PHYSICAL CHEMISTRY 2018

14th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

Proceedings
Volume I

September 24-28, 2018
Belgrade, Serbia

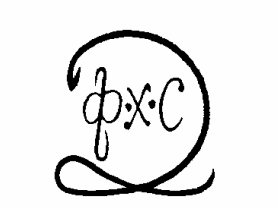
ISBN 978-86-82475-36-1
Title: Physical Chemistry 2018 (Proceedings)
Editors: Željko Čupić and Slobodan Anić
Published by: Society of Physical Chemists of Serbia, Studentski Trg 12-16, 11158, Belgrade, Serbia
Publisher: Society of Physical Chemists of Serbia
For Publisher: S. Anić, President of Society of Physical Chemists of Serbia
Printed by: ″Jovan″, <Printing and Publishing Company, 200 Copies
Number og pages: 550+6, Format B5, printing finished in September 2018

Text and Layout: ″Jovan″

Neither this book nor any part may be reproduced or transmitted in any form or by any means, including photocopying, or by any information storage and retrieval system, without permission in writing from the publisher.

200 - *Copy printing*

CONTENT



PHYSICAL CHEMISTRY 2018

14th International Conference on
Fundamental and Applied Aspects of
Physical Chemistry

Organized by

The Society of Physical Chemists of
Serbia

in co-operation with

Institute of Catalysis Bulgarian Academy of Sciences

and

Boreskov Institute of Catalysis Siberian Branch of
Russian Academy of Sciences

and

University of Belgrade, Serbia:

Faculty of Physical Chemistry
Institute of Chemistry, Technology and Metallurgy
Vinča Institute of Nuclear Sciences
Faculty of Pharmacy
Institute of General and Physical Chemistry, Belgrade, Serbia

Organizing Committee

Chairman: *S. Anić (Serbia)*

Vice-chairmans: *M. Gabrovska (Bulgaria)*
A. A. Vedyagin (Russia)
S. N. Blagojević (Serbia)

Members: *N. Cvjetičanin (Serbia), S. M. Blagojević (Serbia), M. Daković (Serbia), J. Dimitrić-Marković (Serbia), T. Grozdić (Serbia), Lj. Ignjatović (Serbia), D. Jovanović (Serbia),J. Jovanović (Serbia), M. Kuzmanović (Serbia), D. Marković (Serbia), B. Milosavljević (USA), M. Mojović (Serbia), N. Ostrovski (Serbia), N. Pejić (Serbia), M. Petković (Serbia), A. Popović-Bjelić (Serbia), B. Simonović (Serbia), D. Stanisavljev (Serbia), M. Stanković (Serbia), Z. Šaponjić (Serbia), B. Šljukić (Serbia), G. Tasić (Serbia), S. Veličković (Serbia), N. Vukelić (Serbia)*

Scientific Committee

Chairman: *Ž. Čupić (Serbia)*
Vice-chairmans: *V. Bukhtiyarov (Russia)*
S. Todorova (Bulgaria)
B. Adnađević (Serbia)

Members: *S. Anić (Serbia), A. Antić-Jovanović (Serbia), D. J. Biswas (India), R. Cervellati (Italy), G. Ćirić-Marjanović (Serbia), V. Dondur (Serbia), S. D. Furrow (USA), A. Goldbeter (Belgium), R. Jerala (Slovenia), M. Jeremić (Serbia), A. Jovović (Serbia), Y. Kalvachev (Bulgaria), E. Kiš (Serbia), Lj. Kolar-Anić (Serbia), U. Kortz (Germany), T. Kowalska (Poljska), V. Kuntić (Serbia), G. Lente (Hungary), Z. Marković (Serbia), S. Mentus (Serbia), K. Novaković (UK), B. Novakovski (Poljska), S. Otto (Netherlands), V. Parmon (Russia), R. Pascal (USA), M. Perić (Serbia), M. Plavšić (Serbia), J. Savović (Serbia), G. Schmitz (Belgium), I. Schreiber (Czech), L. Schreiberova (Czech), H. W. Siesler (Germany), E. M. Barbosa Souto (Portugal), N. Stepanov (Russia), E. Szabó (Slovakia), R. Tomovska (Spain), Á. Tóth (Hungary), M. Trtica (Serbia), V. Vasić (Serbia), D. Veselinović (Serbia), D. Vučković (Canada), V. Vukojević (Sweden), P. Walde (Switzerland)*

Local Executive Committee

Chairman: *S.N. Blagojević*
Vice-chairmans: *A. Ivanović-Šašić*
A. Stanojević

Members: *M. Ajduković, I. N. Bubanja, A. Dobrota, J. Dostanić, D. Dimić, A. Ignjatović, S. Jovanović, Z. Jovanović, A. Jović, N. Jović-Jovičić, D. Lončarević, M. Kragović, J. Krstić, S. Maćešić, J. Maksimović, S. Marinović, V. Marković, D. Milenković, M. Milovanović, T. Mudrinić, B. Nedić, M. Pagnacco, A. Pavićević, N. Potkonjak, D. Ranković, M. Ristić, B. Stanković, K. Stevanović, M. Stević, A. Stoiljković*

