

Accepted Manuscript

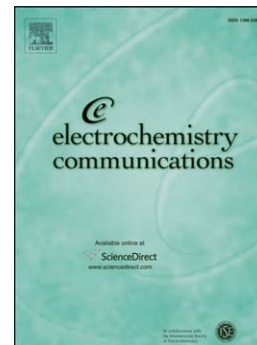
Interaction of water with methanesulfonic acid on Pt single crystal electrodes

Andrea P. Sandoval, Marco F. Suárez-Herrera, Víctor Climent, Juan M. Feliu

PII: S1388-2481(14)00344-0
DOI: doi: [10.1016/j.elecom.2014.11.007](https://doi.org/10.1016/j.elecom.2014.11.007)
Reference: ELECOM 5314

To appear in: *Electrochemistry Communications*

Received date: 21 October 2014
Revised date: 6 November 2014
Accepted date: 7 November 2014



Please cite this article as: Andrea P. Sandoval, Marco F. Suárez-Herrera, Víctor Climent, Juan M. Feliu, Interaction of water with methanesulfonic acid on Pt single crystal electrodes, *Electrochemistry Communications* (2014), doi: [10.1016/j.elecom.2014.11.007](https://doi.org/10.1016/j.elecom.2014.11.007)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Interaction of water with methanesulfonic acid on Pt single crystal electrodes

Andrea P. Sandoval^{a,b}, Marco F. Suárez-Herrera^b, Víctor Climent^a, Juan M. Feliu^{a}*

^a Departamento de Química Física e Instituto Universitario de Electroquímica
Universidad de Alicante, Apartado 99, E-03080 Alicante (Spain)

^b Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia,
Cra. 30# 45-03, Edificio 451, Bogotá (Colombia)

*Corresponding author: juan.feliu@ua.es, Tel: +34 965 909 301, Fax: +34 965 903 537

Abstract

The electrochemical behavior of methanesulfonic acid on platinum single crystal electrode surfaces is investigated by cyclic voltammetry and infrared spectroscopy measurements. The results are compared with those characteristic of perchloric and trifluoromethanesulfonic acids. The differences on the voltammetric profile are interpreted in terms of the effect of the anion on the structure of water. No adsorbed species are detected by infrared spectroscopy.

Keywords: Methanesulfonic acid, platinum single crystal electrodes, cyclic voltammetry, anion adsorption.

1. Introduction

Methanesulfonic acid (MSA) is used as catalyst in organic chemistry [1-4] and electrolyte for electrodeposition (mainly of tin and lead [5-9]) or fuel cells [10-12]. MSA is also one of the atmospheric oxidation products of dimethyl sulfide [13-15] and it is known to be efficient in forming aerosol particles which serve as cloud condensation nuclei [16].

In order to understand all the above processes it is important to study the effect of MSA on the water structure at the interfaces such as the electrode-electrolyte and liquid-gas

interfaces. Since anions can exert a strong influence on the electrochemical reactivity, most often hindering the reaction (for example, the oxygen reduction reaction [17]), it is of major importance to analyze their behavior under controlled conditions. In this work, the behavior of MSA solutions on platinum single crystal electrodes is studied by means of cyclic voltammetry and infrared spectroscopy. Comparison is made with other (weakly) adsorbed anions such as perchlorate [18] and trifluoromethanesulfonate. [19].

2. Experimental

Platinum single crystals prepared following standard procedures [20] were used as working electrodes. The electrodes were heated in a gas-oxygen flame, cooled down in reductive atmosphere ($H_2 + Ar$) and protected with a droplet of water. Solutions were prepared from perchloric acid (Merck suprapur) and MSA (Merck for synthesis, $\geq 99\%$) in ultrapure water ($18.2 M\Omega\cdot cm$, Elga Vivendi) and deaerated with Argon ($Ar \geq 99.995\%$ Alphagaz). Chemicals were used as received without further purification.

In situ external reflection infrared spectroscopic experiments were performed in a Nexus 8700 (Thermo Scientific) spectrometer using SNIFTIRS (Subtractively Normalize Interfacial Fourier Transform InfraRed Spectroscopy) technique [21]. 500 interferograms were collected. The reference spectrum was collected at 0.10V. Attenuated total reflection spectra of the solution (ATR) were obtained using a ZnSe hemicylindrical window and collecting 100 interferograms.

