

New voltammetric method useful for water insoluble or weakly soluble compounds: application to p*K*_a determination of hydroxyl coumarin derivatives

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Abstract Here, we reveal a different way of doing the voltammetric experiments that considers the electroactive species packaged in the electrodic phase instead of dissolved in solution. In this way, it is possible to obtain voltammograms of insoluble species. In this work, the method is exemplified by obtaining voltammograms for weakly soluble coumarins but it could be extrapolated to other weakly soluble compounds. We have studied a comprehensive series of 3-acetyl-hydroxycoumarins derivatives which are insoluble in aqueous medium but capable of being trapped in a three-dimensional multi-walled carbon nanotubes (MWCNT) network. Consequently, an electrodic phase composed of an MWCNT modified glassy carbon electrode (GCE) containing the coumarin derivative is prepared. The voltammetric experiment is performed with the above electrodic phase and an aqueous medium as the solution phase. All the coumarin derivatives show one anodic peak due to the oxidation of the hydroxyl group in the phenyl ring. The oxidation peaks follow a one-electron, one-proton irreversible, pH-dependent process for all monohydroxylated compounds. The *E*_p values are closely dependent of the substituent effect being the 7,8-cum derivative more easily oxidized due to both the electron donor effect of neighboring hydroxyls groups and hydrogen bonding interaction between them. On the other hand, the hydroxyl of the 7-

cum derivative is the most difficult to oxidize due to the electron-attracting effect of the lactone carbonyl group at position 2 and acetyl carbonyl at position 3 which is conjugated with OH at 7 positions. From the breaks in the graphs *E*_p versus pH, we estimate the voltammetric p*K*_a values for all the studied coumarin derivatives.

Keywords Coumarin derivatives · MWCNT · Modified electrode

Introduction

Carbon nanotubes (CNT) have revolutionized the way we do electrochemistry. Its use as electrode materials has expanded exponentially in the last 15 years. In a search carried out using the Scopus database with the keywords “carbon nanotube” and “electrode,” we recovered 653 documents in the year 2002 and 26,810 documents in 2016, representing an increase of more than 40 times in 15 years.

The bonding in CNT is essentially sp²; however, the tube curvature, apart from yielding quantum confinement and quantized conductance, also causes σ–π rehybridization, an effect that is stronger as the CNT diameter decreases [1]. In such case, three σ bonds are slightly out of plane and for compensation, the π orbitals are more delocalized outside the tube. That is the main difference with respect to graphite in which the sp² hybrid orbital form three in-plane σ bonds with an out-of-plane π orbital. The electron cloud distortion induced by the tube curvature, which yields a rich π-electron conjugation outside the tube, can make CNT more electrochemically active and electrically and thermally more conductive. The above is the key for the main advantage of CNTs as electrode material. The high specific surface of CNTs together with the σ–π rehybridization and the presence of structural

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defects facilitate different chemical processes such as chemical derivatization, intercalation, molecular adsorption, doping, charge transfer, etc. [2, 3]. Consequently, their electronic properties and their physical characteristics such as high surface-to-volume ratio and porosity provide many interesting applications as electrode phase. One of the most important advantages of the CNTs is the possibility to modify them with several organic or inorganic chemical compounds changing dramatically the properties of the electrode phase.

The state of the art of the electrochemical study of insoluble compounds has been prodigal in the field of the Solid State Electroanalytical Chemistry (SSEAC) which deals with studies of the processes, materials, and methods specifically aimed to obtain analytical information (quantitative elemental composition, phase composition, structure information, and reactivity) on solid materials by means of electrochemical methods [4]. That review deals with the relationships between molecular electrochemistry (i.e., solution electrochemistry) and solid state electrochemistry as applied to analysis. Special attention is focused on a critical evaluation of the different types of analytical information that are accessible by SSEAC. On the other hand, the strategy of incorporating electroactive species into inorganic matrices such as electrode phases has been profusely developed and very well summarized in a monographic issue of *J. Solid State Electrochem.* [5]. In summary, this monographic issue presents a quite comprehensive view of the electrochemistry of micro and mesoporous silica and aluminosilicate-based materials and layered double hydroxides where the reader can find representative examples of the theoretical and practical aspects, including synthesis, analysis, physical chemistry, and energy management, which are a matter of research in the field of electrochemistry.