ELECTROCHEMICAL BEHAVIOUR OF NICOTINE ADSORBED ON MONTMORILLONITE

T. Mudrinić, N. Jović-Jovičić, Z. Mojović, A. Milutinović-Nikolić, S. Marinović, M. Ajduković and P. Banković

University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Center for Catalysis and Chemical Engineering, Njegoševa 12, 11000 Belgrade, Serbia (tihana@nanosys.ihtm.bg.ac.rs)

ABSTRACT

The montmorillonite (Mt) and acid modified montmorillonite (Mt_A) were used as nicotine adsorbents. The optimal pH values for nicotine adsorption were 6 and 9 for Mt and Mt_A, respectively. Mt and Mt_A, previously saturated with nicotine via adsorption, at these characteristic pH values, were used as modifiers of carbon paste electrode. The cyclic voltammetry was performed at characteristic pH values (6 and 9) in Britton-Robinson buffer. The obtained cyclic voltammograms depended on both modifier and pH regime of the supporting electrolyte.

INTRODUCTION

Nicotine can be found in surface and groundwater because of possible leaching of nicotine from tobacco industry waste. Monitoring of nicotine presence is water is a challenging task. Development of electrochemical sensors for nicotine could be regarded as promising solution. Such sensors are portable, fast and relatively inexpensive and do not require preparation of sample even the opaque ones. In this paper carbon paste electrode modified with montmorillonite was tested as first step in potential development of sensor that enables detection of nicotine and its differentiation from other analytes that might act as interferences.

EXPERIMENTAL

The Wyoming, USA (Mt) with montmorillonite content of 90 – 100 % was obtained from Clay Mineral Society repository. Acid modified montmorillonite (Mt_A) was prepared following the procedure [1]: 4.5M HCl, 2 h 90 °C, solid to liquid ratio 1:4.5. The rinsing until Cl^- free was performed by dialysis.

The adsorption of nicotine (c=0.75 mmol dm^{-3}, V=50.00 cm^3) onto Mt and Mt_A (m_{ads}=50 mg) was performed in a batch system at 25 ºC in thermostated shaker (Memmert WNE 14 and SV 1422). Thermo Electron

Nicolet Evolution 500 UV-Vis was used for monitoring the nicotine concentration before and after adsorption (λ_{max}=261 nm). The materials with adsorbed nicotine were used as modifiers of carbon paste electrode. The electrode was prepared by hand mixing of clay, carbon black (Vulcan-XC 72R) and paraffin oil with mass ratio 10:1:4. The resulting paste was packed into the hollow electrode and used as working electrode. The reference electrode was Ag/AgCl in 3 M KCl, while a platinum rod served as a counter electrode. The cyclic voltammetry was performed using Autolab electrochemical workstation (Autolab PGSTAT302N, Metrohm-Autolab BV). The supporting electrolyte was 0.1 M Britton-Robinson buffer. pH meter (PHM240 MeterLab®) was used to control the solution pH.

RESULTS AND DISCUSSION

The study of the influence of pH on the percent of the adsorbed nicotine onto Mt and Mt_A (Fig. 1) was conducted using pH of initial nicotine solutions in the range from 2 to 12 [2]. The Mt as adsorbent showed the highest efficiency at pH=6, while Mt_A at pH=9. The adsorption of nicotine is governed by the form of nicotine molecule in solution and surface acidity of adsorbents. At different pH nicotine can be found as neutral molecule, mono- and di-protonated cations [3]. At pH<3 diprotonated form of nicotine is dominant. With the increase of pH, the presence of monoprotonated form of the nicotine increases. At pH=6 the molecular form of nicotine appears. With further increase of pH, molecular form of nicotine becomes dominant. At pH≈9, solution contains approx. 90% of nicotine in the molecular form, while the rest is in monoprotonated form. Therefore, the most efficient adsorption onto Mt occurred at pH=6 with monoprotonated form of nicotine as the most dominant form. On the other hand at pH=9, where Mt_A exhibited the best adsorption performance, molecular form of nicotine was mainly adsorbed.

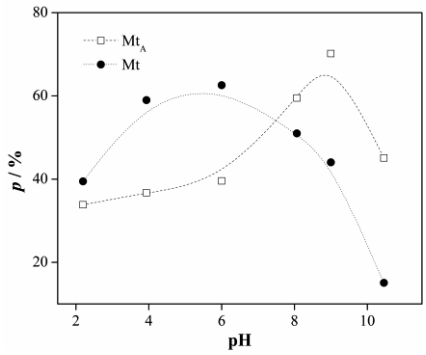


Figure 1. Percent of the adsorbed nicotine vs. pH.

