Electrochemical study of Fe II/Fe III on modified GCE with PAN and PMMA at different temperatures using cyclic voltammetry

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Abstract. Poly (Methyl Methacrylate) (PMMA) was studied as a chemical compound used almost universally for teeth base manufacture. The study was focused on the effect of different temperatures of potassium ferricyanide K3[Fe(CN)6] in 1M KCl as an electrolyte using CV technique at modified glassy carbon electrode (GCE) with poly-acrylonitrile (PAN) and PMMA as working electrode (PAN/PMMA /GCE). The thermodynamic functions such as activated enthalpy (ΔH*), free energy (ΔG*) and entropy (ΔS*) for redox current peaks of K3[Fe(CN)6] in 1M KCl on (PAN/PMMA /GCE) electrodes, using Eyring was explored. The determination of the activation energy (Ea*) determined by Arrhenius equations for the oxidation-reduction current peaks of K3[Fe(CN)6] to compare values obtained by K3[Fe(CN)6] in 1M KCl on various electrodes was studied.

1. Introduction
Because Poly(methyl methacrylate) (PMMA) has significant polymer mechanical and optical implementations, feasibility, perfect stretchy strength and rigidity, high transparency, high surface resistivity, good dielectric properties, and thermal constancy it has a suitable processing properties, excellent thermoforming, and ability modified with dye, flame retardant additives, UV absorbent additives, and abrasion resistant coatings [1] [2]. The physical properties of this polymer are significant in the fabrication of polymeric denture bases as the cured polymer has to be tough, sufficient to leave over the teeth in obstruction during chewing and to reduce the uneven loading of the mucus [3]. On the other hand, poly acrylonitrile (PAN) is suitable for making high execution carbon fibers. The properties and structure of budding fibers prepared by moisten spinning are created by liquid-solid phase disconnection through extension, which affect the development of properties through the preparation of poly acrylonitrile fibers and impact the conclusive properties of carbon fibers [4]. The efficacy of Cyclic voltammetry (CV) results from its ability to rapidly predestine the oxidation and reduction manner over spacious potential range [5,6].

2. Materials and Methodologies
Poly (acrylonitrile) (purity 98% Brand name if applicable. China), Poly (Methyl Methacrylate) (PMMA).

2.1. Apparatus
In this experiment used Potentiostat/Galvanostat EZstat series NuVant Systems Inc. (USA). The Electrochemical Bio-analytical cell was connected to a potentiostat device and was monitored by special software to perform cyclic voltammetry (CV). Platinum wire (1 mm diameter) was used as
counter electrodes, silver-silver chloride as reference electrode (Ag/AgCl in 3M KCl) and GCE as working electrode.

2.2. Preparation the modified GCE with Poly acrylonitrile/ Poly Methyl Methacrylate (PAN/PMMA/GCE)
Prepare the (PAN/PMMA/GCE) working electrode as a sensor by mechanical attachment technical method [7]. The method of the modification of GCE included abrasive application of Poly(acrylonitrile)/Poly(Methyl Methacrylate) PAN and PMMA on the clean surface of GCE, forming an array of acrylonitrile and Poly Methyl Methacrylate as modified working electrode PAN/PMMA/GCE and put in 10 ml of electrolyte in the cyclic voltammetric cell, then connected all electrodes (Platinum wire, Ag/AgCl in 3M KCl and PAN/PMMA/GCE) with the potentiostat [8].

2.3. Measurements at different temperatures
A 10 ml size cell was used to measure the CV. Solutions were replaced for studying at different temperatures. Three electrodes (Platinum wire, Ag/AgCl in 3M KCl and PAN/PMMA/GCE) as well as a thermometer were submerged into the cell to follow the solution temperature, and the three electrodes were connected to the potentiostat. The cell was placed into a water bath to set the required temperature and a hot plate was used to increase the temperature in the CV tests.

3. Results and Discussion
3.1. Effect of varying temperature
K₃[Fe(CN)₆] in 1M KCl solution was studied at different temperatures using modified GCE with PAN and PMMA using CV technique to determine the physical and chemical properties in terms of activation energy and thermodynamic parameters using Arrhenius equations [9] and Eyring equations [10].