Despite the above, the use of multi-walled carbon nanotubes (MWCNTs) as a bed to support the electroactive species in the voltammetric experiment is a rather unexplored matter. Recently, we revealed a new strategy to study the voltammetric behavior of nitrocompounds encapsulated on (MWCNT) or more precisely by being trapped within the pockets of the MWCNTs three-dimensional array, without formation of covalent bonding [6–8]. The procedure involves physical adsorption that is based on weak interactions (e.g., π - π stacking, electrostatic forces, Van der Waals forces, and hydrophobic interactions). It is particularly attractive because it offers the possibility of attaching chemical handles preserving the sp^2 nanotube structure and consequently not affecting the electronic network. Furthermore, this procedure generates a non-conventional way to perform the voltammetric experiment [9].

The above procedure was described only for aromatic nitrocompounds, but our current challenge is to extend it to other compounds in order to generalize it. One of the main advantages of this non-conventional way of performing voltammetry is that it allows the study of poorly soluble

compounds. Therefore, in this work, we will test this new non-conventional form of voltammetry with a series of coumarin derivatives that have very little solubility in aqueous medium, and therefore its conventional voltammetric study in aqueous medium is not possible.

Experimental

Apparatus and reagents

Voltammetric measurements were carried out in a conventional three-electrode cell using a CHI760 100 voltammetric analyzer. We used a glassy carbon electrode (GCE) measuring 3 mm in diameter (model CHI104, CH instruments) as the working electrode. A platinum wire (CHI115) and an Ag/AgCl/KCl electrode (0.3 M) (CHI111) were used as the auxiliary and reference electrodes, respectively. All potentials are referred to the Ag/AgCl reference electrode. MWCNTs (1.5 μ m in length and 10 nm in diameter) were obtained from Dropsens S.L., Spain.

Dimethylformamide (DMF) containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as electrolytic medium was used for non-aqueous voltammetry on GCE.

Britton-Robinson buffer (B-R) as electrolytic medium was used for non-conventional voltammetry on GCE modified with MWCNTs (MWCNTGCE) and coumarin derivatives encapsulated.

A small electrochemical cell containing 8 mL of electrolyte solution was used. pH adjustment was monitored using a PMX 3000 WTW pH/ion meter microprocessor (basic pH) and a pH meter 537 WTW Microprocessor (acidic pH).

All reagents and solvents were purchased by Aldrich and were used as received without further purification. Melting points were determined using a Kofler camera Bock monoscope. A 300-MHz spectrometer (Bruker, WM 300) was used for ¹H NMR analysis.

All coumarin derivatives (Fig. 1) were synthesized in our laboratory according to the following:

General procedure

An equimolar mixture of the respective hydroxyaldehyde and ethyl acetoacetate in ethanol, together with catalytic amounts of piperidine, was added and the reaction undergoes to reflux for 2–3 h. The product is vacuum filtered and recrystallized in ethanol [10]. All compounds were previously reported [11–13], and ¹H NMR analysis corroborates the results of synthesis:

3-acetyl-6-hydroxycoumarin (6-cum): 85%. m.p. 254–256 °C, ¹H NMR (DMSO-d₆ δ (ppm)): (2.57, s, 3 H), (7.16, dd, J = 8.9 y 2.9 Hz, 1H), (7.23, d, J = 2.9 Hz, 1H),

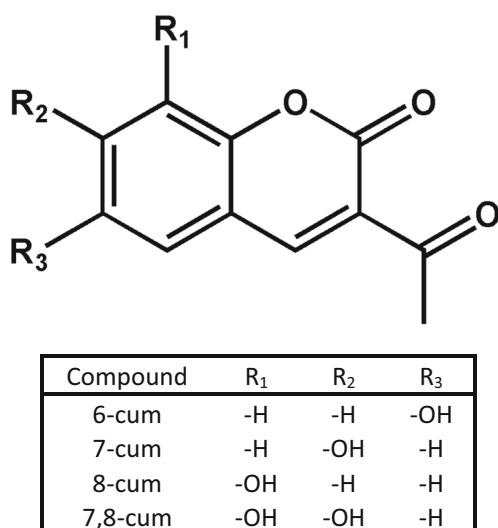


Fig. 1 Molecular structure of 3-acetyl-hydroxycoumarin derivatives

(7.58, d, $J = 8.9$ Hz, 1H), (8.56, s, H-chromene), (9.92, s, OH-Ar).

