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Micellization Behavior of a decavanadate cluster complex $[H_2V_{10}O_{28}][LH]_4$ (L = 2-methyl imidazole)

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ABSTRACT

The title complex was obtained from the reaction of $VOSO_4$ with 2-methyl imidazole in presence of benzoic acid. The interaction of DNA with this structurally characterized decavanadate complex has been studied earlier by UV–visible and fluorescence spectroscopy. Micellization behavior of the complex was studied with cationic surfactant CTAB using conductivity meter and UV-Visible spectrophotometer showing the complex have increased solubility with the addition of surfactant. These initial studies heralded good biological potential of the complex.

Keywords*: Cationic surfactant, CTAB interaction, CMC, decavanadate, micellization, polyoxometalates.*

1. INTRODUCTION

Vanadium occurs as an "essential trace" element in diverse living organisms and has wide spread involvement in enzymatic and physiological activities [1-2]. The coordination chemistry of vanadium complexes are of immense interest due to their significance in various biochemicals, pharmacological and catalytic activities [3-4]. Vanadium possesses the ability to assume various oxidation states ranges from -1, 0, +1, +2, +3, +4, +5 [5]. Under physiological conditions, *in vivo*, vanadium complexes are usually stable in their +4 and +5 oxidation states. Among various transition metal complexes, the importance of vanadium chemistry is currently receiving considerable recognition owing to its diverse applications in biology, pharmacology and their catalytic activity [6-7]. The polyoxovanadate anions e.g. the dimer ($H_2V_2O_7^{2-}$, $HV_2O_7^{3-}$ or $V_2O_7^{4}$), the tetramer ($V_4O_{12}^{4-}$), the pentamer ($V_5O_{15}^{5-}$) and the decamer ($H_2V_{10}O_{28}^{4-}$, $HV_{10}O_{28}^{5-}$ or $V_{10}O_{28}^{6-}$) [8,9] are known to possess different geometric features in aqueous solutions but exhibit nearly identical biological activities. However, decavanadate, $[H_nV_{10}O_{28}]^{(6-n)-}$ (V_{10}), has recently attracted attention as a potential precursor of therapeutic agents against a number of maladies and much effort has been made to shed light on the pathways through which treatment with V_{10} affects lipidic structures, cell surface proteins and microbial targets [10-12]. The present paper reports the aggregation (micellization) behavior of a cationic surfactant CTAB with complex using conductometry and UV-Visible spectrophotometry.

2. EXPERIMENTAL

2.1. Materials and methods Chemicals were of reagent grade and used without further purifcation. Cetyl N,N,N-trimethylammonium bromide (CTAB) were purchased from Sigma Aldrich. Solvents were purifed by distillation prior to use. Electronic spectra were recorded on a Shimadzu 1800 spectrophotometer. Conductance

measurements were made in water/methanol solution by using systronics conductivity meter-304. Throughout the experiments, double distilled water was used.

2.2. Preparation of the complex

To an aqueous solution (5 mL) of $VOSO_4,H_2O$ (1 mmol, 0.181g), methanolic solution (10 mL) of benzoic acid (1 mmol, 0.122g) was added dropwise with constant stirring to obtain a clear solution. To the resulting solution, methanolic solution (5 mL) of 2-methylimidazole (2 mmol, 0.164g) was added dropwise with constant stirring and the resultant mixture was further stirred at room temperature for ca 3 h, giving a light green solution. Solution was filtered and left undisturbed at room temperature, after 2-3 days, the colour of this solution gradually turns into yellow and finally yellow crystals suitable for X-ray diffraction studies were deposited after 5-6 days. Compound was isolated by filtration, washed with a small volume of methanol several times and dried in vacuo over anhydrous $CaCl_2$ to give compound 1. Yield 40%. Anal. Calcd. for $V_{10}O_{28}N_8H_{30}C_{16}$: C, 14.90; H, 2.19; N, 8.69. Found: C, 14.95; H, 3.20; N, 8.75. FTIR (KBr, cm^{-1}): ν(C-H) 2980; ν(N-H) 3148; ν(OH) 3460; ν(C=N) 1620; ν(C=C) 1385; ν(V-OH) 1690; ν(V=O_t) 960; ν_{asym}(V-O-V) 830, 725; ν_{sym}(V-O-V) 580, 552, 520. The crystal structure of the complex has been reported [13] earlier (Fig. 2).

