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Association between ammonium monovanadate and β-cyclodextrin as seen by NMR and transport techniques

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Abstract

The interaction between vanadium (V) and the carbohydrate β-cyclodextrin (β-CD) has been studied in aqueous solutions (pH ≈ 7.5, 298.15 K) using multinuclear NMR spectroscopy, coupled with measurements of diffusion coefficients and electrical conductivity. The transport properties of vanadate ion solutions are markedly influenced by the presence of β-CD. Data from ^{51}V, ^{1}H and ^{13}C NMR spectroscopy show that these effects are due to strong interactions between this carbohydrate and vanadate due to formation of 2:1 (β-CD:vanadate) complexes. The formation of such 2:1 complexes is also supported by molecular mechanics calculations. Complexation is seen by conductometric and diffusion techniques to lead to a significant decrease in the molar conductivity and diffusion coefficient of vanadate solutions in the presence of β-CD. Using the above stoichiometry, it has been possible to calculate the association constant, leading to the value $K = 4.3 \times 10^4\ M^{-2}$ from the analysis of the conductivity data.

Keywords: Carbohydrates; β-Cyclodextrin; Vanadium; Diffusion; NMR; Conductivity

1. Introduction

Although vanadium is a trace element, it has considerable biological relevance due to the great similarity between its chemistry and that of phosphate [1,2]. Vanadium salts display insulin-like activity and may be used in the treatment of diabetes [2]. However, at high concentrations they may be toxic due to alterations on the enzyme activity responsible for phosphate metabolism. This element is commonly present in such systems as vanadium (V) in the form of the vanadate anion, and aqueous solutions consist of a complex mixture of different oligomers with different states of protonation (Fig. 1) [3].

Although some studies involving the interaction of vanadate with carbohydrates have been carried, literature data on the diffusion coefficients of ammonium monovanadate in model biological environments are scarce [3]. We are particularly interested in data on the diffusion and conductance of ammonium monovanadate with cyclodextrins in aqueous solutions. This stems from the importance of cyclodextrins in aqueous solutions in applied research due to their wide range of applications, e.g., those related to pharmaceutical chemistry [4]. The most common pharmaceutical application of cyclodextrins is to enhance the solubility, stability, and bioavailability of drug molecules. In addition, we have been interested in diffusion and electrical conductivity in electrolyte solutions for chemical systems occurring in the oral cavity, to understand and resolve corrosion problems related to dental restorations in systems where such data are not currently available.

Cyclodextrins (CDs) are cyclic oligosaccharides [4–7] having a truncated cone structure with a hydrophilic external surface and a relatively non-polar cavity. Because of the relative non-polar character of the cavity in comparison to the polar exterior, cyclodextrins can form inclusion complexes with a wide variety of guest molecules, predominantly due to hydrophobic interactions [8–12]. However,

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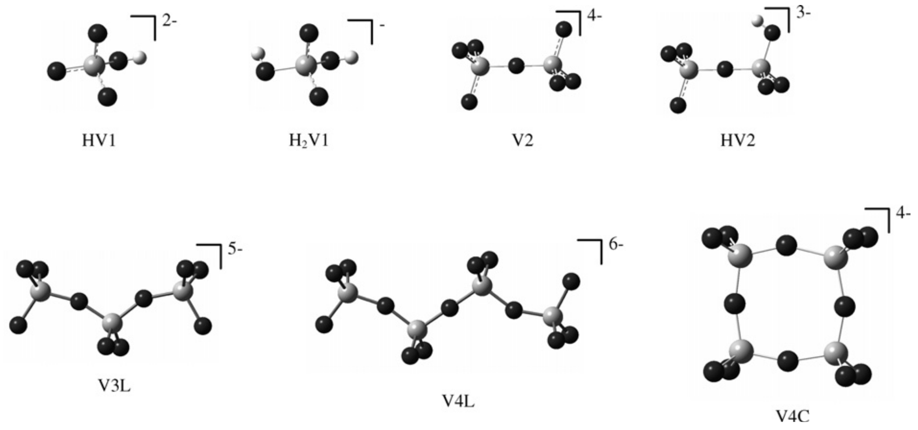