3-acetyl-7-hydroxycoumarin (7-cum): 77%. m.p. 234–236 °C, ^1H NMR (DMSO- d_6 δ (ppm)): (2.49, s, 3 H), (6.41, d, $J = 1.9$, 1H), (6.60, dd, $J = 8.7$ Hz, 1.9 Hz, 1H), (7.58, d, $J = 8.7$ Hz, 1H), (8.44, s, H-chromene).

3-acetyl-8-hydroxycoumarin (8-cum): 41%. Sublimates > 200 °C ^1H NMR (DMSO- d_6 δ (ppm)): (2.58, s, 3H), (7.21–7.17, m, 2H), (7.33, t, $J = 8.8$, 1.9 Hz, 1H), (8.57, s, H-chromene), (10.41, s, OH-Ar) ppm.

3-acetyl-7,8-dihydroxycoumarin (7,8-cum): 65%. Sublimates > 190 °C ^1H NMR (DMSO- d_6 δ (ppm)): (2.5, s, 3H), (6.78, d, $J = 8.71$, 1H), (7.30, d, $J = 8.23$, 1H), (8.54, s, H-chromene), (9.6, s, O-H), (10.67, s, OH-Ar).

Preparation of MWCNT suspensions and modified GCEs

Before each modification, the GCE was cleaned by polishing it with 0.3 μm and 0.05 μm alumina and then was washed thoroughly with water. The MWCNTs were dispersed in 1,3-dioxolane by sonicating for 5 min. The sonication procedure was repeated three times. The MWCNTs were immobilized by casting 5 μL of the MWCNT dispersion on the GCE. Then, the modified electrodes were obtained by drying the dispersion at room temperature.

Adsorption and voltammetry of coumarin derivatives

The voltammetric determination was carried out on GCE modified with MWCNTs (MWCNTGCE) and adsorbed coumarin derivatives. The adsorption process involved the dipping of the MWCNTGCE in dry acetonitrile solution

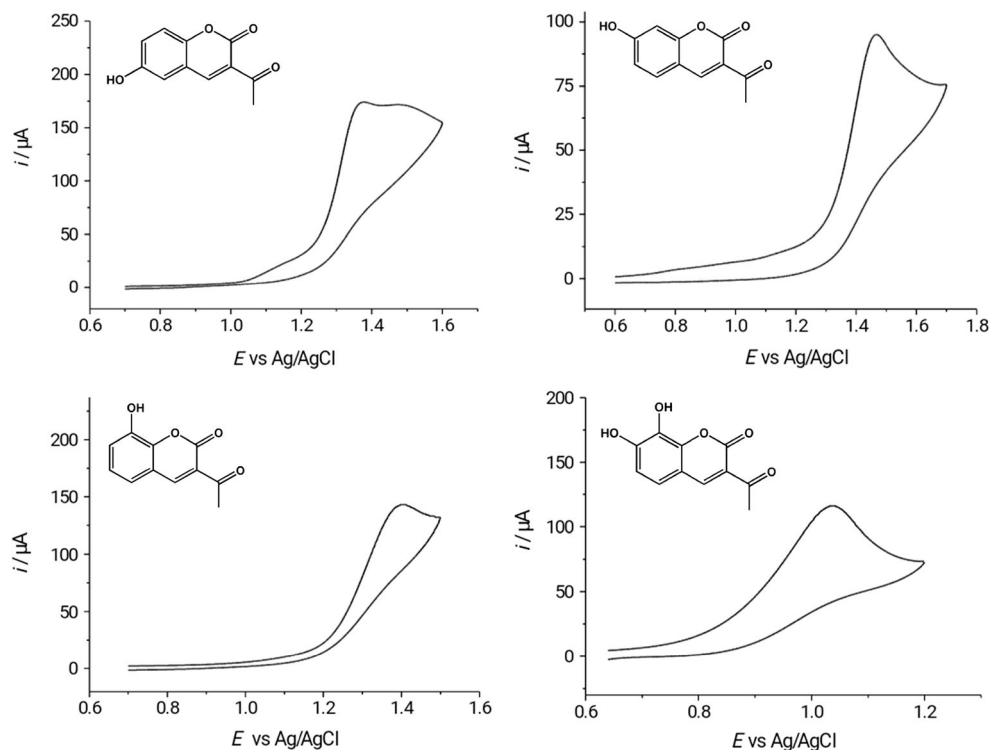
containing 5 mM of coumarin derivative. The optimum dipping time was 60 s, and no potential was applied during the dipping step. Because of the dipping step, the coumarin derivative was adsorbed on the modified electrode. Then, the electrode was washed with milliQ water yielding the modified electrodes: 6-cum-MWCNTGCE, 7-cum-MWCNTGCE, 8-cum-MWCNTGCE, and 7,8-cum-MWCNTGCE. Then, each modified electrode was immersed in an electrochemistry cell containing only (without coumarin derivative) aqueous medium (Britton–Robinson buffer), and then potential was scanned between 0.10 and 1.40 V versus Ag/AgCl to register the voltammetric curve.