3. Results and discussion

Figure 1 compares the voltammograms recorded for the three platinum basal planes in MSA and $HClO_4$. On Pt(111) there is an almost perfect coincidence in the hydrogen adsorption region regardless of the upper potential limit used, 1 V (figure 1a) or 1,2 V (figure 2a). The small peak observed in the negative scan at 0.52 V can be due to some impurity of the reagent, possibly sulfate coming from the degradation of MSA. This feature decreases and becomes negligible when the sweep rate is increased. However, differences

on the voltammetric profile are significant in the OH adsorption zone (0.5 V -0.9 V) and where the monolayer of platinum oxide is formed (1V -1.2 V). The OH adsorption region is characterized by two adsorption states. As it was suggested for perchloric acid [20], the processes correspond to OH adsorption from structured (OH_b , 0.4V - 0.7V) and unstructured water molecules (OH_s , 0.7 V - 0.75 V). The presence of anions that break or promote water structuring modifies the intensity and position of the sharp peak. The MSA causes the separation of the two peaks which shift in opposite directions. The OH_b region has a more rounded shape between 0.52V and 0.75V and is followed by a marked peak at 0.813V. The charge involved in the first peak is $44.7 \mu\text{C cm}^{-2}$ while that in the second peak is $53.4 \mu\text{C cm}^{-2}$. This latter value doubles that calculated for the spike in HClO_4 ($27\mu\text{C cm}^{-2}$)[18].

A similar study with trifluoromethanesulfonic acid (TFMSA) revealed an almost identical voltammetric behavior between TFMSA and perchloric acid [19]. The SO_3 moiety of the trifluoromethanesulfonate ion is less polarizable and it has less negative charge density around it than the SO_3 group of the methanesulfonate ion [22]. This means that the interaction between methanesulfonate and water is stronger than the interaction between trifluoromethanesulfonate and water.

The interaction of MSA with water has been the subject of several studies. Allen et al [16] reported that the presence of MSA enhances the coordination between interfacial water molecules, and that the oxygen atoms of MSA significantly form hydrogen bonds with the free OH. On the other hand, the study of Li et al [23] supports the fact that the hydration of MSA by a small number of water molecules is thermodynamically highly favored. This theoretical study also shows that the hydrogen-bond distance in the monohydrated MSA is 1.715 \AA , which is considerably shorter than that of the water dimer, 1.96 \AA . This indicates a very strong hydrogen bond between acid and water.

It has been reported [18] that ionic kosmotropes (structure makers) shift to higher potential the spike located at about 0,8 V (figure 1a) and ionic chaotropes (structure breakers) shift the spike to lower potentials. The experimental data of Figure 1a support the fact that the

methanesulfonate anion is a strong kosmotrope. As far of the authors knowledge there is no report of an anion that can change in such extension the voltammetric profile of the adsorbed OH on Pt(111) in aqueous media.

Figure 3 shows the fit of different adsorption isotherms to the voltammetric currents in the region of OH adsorption. The three fits are based on the Frumkin isotherm [18], extended to the case of two different sources of OH, structured and unstructured water and correspond to different models: i) Two different water species populate the same adsorbed state following equation (1) where g_1 and g_2 are related to lateral interaction. ii) Two different water species adsorb in two completely independent adsorption states [24]. Each isotherm is simulated by equations (2a) and (2b), and solved by equation (2c). Parameter h_i is the weighting factor for the i adsorbed state. iii) Two water species produce two different adsorbed products that compete for the same surface sites. Parameters n_{ij} in equations (3a) and (3b) represents the number of adsorption sites for species j blocked by species i . Instead of solving equations (3a) and (3b) for θ_1 and θ_2 , an equivalent set of differential equations was solved using the DDEBDF routine from SLATEC package.

$$\frac{\theta}{1-\theta} = \exp\left(\frac{F}{RT}(E-E_1^0) - g_1\theta\right) + \exp\left(\frac{F}{RT}(E-E_2^0) - g_2\theta\right) \quad (1)$$

$$\frac{\theta_1}{1-\theta_1} = \exp\left[\frac{F}{RT}(E-E_1^0) - g_1(\theta_1 - 0.5)\right] \quad (2a)$$

$$\frac{\theta_2}{1-\theta_2} = \exp\left[\frac{F}{RT}(E-E_2^0) - g_2(\theta_2 - 0.5)\right] \quad (2b)$$

$$\theta = h_1\theta_1 + (1-h_1)\theta_2 \quad (2c)$$

$$\frac{\theta_1}{1-n_{11}\theta_1 - n_{21}\theta_2} = \exp\left[\frac{F}{RT}(E-E_1^0) - g_1\theta_1\right] \quad (3a)$$

$$\frac{\theta_2}{1-n_{12}\theta_1 - n_{22}\theta_2} = \exp\left[\frac{F}{RT}(E-E_2^0) - g_2\theta_2\right] \quad (3b)$$

