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Stoichiometry of Vanadium (V) Complexes with Sulphuric Acid: A Conductometric Study

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ABSTRACT-Conductometric method has been used to investigate the stoichiometry of the complex formation between Vanadium (V) and sulphuric acid. The results indicate the formation of 1:1 complex at lower concentration of the sulphuric acid whereas 1:2 complex has been formed at higher concentration of the sulphuric acid. The stoichiometric ratio of the complex formation of vanadium in sulphuric acid formed depends upon the concentration of the acid in aqueous solution.

Keywords: Stoichiometry, Conductometry, Ammonium meta vanadate.

I. INTRODUCTION:

Vanadium has variable valence from 2 to 5 Quinque-valent vanadium is found in anions of two oxy-acids i.e., ammonium meta vanadate $NH_4(VO_3)$ and sodium ortho-vanadate Na_3VO_4. Due to the presence of VO_3 or $H_2VO_4^-$ anion in aqueous solutions of vanadium, it gives yellow color. On addition of sulphuric acid, red polymeric vanadium penta-oxide gives vanadium (IV) cation and forms orange or red color complex ion. Vanadium (V) acts as an oxidant in acidic solution due to the formation of redox couple of vanadium (V) and vanadium (IV). It has been observed that the various reactive species of vanadium (V) in redox reaction are dependent on low and high concentration of acid [1]. The redox system between vanadium (V) and vanadium (IV) in terms of equilibrium between various vanadium species has been established [2, 3].

$$VSO_{4(s)} \leftrightarrow V^{2+} + SO_4^{2-} \quad (1)$$

$$V_2(SO_4)_{3(s)} \leftrightarrow 2V^{3+} + 3SO_4^{2-} \quad (2)$$

$$VOSO_{4(s)} \leftrightarrow VO^{2+} + SO_4^{2-} \quad (3)$$

$$(VO_2)_2SO_{4(s)} \leftrightarrow 2VO_2^{+} + SO_4^{2-} \quad (4)$$

It is now well established that hydrate cations $\{VO(OH_2)_5\}^{2+}$ and $\{VO_2(OH_2)_4\}^{+}$ species of vanadium (V) in aqueous solution are preponderant. The species $\{VO_2H_2SO_4\}^{+}$ or $\{H_2VO_2SO_4\}^{+}$ has also been proposed [4] in sulphuric acid. The specific conductance in dilute aqueous sulphuric acid of ammonium meta vanadate decreased with increase in concentration of salt it is only possible when the sulphuric acid furnished ions in solution, which forms complex with vanadate ion. The reactive species in sulphuric acid are attributed to $V(OH)_3HSO_4^{+}$ and $V(OH)_2(HSO_4)_2^{+}$ [5].

The importance and originality of vanadium (V) complexes still lies in deriving all structural and coordination geometry of complex ion theoretically and practically [6,7,8]. The stoichiometry of vanadium complex with sulphate, bisulphate ions are not studied in which the sulphuric acid act as ligand. In this study we have attempted to investigate the stoichiometry of vanadium complex using the conductometric method. The conductance of ammonium meta vanadate have been measured at different concentration of sulphuric acid in aqueous solution.

II. EXPERIMENTAL:

The stock solution of ammonium meta vanadate was prepared by dissolving weighed quantity of the salt in double distilled water containing very low strength of sulphuric acid. The stock solution was diluted to the desired volume with distilled water and sulphuric acid. The sulphuric acid was used after standardization against standard solution of sodium hydroxide using phenolphthalein as an indicator. A digital conductivity meter 306 (systronic) with a dipping type having platinised electrodes was used for the conductivity measurement. A single phase stabilized A.C. mains of 240 volts/50 Hz was employed throughout the work for conductivity meter. Before used the conductivity cell was soaked in distilled water for 24 hours thereafter standard solution of potassium chloride was used for the calibration of the conductivity meter.

III. RESULT AND DISCUSSION:

In order to investigate the stoichiometric ratio between vanadium ion and sulphuric ion in

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the specific conductance of ammonium meta vanadate has been measured with the increase in the concentration 0.0025 mol dm^{-3} to 0.035 mol dm^{-3} keeping concentration of sulphuric acid constant in aqueous solution the variation of specific conductance at different concentration of ammonium meta vanadate and sulphuric acid has been given in Table 1. The plots of specific conductance of various solutions as function of molar concentration at constant sulphuric acid concentration are given in Fig. 1, 2, 3. It is interesting to note the conductivity decreases significantly by the increasing molar concentration of the salt and attains nearly a constant value after formation of the complex. Conductometric method has been used to investigate the complex formation for electron donor-acceptor complexes [9] for stoichiometric study of complex formation. In all the cases, after complex formation is complete the conductivity of solution becomes almost constant and further increased in salt does not change the conductivity. The point at which the conductivity almost becomes constant corresponds to the stoichiometry of the complex in each case. From the curves, it can be concluded that in Fig. 1 at lower concentration of acid 1:1 complex formed between the vanadium and sulphuric acid. Fig. 2 and 3 shows that the formation of 1:2 complex takes place between the vanadium and sulphuric acid.

