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Solvent-Driven Association and Dissociation of the Hydrogen-Bonded Protonated Decavanadates

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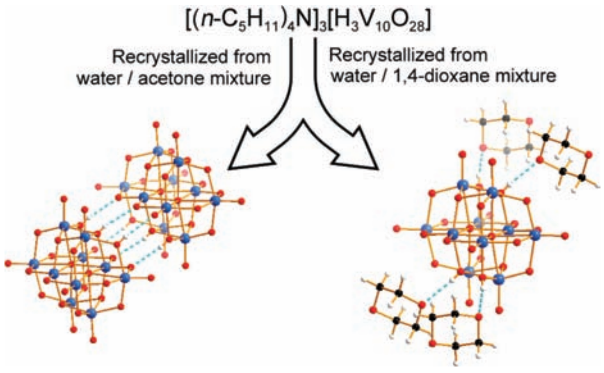
S *Supporting Information*

ABSTRACT: Hydrogen-bond-assisted molecular aggregation of decavanadate anions, $[H_nV_{10}O_{28}]^{(6-n)-}$, in nonaqueous solutions was probed by systematic small-angle X-ray scattering and ^{1}H and ^{51}V NMR spectroscopic measurements in mixtures of acetone and 1,4-dioxane. Under acetone-rich conditions, the decavanadate anion prefers a self-associated hydrogen-bonded dimer of $\{[H_3V_{10}O_{28}]_2\}^{6-}$, which dissociates into monomeric species as the proportion of 1,4-dioxane increases. The association/dissociation behaviors of the decavanadate anions were proven to be reversible and driven by the protophobic/protophilic nature of the solvent.

Polyoxometalates,[1] the molecular oxides of elements in groups 5 and 6, have long been of interest because of their diverse structure- and property-based functionalities. Among them, the polyoxometalates of group 5 elements, which are less acidic than their group 6 counterparts and therefore are protonated at moderate pH,[2] exhibit unique intermolecular interactions both by accepting hydrogen bonds at nonprotonated oxygen atoms and by donating hydrogen bonds at protonated oxygen ones.[3−5] Decavanadate[6] is a typical example showing such bidirectional hydrogen bonding. Day, Klemperer, and Maltbie revealed the protonation sites in triprotonated decavanadate anion dimers, $\{[H_3V_{10}O_{28}]_2\}^{6-}$, both in its solid tetraphenylphosphonium salt and in $CH_3CN/CHCl_3$ solutions of its tetra-*n*-butylammonium salt; moreover, the deliberate addtion of H_2O to CH_3CN solutions of $[(n\text{-}C_4H_9)_4N]_3[H_3V_{10}O_{28}]$ dissociates dimers of decavanadate anions into monomers.[3]

Investigations of solvent effects on the solution chemistry of oxoanion solutes in non-aqueous aprotic media are an important and complementary component to research in protic media, leading to deeper insights into the aggregation/self-assembly behavior of polyoxometalates in general and decavanadates in particular. In this context, we focused our attention on tetraalkylammonium decavanadates that showed both the dimeric and monomeric hydrogen-bonded molecular complexes in the crystalline state, depending upon the protophobic or protophilic nature[7] of the solvent (Scheme 1).[5] On the one hand, protonated decavanadate anions self-assembled into self-complementarily hydrogen-bonded dimers when crystallized with acetone, a solvent molecule that is reluctant to accept hydrogen bonds. On the other hand, they formed hydrogen bonds with solvent molecules and remained monomers when crystallized with 1,4-dioxane, a solvent molecule that is keen to accept hydrogen bonds. Herein we discuss the effect of solvent properties on hydrogen-bond formation of decavanadates in the solution state based on systematic small-angle X-ray scattering (SAXS) as well as ^{1}H and ^{51}V NMR measurements of $[(n\text{-}C_5H_{11})_4N]_3[H_3V_{10}O_{28}]$ dissolved in mixtures of acetone and 1,4-dioxane. The acetone/1,4-dioxane mixed-solvent system was employed as the first target system in order to facilitate direct comparisons with the results obtained from the corresponding solid-state studies. These solvents, which neither accept or liberate protons, allowed us to track the behaviors of protons using ^{1}H NMR spectroscopy. SAXS is a direct method for investigating the morphology of polyoxometalates in solution and probing self-assembly and ion association.[8] The results reported here illustrate that acetone accelerates dimer formation and 1,4-dioxane accelerates dimer dissociation and that the reactions are reversible.