The first case, which allows the best fit for perchloric acid, leads to a poorer fit for MSA and is unable to explain the separation of the two processes. The second case is less realistic and has only been included here as an academic exercise. Finally, the case of competitive adsorption gives better results although it is still unable to perfectly fit the experimental shape. The results obtained with the latter model imply repulsion between the adsorbed species for the OH_b peak (corresponding to a negative values of the interaction parameter of about -5) and attraction between the adsorbed species for the OH_s (corresponding to a positive values of the interaction parameter of about 3.3). More work is in progress to understand these differences and get information about interfacial water interaction with the Pt(111) surface.

It can also be seen in Figure 2a that the first surface oxidation peak shifts toward higher potentials although the charge remains the same as in perchloric acid ($154 \mu\text{C cm}^{-2}$). This points out that the nucleation and growth kinetics leading to O_{ads} formation [25] is affected by the presence of methanesulfonate anions, either because the previously adsorbed OH layer interacts with the anions in solution or because the effect of the anion on the water structure affects the kinetics of the oxidation.

The behavior of Pt(100) dramatically changes in the presence of MSA. Figure 1d shows that the same three peaks found in HClO_4 are present in the first scan. However, these peaks decrease and broaden in subsequent scans, figure 1b. Two couples of peaks remain stable at 0.27 and 0.35V. The increase in potential up to 1.2V produces two oxidation peaks around 0.80 V and 1.05 V (Figure 2b). The first peak is absent in perchloric acid. The hydrogen adsorption region changes in two broad peaks. The changes in the voltammetry can be related with the modification of the competitive H^+/OH adsorption as it has been proposed for perchloric acid [26]. In fact, the region between 0.40 and 0.70V shows a much lower adsorption of OH while the hydrogen adsorption has been displaced to lower potentials. This behavior supports hydrogen adsorption in the first two peaks in perchloric and MSA solutions, and the lower availability of free OH to be adsorbed in MSA in the highest potential region.

In the case of Pt(110) the hydrogen adsorption region is also modified. There are two oxidation peaks at 0.14 and 0.20 V and only one reduction peak at 0.10V (figure 1c). However, the charge involved in the two peaks in perchloric acid ($210 \mu\text{C cm}^{-2}$) has almost the same value as that observed in MSA ($217 \mu\text{C cm}^{-2}$). Besides, when the upper potential limit of the voltammetric scan is restricted to 0.185V (figure 1e), a symmetric reduction peak is observed. This behavior seems to be related to the hydrogen availability in both acids. Despite of the fact that both acids are very strong[27, 28], the energy to transfer an H^+ ion from the solution phase to the electrode surface to form an adsorbed hydrogen atom must be higher in the presence of more structured water. This seems to be the case in the presence of MSA in comparison to perchloric acid. The latter facts can explain the overpotential needed for the first adsorbed state on Pt(110) in the presence of MSA. The excursion to oxidative potentials up to 1.2 V shows two oxidation peaks at 0.81 and 1.047V, slightly shifted to higher potentials than in perchloric acid. Only one broad reduction peak is observed at 0.771 V.

Results show that MSA anions interact weakly with Pt single crystal surfaces, although the modifications of the voltammetric profiles are more important than those observed in the presence of perchlorate, fluoride or trifluoromethanesulfonate anions. This is particularly important with Pt(100) and Pt(110).

SNIFTIR spectra collected in the presence of MSA using p-polarization are compared with the solution spectrum in figure 4. Typical bands of the dissociated acid are seen in the later. The assignment of the bands based on the literature is: $\nu_{\text{asym}} \text{SO}_2$ 1334 cm^{-1} , $\nu_{\text{sym}} \text{SO}_2$ 1184 cm^{-1} , $\delta \text{S-O-H}$ 1111 cm^{-1} , $\nu_{\text{sym}} \text{SO}_3^-$ 1049 cm^{-1} [29, 30]. None of these bands or others related to MSA decomposition were observed in the SNIFTIR spectra. This means that methanesulfonate anion does not adsorb on the Pt basal planes, as it was reported for TFMSA [19]. A small amount of adsorbed species, below the detection limit of the infrared measurement, cannot be discarded, specially for the case of Pt(100).