Fig. 1. Schematic structures of the main species in vanadate aqueous solutions (adapted from Refs. [3,4]) HVO_4^{2-} (HV1), $H_2VO_4^{-}$ (H_2V1), $V_2O_7^{4-}$ (V2), $HV_2O_7^{3-}$ (HV2), $V_3O_{10}^{5-}$ (V3L), $V_4O_{13}^{6-}$ (V4L) and $V_4O_{12}^{4-}$ (V4C).

it should be emphasized that not only hydrophobic interactions will lead to an association between a guest molecules and CD. Ionic solutes, such as non-associated inorganic salts, can also be involved in these complexes [13–15].

The present paper intends to fill this gap, and report conductance measurements and diffusion coefficients for vanadium (V) in aqueous solutions of β-cyclodextrin (β-CD) at 298.15 K. These studies are complemented and supported by nuclear magnetic resonance (NMR) spectroscopic studies in order to identify the dominant species involved in the diffusion and conductivity processes. To obtain a better understanding of the structure of the chemical species formed, we have complemented these studies using molecular mechanics calculations. Finally, a model to calculate the association constant between vanadium (V) and β-CD has been developed and the association constant estimated.

2. Experimental

2.1. Reagents

Ammonium monovanadate (Merck, *pro analysi*, >99%) was used without further purification. β-CD was purchased from Sigma (*pro analysi* >99%), and had a water content 13.1% as verified from thermal analysis.

Aqueous solutions were prepared using bi-distilled (diffusion measurements) or Millipore-Q (conductance measurements) water, and D_2O (NMR spectroscopy).

All solutions were freshly prepared before each experiment.

2.2. Diffusion measurements

Diffusion coefficients were measured with an open-ended capillary cell. The apparatus assembled for use with the open-ended capillary cell in this laboratory is essentially the same as previously reported [16]. The cell has two vertical capillaries, each closed at one end by a platinum electrode and positioned one above the other with the open ends separated by a distance of about 14 mm.

The upper and lower tubes, initially filled with solutions of concentrations 0.75*c* and 1.25*c*, respectively, were surrounded with a solution of concentration *c*. This ambient solution was contained in a glass tank (200 × 140 × 60) mm immersed in a thermostat at 298.15 K. The tank was divided internally by Perspex sheets and a glass stirrer created a slow lateral flow of ambient solution across the open ends of the capillaries. Experimental conditions were such that the concentration at each of the open ends was equal to the ambient solution value *c*. That is the physical length of the capillary tube coincided with the diffusion path, such that the boundary conditions described in the literature [16] to solve Fick's second law of diffusion are applicable. As a consequence, the so-called Δl-effect [16] is reduced to negligible proportions. In contrast to a manual apparatus, where diffusion is followed by measuring the ratio of resistances of the top and bottom tubes, $w = R_t/R_b$, by an alternating current transformer bridge, in our automatic apparatus w was measured by a Solartron digital voltmeter (DVM) 7061 with 6 1/2 digits. A Bradley Electronics Model 232 power source supplied a 30 V sinusoidal signal of 4 kHz (stable up to 0.1 mV) to a potential divider that applied a 250 mV signal to the platinum electrodes at the top and bottom capillaries. By rapidly (<1 s) measuring the voltages V' and V'' from top and bottom electrodes to the central electrode at ground potential, the value $w = R_t/R_b$ was then calculated from the DVM reading.

To measure the differential diffusion coefficient, D, at a given concentration c, a "top" solution of concentration 0.75*c* and a "bottom" solution of concentration 1.25*c* were prepared, each in a 2 L volumetric flask. The "bulk" solution of concentration *c* was produced by mixing accurately measured volumes of 1 L of "top" solution with 1 L of "bottom" solution. The ammonium monovanadate solutions were prepared by heating to 353.15 K and then allowing them to cool to 298.15 K. The glass tank and the two capillaries were filled with solution *c*, immersed in the