Scheme 1. (left) Structure of a Dimer of Triprotonated Decavanadate Anions Obtained from a Mixed Solvent Containing Protophobic Acetone and Water, Showing Six Interanion Hydrogen Bonds; (right) Structure of a Tetraprotonated Decavanadate Anion Monomer Obtained from a Mixed Solvent Containing Protophilic 1,4-Dioxane and Water, Showing Hydrogen Bonds to Four 1,4-Dioxane Molecules[a]



[a] Color key: blue, V; red, O; black, C; white, H.

SAXS from 10 mmol/L $[(n\text{-}C_5H_{11})_4N]_3[H_3V_{10}O_{28}]$ solutions in mixtures of acetone and 1,4-dioxane was measured at the 12-ID-C beamline of the Advanced Photon Source (APS).[9,10] The solution composition was systematically varied by mixing acetone and 1,4-dioxane in volumetric ratios of 10/0, 9/1, 8/2, ...,

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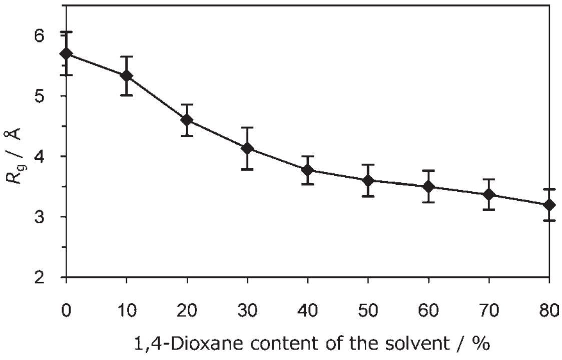

Figure 1. Dependence of the average R_g obtained from analyses of the SAXS data for the 10 mmol/L $[(n\text{-}C_5H_{11})_4N]_3[H_3V_{10}O_{28}]$ solutions prepared with volumetric mixtures of acetone and 1,4-dioxane.

and 2/8. Plots of the scattering intensity $I(Q)$ versus the momentum transfer Q (in Å^{-1}) experienced by the incident photons[11] varied with the composition of the mixed solvent, as shown in the Supporting Information. Three fitting methods (Guinier, form factor, and pair-distribution analyses) were used to determine the average radius of gyration R_g (a shape-independent measure of particle size given by the root-mean-square distance of the atoms in a particle from its center of mass) of the species dissolved in each solution.[12] Figure 1 shows a plot of R_g as a function of the 1,4-dioxane content in the mixed solvent. R_g for the solution in 100% acetone was 5.7(4) Å, whereas R_g for the solution in the mixed solvent consisting of 20% acetone and 80% 1,4-dioxane was 3.2(3) Å. These values agree with those calculated from the crystal structure (5.1 Å for the dimer, $\{[H_3V_{10}O_{28}]_2\}^{6-}$, and 3.5 Å for the monomer, $[H_3V_{10}O_{28}]^{3-}$).[13] The variation in the experimentally determined R_g values clearly shows that the particle scatterers assembled into larger entities in acetone-rich solutions and disassembled into smaller entities as the ratio of 1,4-dioxane increased. This is consistent with the formation of the sextuply hydrogen-bonded $\{[H_3V_{10}O_{28}]_2\}^{6-}$ dimer (Scheme 1 left) in acetone-rich solutions and its dissociation into monomeric anions with different degrees of protonation (see below). Fits to the $I(Q)$ data for the 10 mmol/L $[(n\text{-}C_5H_{11})_4N]_3[H_3V_{10}O_{28}]$ solutions using different form factors confirmed the trend shown by the average R_g values in Figure 1. Specifically, the particle scattering data corresponding to volumetric 10/0, 9/1, 8/2, 7/3, and 6/4 acetone/1,4-dioxane mixtures were best fit with ellipse models of dimers (11.2 Å × 5.2 Å semiaxes for 10/0 and 5.6 Å × 4.2 Å semiaxes for 6/4). Thereafter, for solutions of $[(n\text{-}C_5H_{11})_4N]_3[H_3V_{10}O_{28}]$ in 5/5, 4/6, 3/7, and 2/8 solvent mixtures, the axis lengths converged, and the data were best fit with solid-sphere models with a radius of 4.7(2) Å, consistent with the physical dimensions of the monomer. The variations of the axis lengths with solvent composition are shown in the Supporting Information.