4. Conclusions

MSA is an electrolyte that does not adsorb on platinum surfaces. However, its interaction with water causes some changes in the shape of the characteristic voltammetric profiles. The voltammetry of Pt(111) in MSA and HClO₄ are very different in the region of OH adsorption, exhibiting stronger separation of the two processes in this region. This has been explained in terms of the effect of the anion on the structure of water. Hence, the use of single crystal electrodes is very useful and sensitive to point out the effect of ions on the water structure at the electrode-electrolyte interface.

Acknowledgements

APS acknowledges the scholarship “Estudiantes sobresalientes de posgrado” at the UNC and COLCIENCIAS National Doctoral Scholarship (567) MFS acknowledges support of UNC (Research Project 19030). JMF thanks Generatitat Valenciana (Feder) through project PROMETEOII/2014/013.

References

1. C. Wang, X. Ma, J. Zhang, Q. Tang, W. Jiao, H. Shao, *Eur. J. Org. Chem.*, 2014 (2014) 4592.
2. B. X. Luong, A. L. Petre, W. F. Hoelderich, A. Commarieu, J. A. Laffitte, M. Espeillac, J. C. Souchet, *J. Catal.*, 226 (2004) 301.
3. L. Fabian, M. Gómez, J. A. C. Kuran, G. Moltrasio, A. Moglioni, *Synth. Commun.*, 44 (2014) 2386.
4. L. M. Goldenberg, S. Aeiyaich, P. C. Lacaze, *Synt. Met.*, 51 (1992) 349.
5. M. D. Gernon, M. Wu, T. Buszta, P. Janney, *Green Chem.*, 1 (1999) 127.
6. I. Sirés, C. T. J. Low, C. Ponce-de-León, F. C. Walsh, *Electrochem. Commun.*, 12 (2010) 70.
7. N. Pewnim, S. Roy, *Trans. Inst. Met. Finish.*, 89 (2011) 206.
8. R. Sekar, S. Jayakrishnan, *Trans. Inst. Met. Finish.*, 90 (2012) 324.
9. C. T. J. Low, F. C. Walsh, *Surf. Coat. Technol.*, 202 (2008) 1339.

10. J. Ahmad, T. H. Nguyen, R. T. Foley, *J. Electrochem. Soc.*, 128 (1981) 2257.
11. J. Maruyama, I. Abe, *J. Power. Sources.*, 148 (2005) 1.
12. A. Oury, A. Kirchev, Y. Bultel, *J. Power. Sources.*, 264 (2014) 22.
13. H. Berresheim, F. L. Eisele, *J. Geophys. Res.*, 103 (1998) 1619.
14. S. P. Urbanski, P. H. Wine, in Z.B. Alfassi (Ed.), *S-centered Radicals*, Wiley, 1999.
15. K. Sehested, J. Holcman, *Rad. Phys. Chem.*, 47 (1996) 357.
16. H. C. Allen, E. A. Raymond, G. L. Richmond, *J. Phys. Chem. A.*, 105 (2001) 1649.
17. M. Teliska, V. S. Murthi, S. Mukerjee, D. E. Ramaker, *J. Electrochem. Soc.*, 152 (2005) A2159-A2169.
18. A. Berná, V. Climent, J. M. Feliu, *Electrochem. Commun.*, 9 (2007) 2789.
19. A. Berná, J. M. Feliu, L. Gancs, S. Mukerjee, *Electrochem. Commun.*, 10 (2008) 1695.
20. C. Korzeniewski, V. Climent, J. M. Feliu, in A.J. Bard, C.G. Zoski (Eds.), *Electroanalytical Chemistry: A Series of Advances*, vol. 24, CRC Press, Boca Raton, 2012.
21. A. Berná, A. Kuzume, E. Herrero, J. M. Feliu, *Surf. Sci.*, 602 (2008) 84.
22. A. Krishtal, P. Senet, C. Van Alsenoy, *J. Chem. Theory Comput.*, 4 (2008) 2122.
23. S. Li, W. Qian, F.-M. Tao, *Chem. Phys. Lett.*, 438 (2007) 190.
24. D. Armand, J. Clavilier, *J. Electroanal. Chem.*, 225 (1987) 205.
25. A. M. Gómez-Marín, J. M. Feliu, *Electrochim Acta*, 104 (2013) 367.
26. N. Garcia-Araez, V. Climent, J. M. Feliu, *J. Electroanal. Chem.*, 649 (2014) 69.
27. J. Zhang, Y. Sun, C. Mao, H. Gao, W. Zhou, Z. Zhou, *J. Molec. Struc. THEOCHEM*, 906 (2009) 46.
28. S. Patai, Z. Rappoport, *The Chemistry of Sulphonic Acids, Esters and their Derivatives*, John Wiley and Sons, New York, 1991.
29. A. Givan, A. Loewenschuss, C. J. Nielsen, *J. Molec. Struc.*, 748 (2005) 77.
30. X. Chen, B. Minofar, P. Jungwirth, H. C. Allen, *J. Phys. Chem. B*, 114 (2010) 15546.