3.2. Activation energy (E*a)
K₃[Fe(CN)₆] in 1M KCl solution was studied at different temperatures using PAN and PMMA/GCE to determine the activation energy(E*a). It was found that the cathodic current peak was enhanced gradually at the range of temperature from 9-78 °C. Figures 1 and 2 show the plot of Ln(Ipc) of K₃[Fe(CN)₆] different reciprocal of temperature on PAN and PMMA/GCE respectively, which is found to be fairly linear in agreement with thermodynamic expectation of Arrhenius equation; see Eqs (1) and (2) [8].

\[
\sigma = \sigma^0 e^{-Ea/RT} \quad \text{............ (1)}
\]

\[
D = D^0 e^{-Ea/RT} \quad \text{............ (2)}
\]

Where: \( \sigma / D \) = conductivity/diffusibility. \( \sigma^0 / D^0 \) = standard conductivity/initial diffusibility. \( Ea \) = activation energy. \( R \) = universal gas constant, \( T \) = temperature.

Figure 3 illustrates CV of K₃[Fe(CN)₆] in 1M KCl solution using modified electrode PAN and PMMA/GCE at 9 and 78 °C. It shows that increasing the temperature results in the enhancement of both the redux current peaks of K₃[Fe(CN)₆]. Moreover, the PAN and PMMA/GCE results in the improvement of the current as an electro-catalyst in 1M KCl.
Figure 1. Plot of Ln(Ipc) reduction current peak of K$_3$[Fe(CN)$_6$] in 1M KCl solution against inverse temperature at PAN and PMMA /GCE versus Ag/AgCl as a reference electrode.

Figure 2. Plot of Ln(Ipa) oxidation current peak of K$_3$[Fe(CN)$_6$] in 1M KCl solution against inverse temperature at PAN and PMMA /GCE versus Ag/AgCl as a reference electrode.

Figure 3. Cyclic voltammogram of K$_3$[Fe(CN)$_6$] in 1M KCl on the PAN and PMMA /GCE versus Ag/AgCl as a reference electrode.

The cathodic activation energy value (E*apc) and anodic (E*apa) current peaks of K$_3$[Fe(CN)$_6$] in 1M KCl solution at PAN and PMMA /GCE are 7.687 kJ/mol.K and 83.289 kJ/mol.K respectively as shown in Table 1.

Table 1. Activation energy and thermodynamic functions of K$_3$[Fe(CN)$_6$] in 1M KCl solution at PAN and PMMA /GCE.

| Reaction status           | $E_a^*$ | $\Delta S^*$ | $\Delta H^*$ | $\Delta G^*$ | Type of Reaction |
|--------------------------|--------|-------------|-------------|-------------|-----------------|
| Spontaneous reaction     | 7.687  | 0.20        | -66.1101    | -2.64193    | reduction       |
| Nonspontaneous reaction  | 83.289 | -0.218      | -2.566      | 67.088      | oxidation       |
3.3. Thermodynamic functions

Activation free energy ($\Delta G^*$), enthalpy ($\Delta H^*$) and entropy ($\Delta S^*$) of $K_3[Fe(CN)_6]$ in 1M KCl solution at PAN and PMMA /GCE were determined from Eyring equation, see Eq. (3) [9] and thermodynamic equations [11]:

\[
\Delta G^* = -RT \ln \left( \frac{k h}{T k_B} \right) \quad (3)
\]

\[
\Delta H^* = \Delta G^* + T \Delta S^* \quad (4)
\]

\[
\Delta H^* = \Delta G^* + T \Delta S^* \quad (5)
\]

The different units are accounted for in using either the gas constant $R$ (8.314 J.mol$^{-1}$k$^{-1}$), the Boltzmann constant $k_B$ (1.381×10$^{-23}$ m$^2$kg.sec$^{-2}$k$^{-1}$), and Planck constant $h$ (6.66×10$^{-34}$ J.sec) as the multiplier of temperature $T$ (K). Table 1 illustrates the thermodynamic functions of $K_3[Fe(CN)_6]$ in 1M KCl solution, the results shows the spontaneous reaction was depended on more than one factors according to the law of Gibbs free energy, not only depend on change in enthalpy ($\Delta H^*$) to interact and build on the Gibbs law, the reaction is becoming spontaneous when the free energy change ($\Delta G^*$) is negative and enthalpy change ($\Delta H^*$) is also negative, but entropy ($\Delta S^*$) is positive [10]. The electrochemistry reactions such as the oxidation – reduction process for $K_3[Fe(CN)_6]$ in 1M KCl solution to know spontaneous or nonspontaneous reaction was studied different temperatures. In this study, the modified working electrode PAN and PMMA /GCE was used to determine the functions as shown in Table 1 to study the reduction and oxidation current peaks of $K_3[Fe(CN)_6]$ in 1M KCl.

