Experimental investigation of doping process of a Polyaniline film as a Langmuir adsorption

Fatemeh Ziaei Moghaddam and **Reza Arefinia**[*]

Department of Chemical Engineering, Ferdowsi university of Mashhad, Mashhad, Iran
Corresponding author E-mail: arefinia@um.ac.ir

Introduction

The conductive nature of polyaniline (PANI) is risen from repeated conjugated double bound along with the doping process [1, 2]. According to the previous work [3], it was concluded that almost all the redox sites, consumed during the first oxidation peak in PANI voltammograms, were presented in the doping process. The aim of this work is experimentally confirming that the doping process can be dealt as a separate Langmuir adsorption. In this regard, the cyclic voltammetry method was applied on a thin PANI film in solutions with different concentration of hydrogen ions (H$^+$) and anions (A$^-$).

Methods

A PANI film was electropolymerized on the surface of a gold electrode (1 cm^2) in a conventional three electrodes cell with an Autolab PGSTAT 302N. The obtained PANI film was immersed in electrolytes, containing different chloride and hydrogen activities, presented in Table 1. Accordingly, solutions of series (i) were prepared by addition of different HCl concentrations; while series (ii) by addition of the certain amounts of sodium hydroxide to a define HCl solution. Then, the cyclic voltammetry was conducted between -0.2 and 0.4 V at the potential scan rate of 10 mV s^{-1}.

Table 1 solutions with different chloride and hydrogen activities

Solution	(i)		(ii)	
	a_{H^+}	a_{Cl^-}	a_{H^+}	a_{Cl^-}
1	12.9	12.9	12.9	12.9
2	7.5	7.5	10.3	12.9
3	4.1	4.1	7.7	12.9
4	2	2	5.2	12.9

Results and discussion

The doping process can be stated as follows:

$$Ox + A^- + H^+ \underset{de}{\overset{ad}{\rightleftharpoons}} OA \qquad (1)$$

where Ox represents the oxidize site, OA the adsorbed sites, H$^+$ the hydrogen ions and A$^-$ the anion. Moreover, the doping process can be considered as a Langmuir adsorption if the experimental data are adopted the Langmuir isotherms according to the following equation [4]:

$$\frac{a_{H^+} a_{A^-}}{\Gamma} = -\frac{1}{B_{ad}\Gamma_{max}} + \frac{a_{H^+} a_{A^-}}{\Gamma_{max}} \qquad (2)$$

where   and   are the activity of hydrogen ion and anion, respectively; B_{ad} reflects the affinity of ions towards the adsorption sites, Γ (mol cm^{-2}) is the surface concentration of adsorbed sites and Γ_{max} the maximum concentration of adsorbed sites. Γ was calculated from the charge pass during the first oxidation peak of the PANI voltammogram.