Cyclovoltammograms (CV) were recorded on different pH values: the pH where adsorption was performed (Fig. 2a) and on opposite pH (Fig. 2b) i.e. if the adsorption was performed at pH=6 the CV was recorded at pH=9 and vice versa.

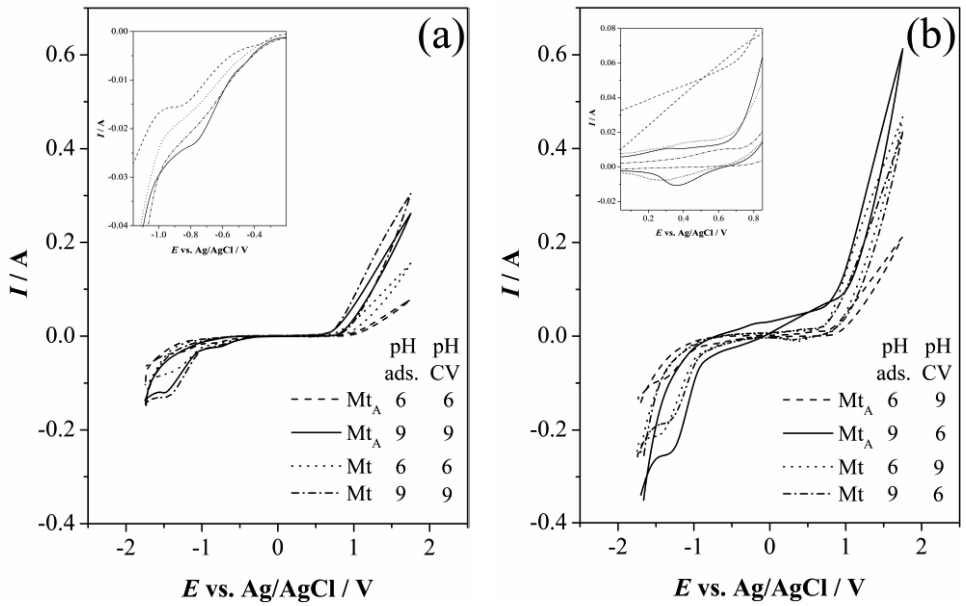


Figure 2. CV of nicotine adsorbed on Mt and Mt_A in buffered solution. Adsorption and CV were performed: a) at same pH, b) at opposite pH

All CV exhibited increase of anodic current due to nicotine oxidation and cathodic peak due to nicotine reduction. These characteristic currents were lower for CV performed at pH where adsorption was performed in comparison to CV performed at opposite pH. CV recorded at pH where the adsorption was performed exhibited additional cathodic wave at lower potential than main cathodic peak (inserted graph in Fig. 2a). This peak was more expressed with carbon paste electrode modified with Mt_A. CV recorded at the opposite pH exhibited additional pair of peaks at the foot of the anodic increase (inserted graph in Fig. 2b) due to nicotine oxidation. The peaks were best developed for CV recorded at pH=9 for electrode modified with Mt where nicotine was adsorbed at pH=6. CV recorded at pH=6 for electrode modified with Mt_A where nicotine was adsorbed at pH=9 exhibited hysteresis.

Additional experiments are needed in order to clarify electrochemical behavior of nicotine particularly since literature data on this subject are deficient. Suffredini et al. [4] has suggested mechanism of nicotine electrooxidation that is not sufficient to elaborate the results obtained in this paper.

CONCLUSION

The optimal pH values for nicotine adsorption on montmorillonite (Mt) and acid modified montmorillonite (Mt_A) were 6 and 9, respectively. Mt and Mt_A were saturated with nicotine by adsorption at pH 6 and 9. Materials prepared in this manner were used as modifiers of carbon paste electrode. The cyclic voltammetry was performed at same characteristic pH values in Britton-Robinson buffer. All CV exhibited increase of anodic current due to nicotine oxidation and cathodic peak due to nicotine reduction. These characteristic currents were lower for CV performed at pH where adsorption was performed in comparison to CV performed at opposite pH (meaning that if the adsorption was performed at pH=6 the CV was recorded at pH=9 and vice versa).

Acknowledgement

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (III 45001).

REFERENCES

[1] Z. Vuković, A. Milutinović-Nikolić, Lj. Rožić, A. Rosić, Z. Nedić, D. Jovanović, Clays and Clay Minerals, 2006, 54, 697-702.
[2] I. Ilić, N. Jović-Jovičić, P. Banković, Z. Mojović, D. Lončarević, I. Gržetić and A. Milutinović-Nikolić, Science of Sintering, 2018 *in Press*.
[3] D. Hoffmann, I. Hoffmann, Journal of Toxicology and Environmental Health, 1997, 50, 307-364.
[4] H. B. Suffredini, M. C. Santos, D. De Souza, L. Codognoto, P. Homem-de-Mello, K. M. Honório, A. B. F. da Silva, S. A. S. Machado, L. A. Avaca, Analytical Letters, 2005, 38, 1587–1599.