Electrochemical Behavior of Lead and Vanadium as Technologically Important Metals in Aqueous Solutions

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Summary

Lead and Vanadium are technologically important metals due to the wide range of their industrial applications. The importance of lead metal arises from its wide industrial applicability, especially, in lead batteries. The metal is also an important alloying element: for example, it is used to improve the mechinability of brass alloys. Vanadium is a light transition metal, largely used in metallurgy and batteries and also well known as catalyst in combination with oxygen and phosphorous for the mild oxidation of light alkenes. One of its important applications is its use in vanadium- based redox flow batteries.

The present work represents a systematic and detailed investigation concerning the corrosion and passivation behaviors for lead and vanadium metals in aqueous solutions of different pH covering the acidic, neutral and basic media. Also, the inhibition of the corrosion process in these media was considered. The use of different amino acids as environmentally safe corrosion inhibitors for Pb and V was investigated.

The work presented in this thesis is divided into three chapters. Chapter I is subdivided into two sections. The first one is an introduction reviewing the relevant literature, and the second summarizes the aim of the whole investigation.

Chapter II is devoted to the experimental part. It includes specification of the electrodes and chemicals beside the details of the electrochemical cell and measuring systems. It describes also details of the electrode pretreatment, polarization and impedance techniques.

The experimental data are presented and discussed in chapter III where, they are divided into three main parts. In the first part the electrochemical behavior of Pb

metal in aqueous solution covering the acidic, neutral and basic media were described. The obtained results show that in acidic solutions of pH=2, a continuous corrosion is taking place until the steady state is reached. In neutral solutions, pH=7, a passive film develops on the metal surface. In basic solutions, pH=12, a corrosion/passivation process occurs. The presence of Cl^- ions in the acidic solutions increases the rate of corrosion of lead. These observations explained by higher reactivity of lead with Cl^- leading to the formation of $PbCl_2$ which cannot adhere to the metal surface. The calculated activation energy of the lead metal dissolution process reveals that the rate determining step for the dissolution process is one electron transfer process. The electrochemical impedance data were analyzed using the simple equivalent circuit model (RC model). The results of the DC measurements are consistent with those of the EIS, investigation.

The second part presents the electrochemical behavior of V metal in aqueous solutions of different pH (pH=2,7 and 12). The corrosion rate of V electrode in aqueous solutions increases as the pH of the solution increases. The values of corrosion rates are relatively low indicating a passive behavior for V. The corrosion rate in the presence of Cl^- ions is less than that in their absence, which may be attributed to the high tendency of Cl^- to be adsorbed on the electrode surface or the complex formation between V ions and the Cl^- ions. The activation energy of the corrosion of the V metal in aqueous solutions of pH(2,7 and 12) indicates that the dissolution of the metal is a one electron charge transfer process, which supports the mechanism suggested by Armstrong and Henderson. The impedance data were fitted to theoretical data obtained according to an equivalent circuit model describing the electrode/ electrolyte interface.

The third part takes account of the inhibition of corrosion process in acidic, neutral and basic aqueous solutions by using different aminoacids (such as glycine, alanine, valine, histidine, glutamic acid and cysteine) as inhibitors. This part is subdivided into two main sections. The first section includes the inhibition of the corrosion process of Pb electrode in aqueous solutions by different aminoacids and it is subdivided into three subsections. The first subsection describes the effect of the six aminoacids on the corrosion inhibition of Pb in chloride free and chloride containing acidic solutions of pH=2. The inhibition efficiencies of the amino acids were found to decrease in the presence of Cl^- ions. In the second subsection the calculated inhibition efficiencies in neutral solutions (pH=7) are higher than these obtained in the acidic solutions and the aminoacids is adsorbed through the Zwitter ion and act as cathodic inhibitor. The third subsection includes the effect of the six different aminoacids in the basic solution. The anion form of the amino acids is adsorbed on the anodic regions of the electrode surface. Generally, glutamic acid shows the best inhibition efficiency for Pb in the aqueous solutions. The activation energy values were calculated and the adsorption isotherms for Pb electrode in the presence of glutamic acid in neutral solutions were recorded and found to fit the Langmuir adsorption isotherm.

In the second section, the inhibition of the corrosion process of V in aqueous solutions by the six different amino acids was investigated; it is subdivided into three subsections. The first subsection describes the effect of the six different aminoacids on the corrosion of V in chloride free and chloride containing acidic solutions of pH=2. It was noted that in most cases the inhibition efficiency $\eta(\%)$ has lower values in the presence of Cl^- ions. The second and the third subsections deal with the effect of these aminoacids on the V electrode in the neutral and basic solutions. The aminoacids shift the corrosion potential, E_{corr}, to more positive values. The positive shift of E_{corr} is an indication that the addition of the aminoacids influences the anodic process. The activation energy values and the adsorption isotherm for V electrode in the presence of valine (as representative example) were recorded and found to fit the Freundlich adsorption isotherm.