TABLE 1
Conductance of ammonium meta vanadate in different concentration of sulphuric acid at temperature 284K.

S.No.	Concentration (mol dm^{-3})	Specific conductance κ (m S cm^{-1})		
		0.01(mol dm^{-3})	0.03(mol dm^{-3})	0.05(mol dm^{-3})
1	0.0000	4.97	13.40	21.20
2	0.0025	4.43	12.20	20.60
3	0.0050	3.88	11.00	19.40
4	0.0075	3.33	10.20	18.60
5	0.0100	3.03	9.43	17.80
6	0.0150	2.97	8.58	16.60
7	0.0200	2.92	8.00	15.80
8	0.0250	2.90	7.90	15.10
9	0.0300	2.88	7.84	14.80
10	0.0350	2.87	7.80	14.70

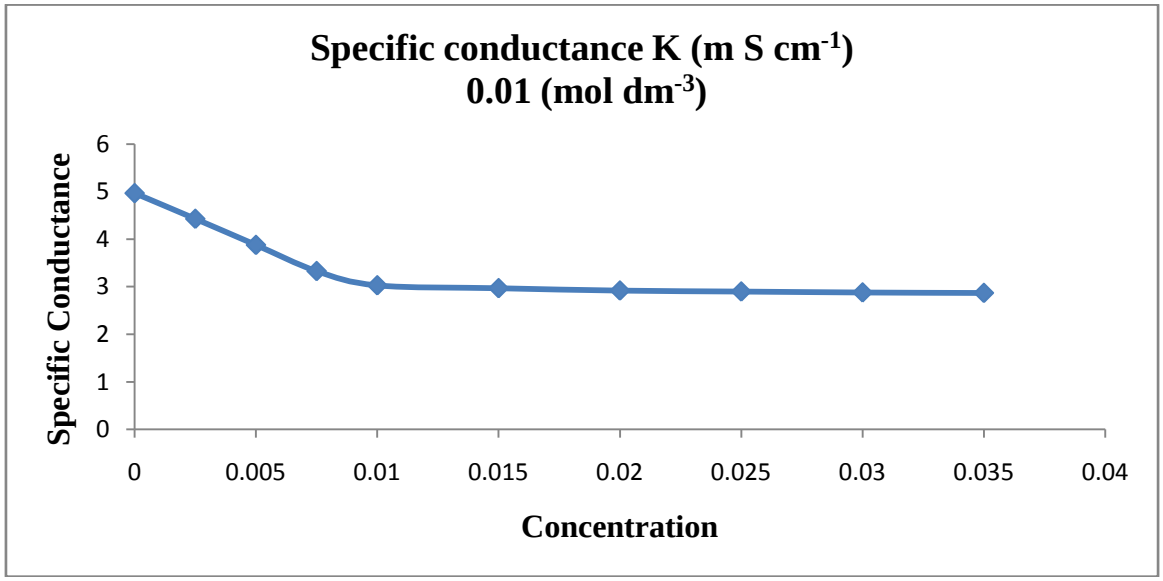

Fig.1

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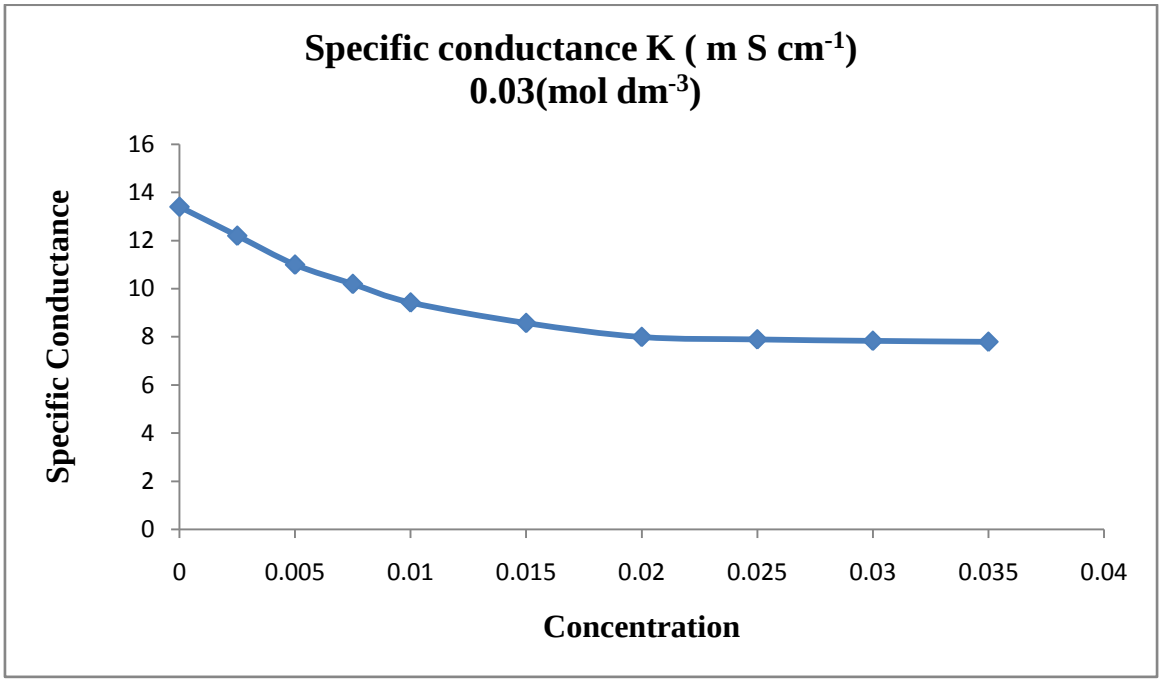