With respect to Eq. (3), the plot of versus for the data obtained in the present work are shown in Fig. 1. The straight line of this figure approves explicitly that the doping process can be dealt by the Langmuir adsorption. Moreover, Γ_{max} and B_{ad} can be calculated from the slope and intercept respectively, and are for series (i): 6.62×10^{-9} and 0.45, for series (ii): 6.85×10^{-9} and 0.05. Therefore, it is resulted that the maximum adsorbed sites do not change significantly; however, adsorption affinity decrease probably due to the decrease of hydrogen ions.
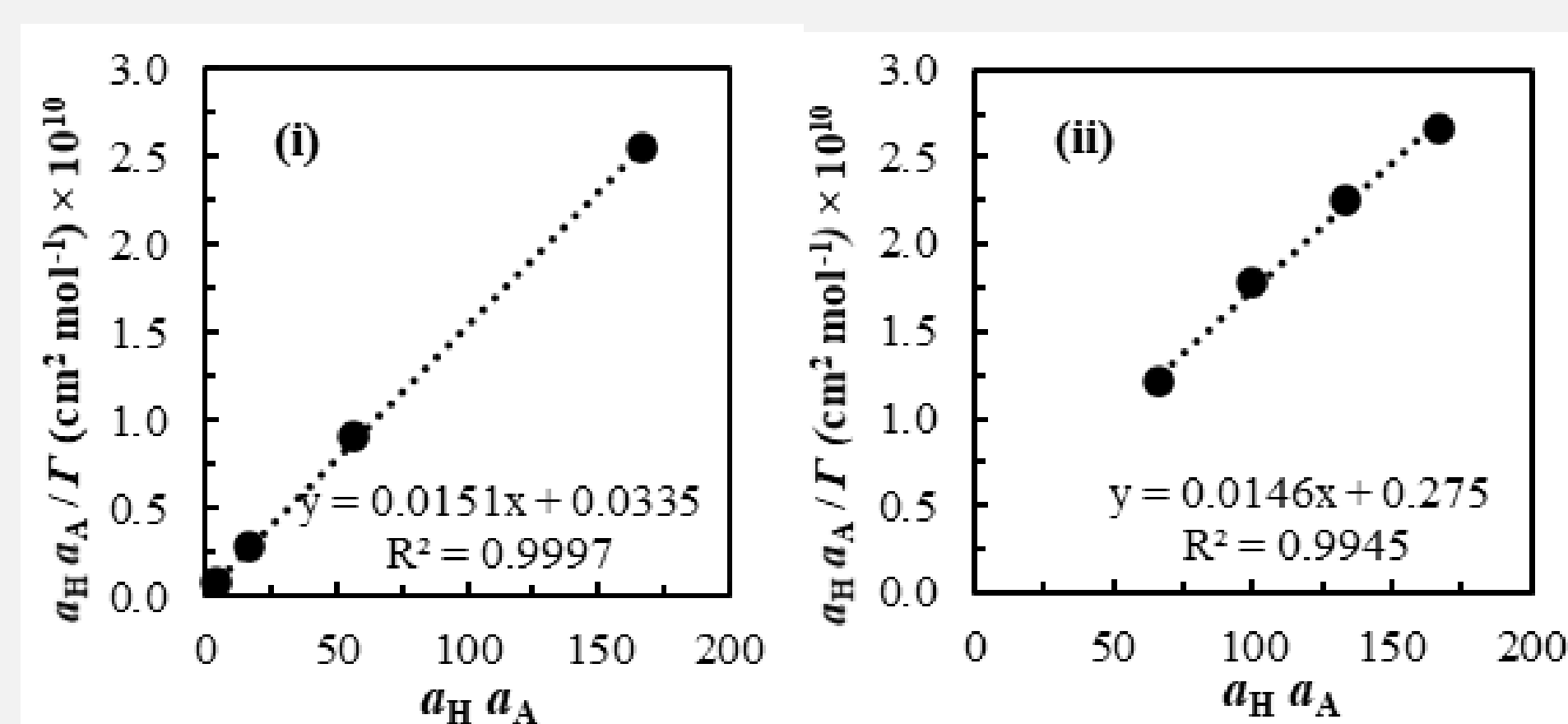

Fig. 1 Langmuir isotherm for two series of data (i) and ii

Conclusion

The assumption of doping process as a Langmuir adsorption for a PANI thin film was experimentally approved. The values for Γ_{max} and B_{ad} obtained for two sets of solution, indicate the significant role of hydrogen ion concentrations in the adsorption affinity. Moreover, the linearity of both figures suggests the contribution of proton along with anion in the doping process.

References

1. Le,T. H., Kim, Y., Yoon, H., Polymers, 2017, 9, 150.

2. MacDiarmid, A. G., Epstein A. J., Faraday Discuss. Chem. Soc., 1989, 88, 317-332.

3. Moghaddam, F. Z., Arefinia, R., J. Electroanal. Chem, 2020, 856, 113652.

4. Farcas, M., Cosman, N. P., Ting, D. K., Roscoe, S. G., Omanovic, S., J. Electroanal. Chem, 2010, 649, 206-218.