4. Conclusion

The effects of different working temperature on oxidation-reduction process of $K_3[Fe(CN)_6]$ in 1M KCl was studied at PAN and PMMA /GCE in CV method to determine the thermodynamic functions and activation energy using Arrhenius equations and Eyring equation. $K_3[Fe(CN)_6]$ has oxidation–reduction current peaks 1M KCl, so it can be considered that $K_3[Fe(CN)_6]$ is an oxidative reagent in 1M KCl with the oxidation current peak at 291 mV. Activation energy values were determined from Arrhenius equations at both PAN and PMMA /GCE electrodes for both cathodic and anodic peaks, Activation of free energy ($\Delta G^*$), enthalpy ($\Delta H^*$) and entropy ($\Delta S^*$) of $K_3[Fe(CN)_6]$ in PAN and PMMA /GCE can be calculated from Eyring equation and other thermodynamic equations. The same values were found for each electrode PAN and PMMA /GCE, so the values of thermodynamic functions are not affected by the electrode, but the spontaneous redox reaction depended on these functions.

5. References

[1] Chatterjee, A., Properties improvement of PMMA using nano TiO2 (2010), J. Appl. Polym. Sci., Vol 118, p. 2890.

[2] Negim, E., Nurlybayeva, A., Irmukhametova, G.S., Makhatova, A., Basharimova, A., Serikkali, A., Sakhy, M., Iskakov, R., and Mun, G.A., (2015) Effect of methyl methacrylate and butyl methacrylate copolymer on the physico-mechanical properties of Acryl syrup paints, International Journal of Biology and Chemistry., Vol 8, p. 60.

[3] Elshereksi, N.W., Mohamed, S.H., Arifin, A., and Ishak, Z.A., (2014). Thermal Characterisation of Poly(Methyl Methacrylate) Filled with Barium Titanate as Denture Base Material, J. Phys. Sci., Vol 25, p. 15.
[4] Zhang, H., Quan, L., Gao, A., Tong, Y., Shi, F., and Xu, L., (2019). The Structure and Properties of Polyacrylonitrile Nascent Composite Fibers with Grafted Multi Walled Carbon Nanotubes Prepared by Wet Spinning Method, Polymers, , Vol 11, p. 422.

[5] Pujado, M.P., (2012). Carbon Nanotubes as platforms for Biosensors with electrochemical and Electronic Transduction, , P. 52.

[6] Elgrishi, N., Rountree, K.J., McCarthy, B.D., Rountree, E.S., Eisenhart, T.T., and Dempsey, J.L., (2018). A Practical Beginner’s Guide to Cyclic Voltammetry, Chem. Educ., , Vol 95, p. 197.

[7] Tan, W.T., and Ng, G.K., and Bond, A.M., (2000). Electrochemical of microcrystalline tetra thiafulvalene at an electrode solid aqueous KBr interface, M. J. Chem., , Vol 2, p. 34.

[8] Muhammed Mizher Radhi, Y. K. A. Amir2 , S. H. Alwan1 and T. W. Tee . (2013) Conference Series Electrochemical Effect of Different Modified Glassy Carbon Electrodes on the Values of Diffusion Coefficient for Some Heavy Metal Ions. Journal of Physics: Conference Series. Vol. 431.

[9] Tan, W.T., and Goh, J., (2008). Electrochemical oxidation of methionine mediated by a fullerene-C60 modified gold electrode, Electroanalysis, , Vol 20, p. 2447.

[10] Chapman, S., and Cowling, T.G., (1991).The Mathematical Theory of Non-uniform Gases: An Account of the Kinetic Theory of Viscosity, Thermal Conduction and Diffusion in Gases (3rd Edition). Cambridge University Press.

[11] Daniels, F., and Alberty, R.A., (1984). Physical Chemistry, John Wiley & Sons Inc; 6th edition.