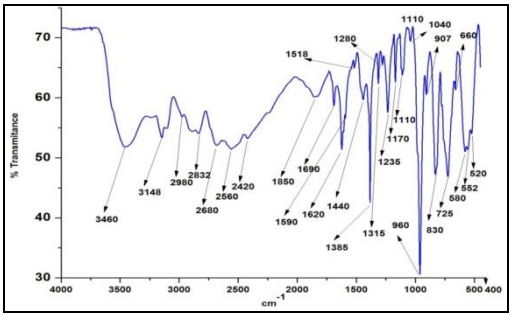

Fig. 1. Infrared spectra of the complex $[H_2V_{10}O_{28}][C_4N_2H_7]_4$

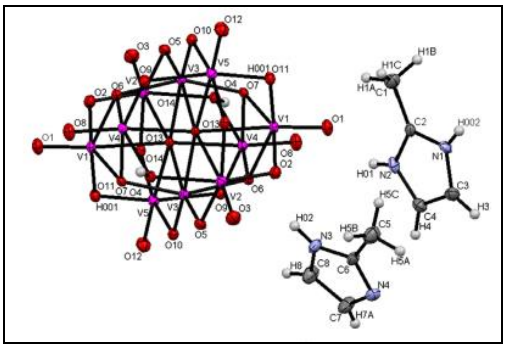

Fig. 2. Ortep view of the structural representation of the complex

2.3. Micellization behavior by conductance analysis

To measure the interaction between surfactant (CTAB) and complex, 0.5 mM concentration of CTAB was prepared in mixture of water, methanol solvents in the ratio of (1:3). A 2 mM concentration of the complex was

prepared in pure methanol. The specific conductance of each complex was measured with and without surfactant.

2.4. Micellization behavior by absorbance analysis

The change in absorbance is a clue for the interaction of complex with surfactant (CTAB). The absorbance of complex with and without surfactant was measured by a double-beam UV–Visible spectrophotometer Shimadzu Mod. UV 1800-240V. The complex solution was taken constant during analysis while the concentration of surfactant was increased.

3. RESULT AND DISCUSSION

3.1. Measurement of surfactant interaction with complex using conductometery

The solubility of mixed ligand complexes was determined conductometrically as well as spectroscopically by using cationic surfactant CTAB. The conductometric plots were made between conductance of solution and the concentration of surfactant in a solution. The conductance report revealed increase in conductance by adding surfactant to the complex solution. An inflection is observed in conductance graph. The concentration at which inflection was observed is called Critical micelle concentration (CMC). At CMC the surfactant monomers encircle from the complex and form an aggregated structure called micelle which is formed due to attraction of surfactant and complex which may be electrostatic or weak van der Waals forces [14]. In pre-micellar region, the conductance is small but in post-micellar region the conductance is abruptly increased which is attributed to the ionic product of the surfactant and charge transfer between the surfactant and complex molecules. Fig.3. shows the conductance plot of CTAB-complex and the CMC value from conductance analysis is $2.3x10^{-3}$ M.

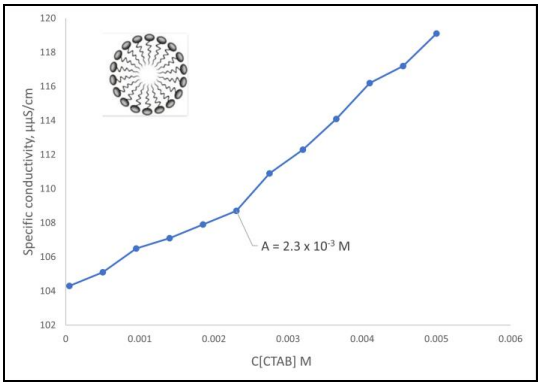

Fig.3. Specific conductivity plot of CTAB with 2 mM of complex at room temperature and constant pH in a mixture of water:methanol solvents in the ratio of 1:3.

3.2. Interaction of surfactant with complex using UV–Visible spectrophotometry

Solubility enhancement of V(IV) was also assessed through spectral analysis with cationic surfactant (CTAB). The increase in absorption with respect to increase in surfactant addition confirms the interaction. The abrupt increase in absorbance at a certain concentration of surfactant is due to the encapsulation of complex into the

micelle [15]. The changes in λ_{max} in the absorbance plots show strong interaction with respective surfactant [16]. Fig.4. is UV–Visible spectra of complex with CTAB (surfactant).

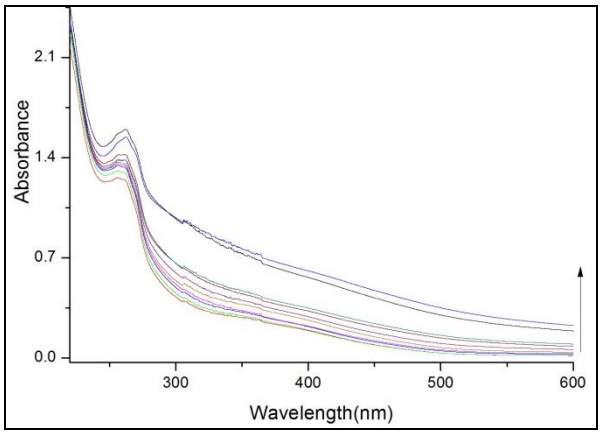

Fig.4. Absorption spectra of complex (2 mM) with increasing amounts of CTAB (0.5 mM) at room temperature and constant pH.

4. CONCLUSSIONS

Micellization behaviour of the complex was determined by using cationic surfactant, CTAB that revealed that the complex has different behaviour from other analogous complexes and the solubility were increased tremendously after opening of the micelle. The complex also has DNA binding abilities were checked earlier by various spectroscopic techniques. These preliminary studies showed the inherent biological potential of the synthesized complex and opened up further avenues for the further studies on such and other complexes.

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