Fig. 2

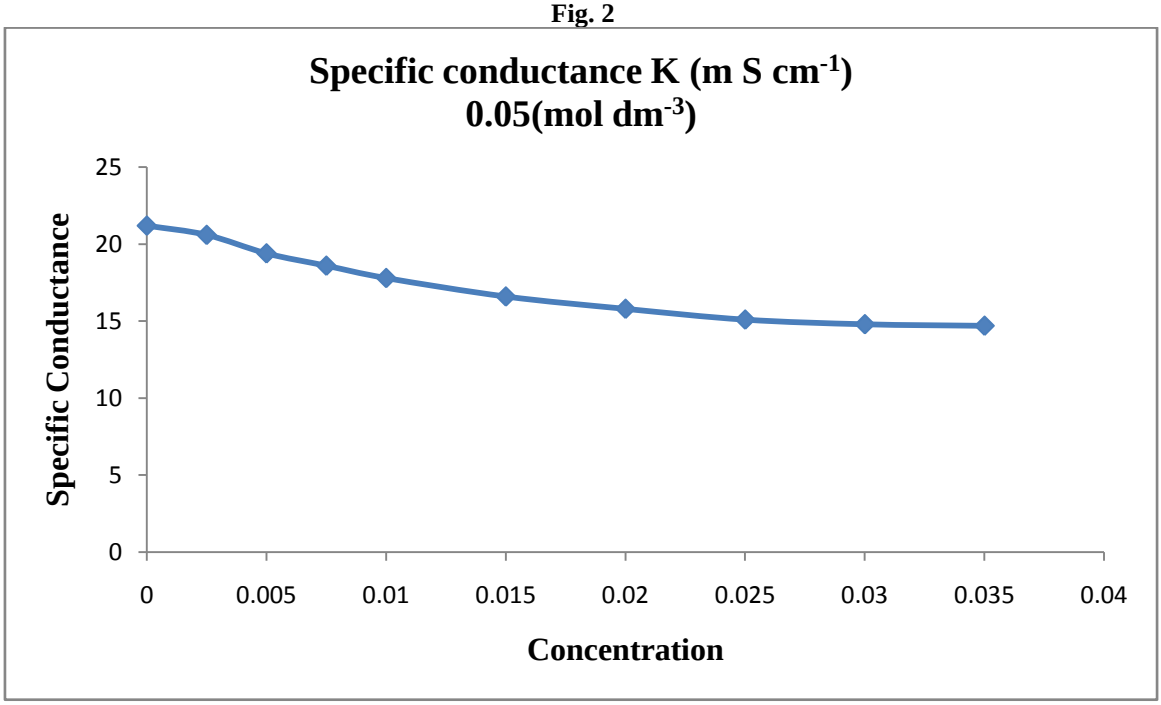

Fig. 3

IV. CONCLUSION:

In our investigation, the complex formation between the vanadium (V) and sulphuric acid shows that lower the concentration of HSO_4^- ions has more possibility to react with the metal ion hence the ionic species VO_2^+ , HSO_4^- is favoured because we have studied the presence of HSO_4^- in dilute and aqueous sulphuric acid . At higher concentration above 0.0150 mol dm^{-3} of sulphuric acid, the complex formation takes place by participation of one more molecule of sulphuric acid the stoichiometry above this concentration between vanadium and sulphuric acid was 1:2. This type of complexation may takes place through the second oxygen atom of VO_2^+ ion with HSO_4^-/ SO_4^{2-} ion.

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