Figure captions

Figure 1 Cyclic Voltammetry of a) Pt(111), b) Pt(100), c) Pt(110) in 0.1M HClO₄ (black line), and 0.1M MSA (red line). d) First scan of Pt(100) in MSA. e) MSA limited to 0.185V Scan rate 50mVs⁻¹.

Figure 2 Cyclic Voltammetry of a) Pt(111), b) Pt(100), c) Pt(110) in 0.1M HClO₄ (black line), and 0.1M MSA (red line). Scan rate 50mVs⁻¹.

Figure 3 Fit of several isotherms to the voltammetric currents in the OH adsorption region. (dashed line) experimental data; (red line) two different water species populating the same adsorbed state; (blue) two independent Frumkin isotherms and (green) Competitive Frumkin adsorption. See text.

Figure 4 Infrared spectra of 0.1M MSA on a) Pt(111), b) Pt(100), c)Pt(110) and d) ATR solution spectrum.

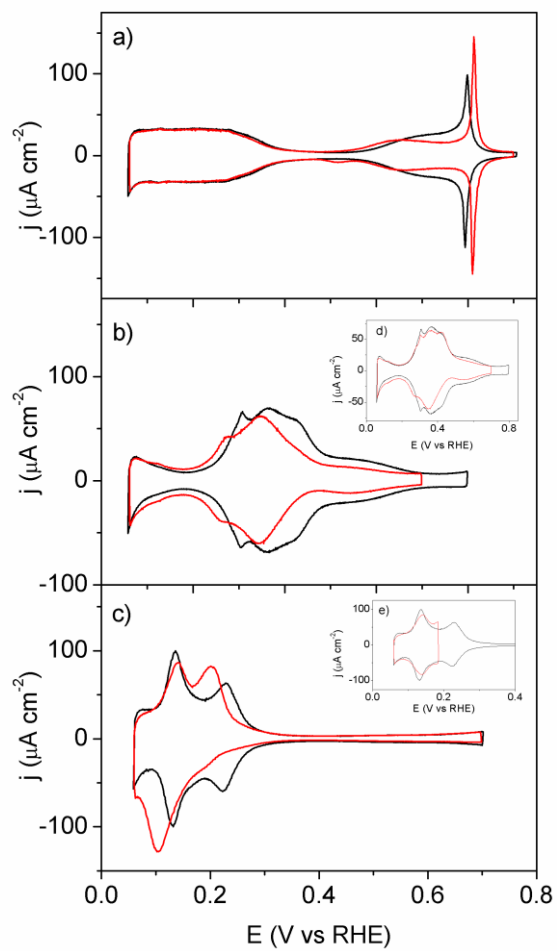


Figure 1

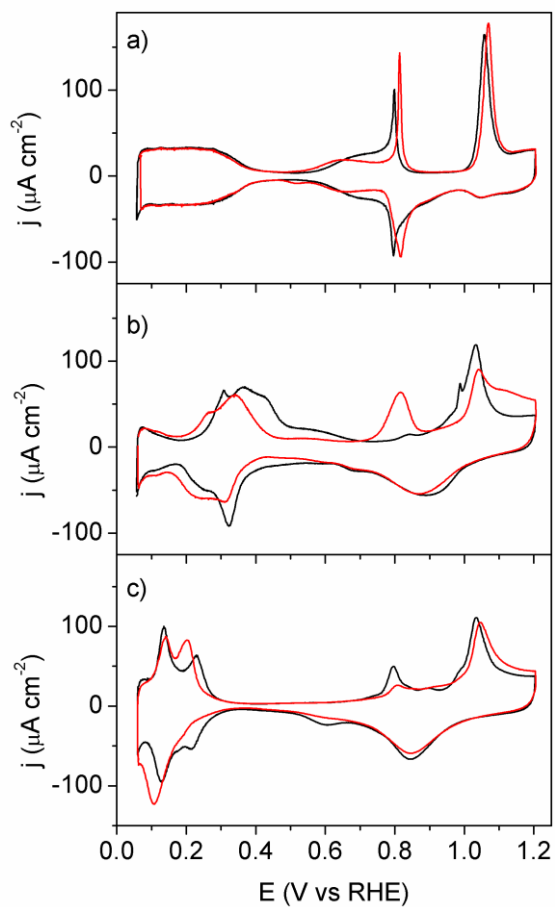


Figure 2

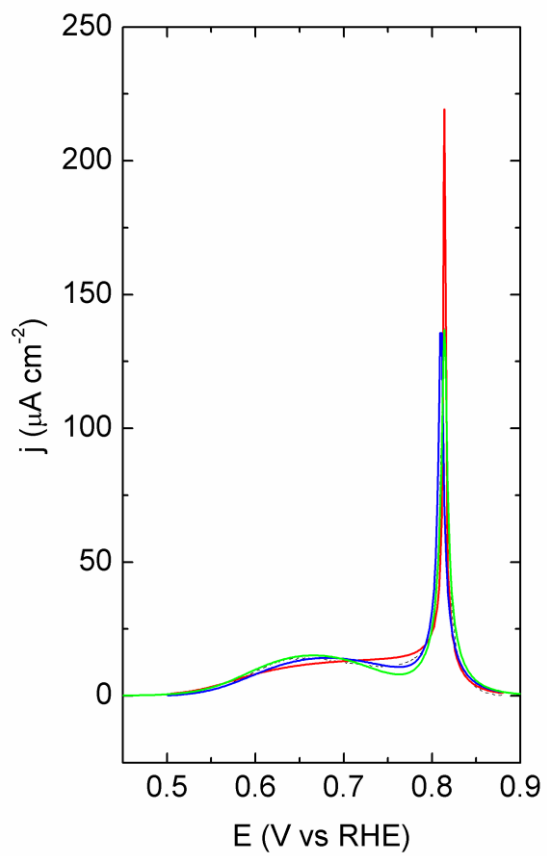


Figure 3

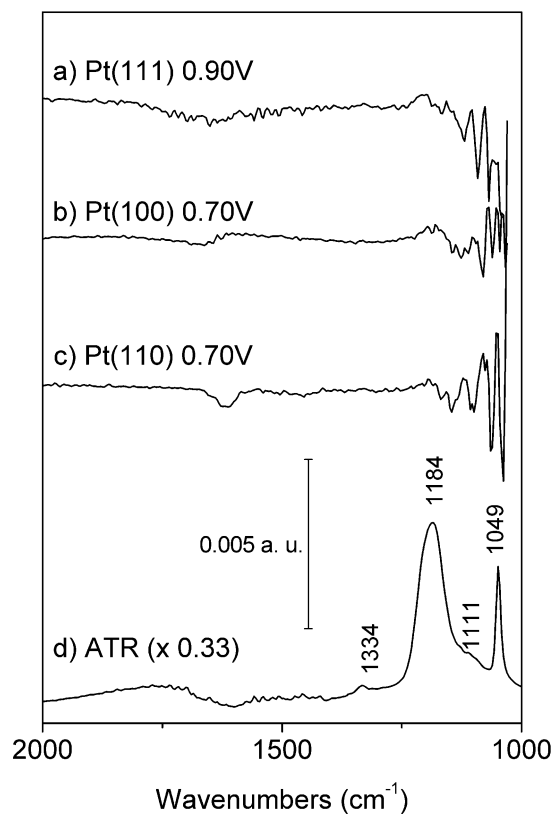


Figure 4

Highlights

- MSA was studied on platinum single crystals.
- MSA does not adsorb on platinum surfaces.
- MSA voltammetric profile differs from that of perchloric and TFMSA.
- High separation between structured and unstructured water observed on Pt(111).
- Voltammetry of Pt(111) indicates interaction of water and MSA.

ACCEPTED MANUSCRIPT