Results and discussion

All the studied coumarins (Fig. 1) are insoluble in aqueous medium, and therefore, the only way to perform a conventional voltammetric study is in non-aqueous medium. Figure 2 shows the cyclic voltammograms of all the studied coumarin derivatives on a glassy carbon electrode (GCE) in a non-aqueous medium containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as electrolytic medium. From these voltammograms, we can observe that all compounds show one irreversible oxidation peak due to the oxidation of the OH phenolic group. There are several evidences in the literature showing that the electroactive group in hydroxycoumarins derivatives is the OH group [14–17]. In our case, depending on the nature of the coumarin derivative, the observed peak potentials (E_p) due to the OH group oxidation are 1.38, 1.47, 1.41, and 1.04 V versus Ag/AgCl for 6-cum, 7-cum, 8-cum, and 7,8-cum, respectively. From the comparison of the peak potential values, we can conclude that the oxidation of all monohydroxylated derivatives occurs with approximately the same degree of difficulty in non-aqueous medium. However, the dihydroxylated 7,8-cum derivative is oxidized significantly easier. This difference is probably due to both the electron donor effect of the neighboring hydroxyl groups and hydrogen bonding interaction between them.

On the other hand, from the extensive bibliographical evidence, it is clear that the oxidation of the OH phenolic group depends on the activity of the protons in the medium. Therefore, the proper way to study oxidations of OH phenolic group is in aqueous medium with control of the proton activity. In the case of the coumarin derivatives, the situation is rather difficult due to the insoluble character of these compounds. However, we can overcome this difficulty by applying a different procedure, recently developed in our laboratory [9], that allows us to perform voltammetry in a non-conventional way. In fact, this non-conventional mode involves working with the coumarin derivatives trapped in the electrode rather than being dissolved in the solution phase. In this case, we trapped the coumarin derivatives in the electrode

Fig. 2 Cyclic voltammograms of all the studied coumarin derivatives on GCE in a non-aqueous medium containing 0.1 M TBAPF₆. Sweep rate = 100 mV/s



phase, and then the modified electrode with coumarin derivatives is immersed in aqueous solution and then potential scan was applied. In this way, we can work with insoluble or weakly soluble electroactive species such as the coumarin derivatives.