^{51}V and ^{1}H NMR data were measured for 10 mmol/L solutions of $[(n\text{-}C_5H_{11})_4N]_3[H_3V_{10}O_{28}]$ dissolved in mixtures of acetone-d_6 and 1,4-dioxane-d_8 at volumetric ratios of 10/0, 8/2, 6/4, 4/6, and 2/8.[10] Like the SAXS data, the ^{51}V NMR and ^{1}H NMR spectra depended on the composition of the solvent (Figure 2). The ^{51}V NMR spectrum of the solution in 100% acetone-d_6 was similar to the spectrum that was assigned to the dimer of decavanadate anions by Day et al.[3] It showed two broad signals at −394.1 and −429.2 ppm (Figure 2c, top trace) derived from the two nonequivalent vanadium sites I_A and I_B (see Figure 2b) in the dimer. The spectrum changed as the ratio of 1,4-dioxane-d_8 increased, with the two broad signals characteristic of the dimer merging into one signal at −415.4 ppm (Figure 2c, bottom trace), indicating that the decavanadate anion dimers dissociated into the constituent monomers.

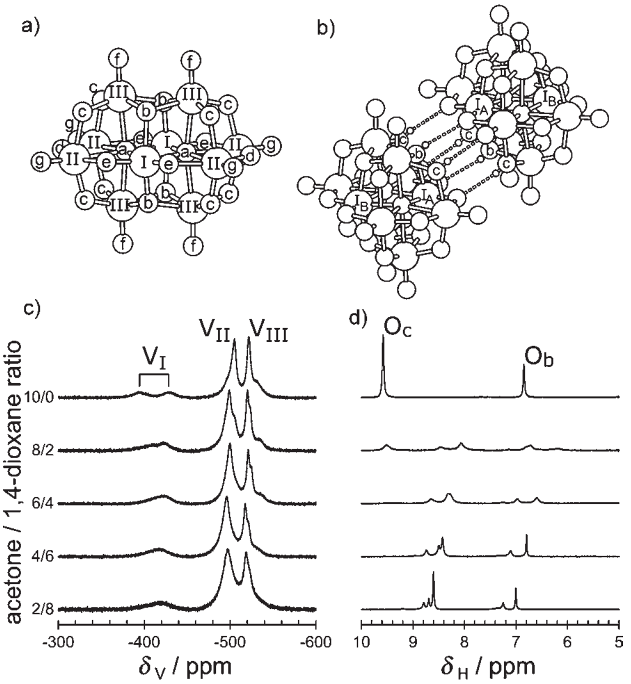

Figure 2. (a) Structure of $[V_{10}O_{28}]^{6-}$ with atom-type labeling (I−III for V and a−g for O). (b) Structure of the hydrogen-bonded dimer $\{[H_3V_{10}O_{28}]_2\}^{6-}$ showing how type-I vanadium atoms become nonequivalent (labeled as I_A and I_B) upon dimerization. (c) ^{51}V NMR and (d) ^{1}H NMR spectra of 10 mmol/L solutions of $[(n\text{-}C_5H_{11})_4N]_3[H_3V_{10}O_{28}]$ in acetone-d_6/1,4-dioxane-d_8 mixed solvents. Assignments of the spectra for the pure acetone solution are given, showing the splitting of the ^{51}V NMR signal for the type-I vanadium atoms into two peaks (assignable to type I_A and I_B vanadium atoms) as a result of dimer formation.

In the ^{1}H NMR spectrum of the solution in 100% acetone-d_6, two signals at 9.58 and 6.85 ppm with a 2:1 intensity ratio were observed (Figure 2d, top trace). These signals are consistent with the results for $[(n\text{-}C_4H_9)_4N]_3[H_3V_{10}O_{28}]$, which forms a dimer in acetonitrile-d_3 as reported by Day et al.[3] This spectrum changed as the 1,4-dioxane-d_8 content increased. The intensities of these two signals, which were assigned to three protons in the dimer, decreased as the 1,4-dioxane-d_8 content increased from 0 to 40%. Simultaneously, two other sets of signals appeared at 8.07−8.79 and 6.19−7.25 ppm. From the combination of SAXS and ^{51}V NMR results, this change in the spectra indicates that protonation on the surface of the decavanadate anion changed with the dissociation from the dimer to the monomer.