When these coumarin derivatives are incorporated in the electrode phase and then the electrode immersed in a solution containing only the buffer, we obtained voltammograms of coumarin derivatives at different pHs. Figure 3 shows the cyclic voltammograms (CVs) of all the studied coumarin derivatives entrapped on the electrode phase and immersed in a Britton-Robinson aqueous buffer at pH = 7.0. All the CVs showed a single anodic peak due to the OH group oxidation. The observed E_p values depend on the nature of the coumarin derivative being 0.75, 0.80, 0.62, and 0.44 V versus Ag/AgCl for 6-cum, 7-cum, 8-cum, and 7,8-cum, respectively. From the comparison of the CVs obtained according to the conventional voltammetry (Fig. 2) and the CV obtained with the non-conventional voltammetry (Fig. 3), it is clear the adsorptive character of the peaks obtained by the latter. However, some qualitative characteristics of the oxidation signals are equivalent since in both cases, the oxidation of the dihydroxylated derivative is significantly easier than the rest of the monohydroxylated ones. The qualitative similarities of the oxidation obtained according to the conventional procedure with the non-conventional procedure is a proof that the binding of the coumarin derivatives with the carbon nanotubes does not imply a covalent bond. Using conventional voltammetry, it is not possible to follow the pH dependence of the E_p

because it is not possible to maintain the coumarin derivatives solubilized in aqueous buffer.

The selectivity of voltammetric method depends on the difference of peak potential, with a minimum difference of 0.2–0.3 V for a linear potential scan and 0.04–0.05 V for differential pulse voltammetry (DPV) [18]. Consequently, in order to

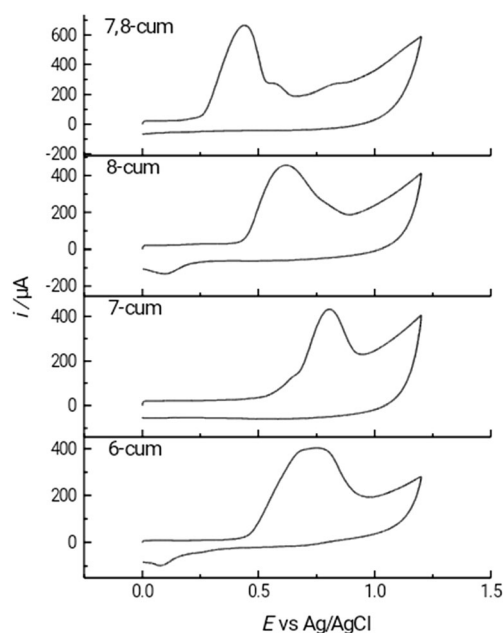


Fig. 3 Cyclic voltammograms of all the studied coumarin derivatives entrapped on a modified MWCNTGCE immersed in a Britton-Robinson buffer pH = 7.0. Sweep rate 100 mV/s

obtain more accurate oxidation potential values, we try DPV using a modified GCE as working electrode. In Fig. 4, we can appreciate DPV curves of the monohydroxylated 7-cum and the dihydroxylated 7,8-cum derivatives trapped in the modified electrode at three different pHs buffer solutions. The hydroxyl group in the phenyl ring undergoes electrochemical oxidation on the expected potential of phenolic compounds. In Table 1, we display the obtained E_p values for all the 3-acetyl-hydroxycoumarin derivatives at pH 7. The E_p values are closely dependent of the substituent effect. In similar way as it was observed previously in non-aqueous medium, the 7,8-cum derivative is more easily oxidized due to the electron donor effect of the neighboring OHs and hydrogen bonding formation between them. Furthermore, in this aqueous medium, it is possible to distinguish other substituent effects between the monohydroxylated compounds. In fact, the 7-cum derivative is the most difficult to oxidize due to the electron-attracting effect of the carbonyl groups at positions 2 and in the acetyl group at position 3 which are conjugated with OH at 7 positions. On the other hand, in the case of 6-cum and 8-cum, the OH group is conjugated to the lactonic-O- group in position 1, which acts by increasing the electron density on the OH group facilitating its oxidation. This effect is increased in 8-cum due to the proximity of interacting groups, which explains that 8-cum is oxidized easier than 6-cum.

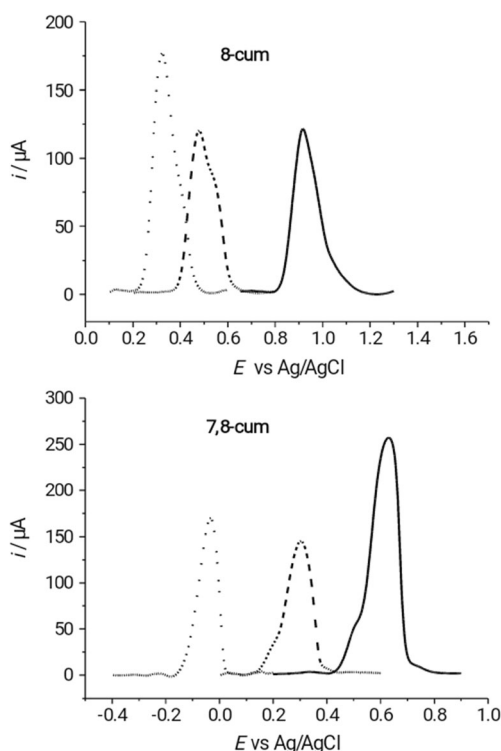


Fig. 4 Differential pulse voltammograms of 7-cum and 7,8-cum derivatives entrapped on a modified MWCNTGCE immersed in a Britton-Robinson buffer at three different pHs. pH = 2 (dotted line); pH = 7 (dashed line); pH = 11 (whole line)

Table 1 Peak potentials (E_p) values obtained from differential pulse voltammetry at pH 7 for all the 3-acetyl-hydroxycoumarin derivatives

Compound	$E_{p_a}/(V)$	pKa	Slope/(mV/pH)
6-cum	0.56	10.37	− 69.35
7-cum	0.66	6.85	− 69.09
8-cum	0.48	9.07	− 73.96
7,8-cum	0.30	9.10	− 64.85

Slope and pKa values obtained from the E_p versus pH plot

On the other hand, all the above-observed substituent effects in the voltammetric behavior reveal that the coumarin derivatives are electronically unaltered on the electrode phase discarding covalent bond between coumarin derivatives and MWCNTs.

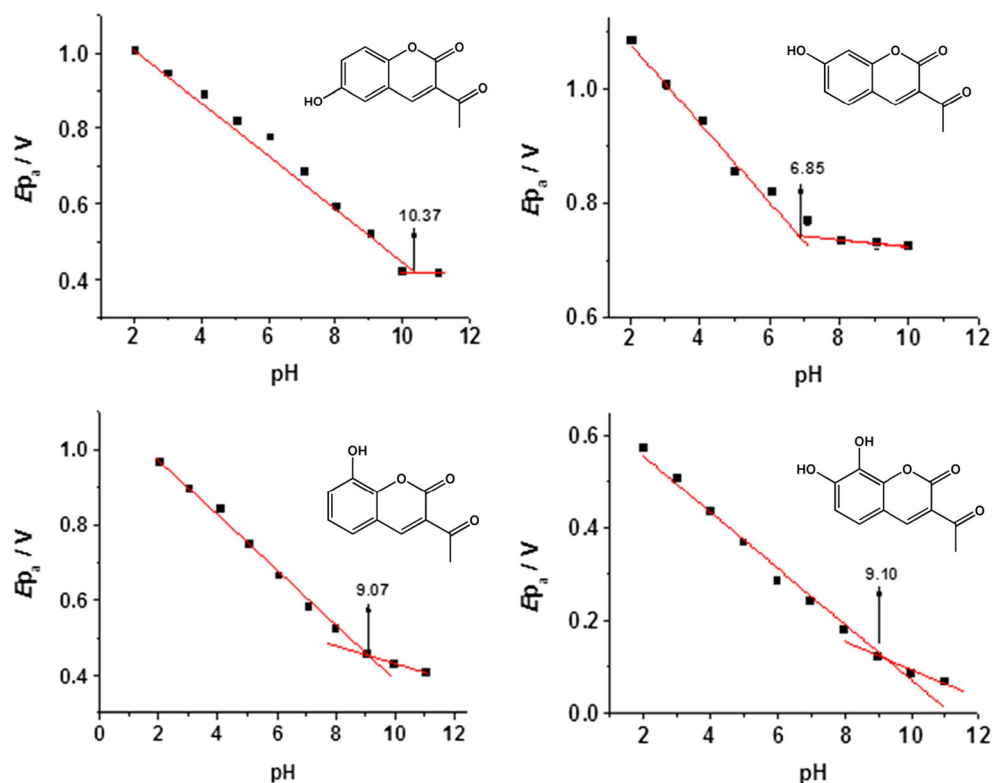
In addition, we studied the pH dependence of the anodic peak on a wide pH range (pH 2.0 to 11.0). The peak potentials shifted to lower values with pH increase in a linear way up to a certain value depending on the type of coumarin derivative. In Fig. 5, we show the E_p versus pH plots obtained from the DPV measurements. In Table 1, we summarize the slope values obtained from the E_p versus pH plots. The slopes are approx. 70 mV per pH unit thus showing that the oxidation of 3-acetyl-hydroxycoumarin derivatives entrapped at MWCNTGCE, in aqueous media, involves the same number of electrons and protons. Furthermore, from the similarity of the slopes, we can conclude that all compounds follow the same mechanism. Consequently, the oxidation peaks follow a one-electron, one-proton irreversible, pH-dependent process as was previously revealed for a related compound [16].