Although both the SAXS and ^{51}V and ^{1}H NMR results for the pure acetone solution were consistent with the solid-state structure of the dimer, the ^{1}H NMR spectra in the dioxane-rich regime differed not only from the spectrum expected for the simply dissociated $[H_3V_{10}O_{28}]^{3-}$ monomer but also from the one expected for the tetraprotonated monomer in the crystal (Scheme 1 right). The tetraprotonated anion should give two signals with a 1:1 intensity ratio because of the four protons attached to four oxygen atoms, namely, two type-b and two type-c oxygen atoms. Instead, there were five prominent signals at

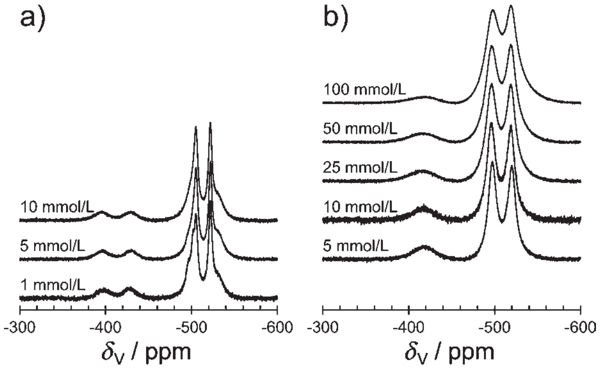

Figure 3. Concentration-dependent ^{51}V NMR spectra of $[(n\text{-}C_5H_{11})_4N]_3[H_3V_{10}O_{28}]$ in (a) 100% acetone-d_6 and (b) an acetone-d_6/1,4-dioxane-d_8 mixed solvent with a volumetric ratio of 20/80.

8.79, 8.69, 8.60, 7.25, and 7.00 ppm in the spectrum for the solutions at acetone/1,4-dioxane ratio of 2/8. Therefore, more than one monomeric species existed in these solutions. The addition of 1,4-dioxane not only dissociated the $\{[H_3V_{10}O_{28}]_2\}^{6-}$ dimer into the constituent $[H_3V_{10}O_{28}]^{3-}$ monomers but also gave rise to the rearrangement of protons. For all of the spectra, the sum of the integrated intensities of the protons remained approximately constant (see the Supporting Information). Because both acetone and 1,4-dioxane are aprotic, proton transfer could occur only on the surface of the decavanadates. The rearrangement of the protons could take place not only within a monomer but also between two monomers, leading to a disproportionation reaction formulated as $\{[H_3V_{10}O_{28}]^{3-}\}_2 \rightleftarrows [H_4V_{10}O_{28}]^{2-} + [H_2V_{10}O_{28}]^{4-}$. A nuclear Overhauser effect (NOESY) spectrum of the 2/8 acetone-d_6/1,4-dioxane-d_8 solution exhibited correlation peaks between all of the protons of the decavanadate monomers and adventitious water (~140 ppm). This result indicates that the protons exchanged between the decavanadate monomer anions directly and/or via water molecules, making the complete assignment of the ^{1}H NMR signals extremely difficult. Nevertheless, it demonstrates the existence of several monomeric species in the 1,4-dioxane-rich solutions. Insofar as the X-ray scattering contrast was dominated by the V atoms in the decavanadate anion, the SAXS response, unlike that for ^{1}H NMR spectroscopy, had insufficient sensitivity to provide information that could be used to distinguish between different monomers, $[H_nV_{10}O_{28}]^{(6-n)-}$ with $n = 2-4$, in solution.

As shown in Figure 3, the decavanadate anions existed as dimers in pure acetone at concentrations as low as 1 mmol/L. In contrast, they existed as monomers and did not aggregate into dimers in 1,4-dioxane-rich mixed solvents even at concentrations as high as 100 mmol/L. In the intermediate range of solvent compositions, the dimerization equilibrium was concentration-dependent (see the Supporting Information).

The reversibility of the dimer association/dissociation reactions was confirmed by monitoring ^{1}H and ^{51}V NMR spectra of a $[(n\text{-}C_5H_{11})_4N]_3[H_3V_{10}O_{28}]$ solution in pure acetone to which 1,4-dioxane was added up to a volumetric ratio of 5/5 and then acetone was added until the volumetric ratio returned to 9/1 (see the Supporting Information).

By using SAXS and ^{51}V and ^{1}H NMR spectroscopy, we have shown that the association and dissociation behaviors of the protonated decavanadate anions in solution are solvent-driven, depending on the protophobic or protophilic nature (i.e., the preference to accept hydrogen bonds) of the solvent. Also, by using aprotic solvents, we were successful in following the proton transfer reactions on the surface of the decavanadates and revealing the reversible nature of the hydrogen-bonded dimer formation reaction. Such tunable hydrogen-bonding equilibria provide an important and recently recognized control toward the formation of much larger supramolecular systems based on polyoxometalates.[14] Further investigations covering a wider range of solvents are now in progress in order to elucidate the origin of this solvent effect.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, details of SAXS analyses, and ^{1}H and ^{51}V NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) See the Supporting Information for experimental details, including the control of water content and evaluation of the effect of water contamination.

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