The oxidation of the coumarin derivatives processes is electrochemically irreversible. Consequently, the determined peak potentials have no thermodynamic meaning and would be, in principle, unable to be used for determining thermodynamic parameters, such as pKa. However, based in the previous work of Stradins [19], who studied the influence of pH on electro-oxidation potentials of about 100 substituted phenols and evaluated pKa from anodic voltammetry data, we can validate the determination from the oxidation potentials of irreversible processes. That paper showed that the method was found to be successful in spite of the irreversibility of the overall electrochemical reactions of most of the phenols studied, but good correspondence between pKa values, determined by spectrometry and by anodic voltammetry, proved the validity of the approach.

Consequently, from the breaks in the graphs E_p versus pH, we can estimate the voltammetric pKa values for all the studied coumarin derivatives.

In Table 1, we can observe the pKa values for all the studied compounds. From these pKa values, we can conclude that the 7-cum derivative has the most acidic OH, probably due to the influence of the electron-withdrawing carbonyl groups at

Fig. 5 E_p versus pH plots for all 3-acetyl-hydroxycoumarin derivatives



positions 2 and 3 which are conjugated to the OH at position 7. In a separate study, a pK_a value of 6.6 was informed for the 7-cum derivative given validity to our results (<http://www.sigmaaldrich.com/catalog/product/sigma/01545?lang=es®ion=CL>). Furthermore, pK_a values of compounds very close to those studied here such as 7-hydroxycoumarin ($pK_a = 7.8$) [20] and 3-carboxylic acid-7-hydroxycoumarin ($pK_a = 7.04$) [21] show values of pK_a very consistent with those found in this work.

Conclusions

We have shown that by the appropriate modification of a GCE with MWCNTs and the subsequent trapping of 3-acetyl-hydroxycoumarins within the three-dimensional array of the MWCNTs, it is possible to perform voltammetry with insoluble or weakly soluble compounds. In this work, it is exemplified by obtaining voltammograms for weakly soluble coumarins but can be extrapolated to others weakly soluble compounds.

All the synthesized coumarin derivatives show one anodic peak due to the oxidation of the hydroxyl group in the phenyl ring showing to undergo electrochemical oxidation on the expected potential for phenolic compounds. The oxidation peaks follow a one-electron, one-proton irreversible, pH-dependent process as was previously revealed for a related compound [16].

The E_p values are closely dependent of the substituent effect. The 7,8-cum derivative results to be more easily oxidized due to the electron donor effect of the neighboring OH that increases the electron density in the electroactive OH. On the other hand, the 7-cum derivative is the most difficult to oxidize due to the electron-attracting effect of the carbonyl groups at positions 2 and 3 which are conjugated with OH at 7 positions.

From the breaks in the graphs E_p versus pH, we can estimate the voltammetric pK_a values for all the studied coumarin derivatives. From these pK_a values, we can conclude that the 7-cum derivative has the most acidic OH, also due to the influence of the electron-withdrawing carbonyl groups at positions 2 and 3 which are conjugated to the OH at position 7.

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