



Electrochemical study of the metal extractant 4-chloro-*N*-8-quinolinybenzenesulfonamide

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ABSTRACT

The electrochemical behaviour of the reagent 4-chloro-*N*-8-quinolinybenzenesulfonamide has been studied by sampled direct current and differential pulse polarography as well as by cyclic voltamperometry techniques. Three reduction waves are obtained and the reversibility and nature of the electrodic processes are discussed. The first and third reduction waves have been explained through chemical reactions and adsorption processes involving the interaction with mercury as electrodic material, whereas the second wave is attributed to the reduction process of the reagent itself. Acidity constant values of the compound in 0.1 M KCl / 25 % methanol medium through polarographic measurements are also given. The influence of the addition of copper to the hydroalcoholic solution in the electrochemical reduction of the reagent is also described.

1. Introduction

Despite the scarce use of electrochemical techniques in hydrometallurgy, different aspects of the extraction processes have been studied through these methods. The extraction mechanism of several lanthanides by β -dicetones [1] phosphine oxides [2] and amines [3] has been studied recording polarograms of the aqueous phases during the extraction processes. On the other hand, cyclic voltamperometry has been applied to obtain distribution constant values of chelating extractants between organic and aqueous phases [4]. Recently, the distribution ratio of copper with the chelating agent 1-phenyl-3-methyl-4-benzoyl-pyrazolone has been evaluated using voltamperometric techniques [5].

4-chloro-*N*-8-quinolinybenzenesulfonamide is a compound closely related to the commercial extractant LIX 34. This extractant, proposed for copper extraction from acidic leach liquors [6], contains 4-alkyl-*N*-8-quinolinybenzenesulfonamide as active component [7]. However, the presence of several isomers of the active component in the commercial reagent often hinders the study of the extractant properties. Therefore, the use of analogous compounds becomes useful. In this sense, 4-methyl-*N*-8-quinolinybenzenesulfonamide was used as model compound and its behaviour in organic solvents [8,9], extractive capacity for several metals ions [10,11], acid-base properties [12] and electrochemical behaviour [13] were reported.

The substitution in the quinolinybenzenesulfonamide molecule of an alkyl group by an electronegative one such as chloro is expected to increase the acidity of the reagent and, consequently, to improve its extractive properties. For this purpose, 4-chloro-*N*-8-quinolinybenzenesulfonamide was synthesized and the increase of the extraction ability for copper was corroborated [14].

In a previous work, the electrochemical reduction of 4-methyl-*N*-8-quinolinybenzenesulfonamide was studied by differential pulse polarography (DPP) and cyclic voltamperometry [13]. Three reduction waves were reported, the second one (≈ -900 mV) attributed to the reduction of 4-methyl-*N*-8-quinolinybenzenesulfonamide, was performed through the cleavage of the S-N bound. On the other hand, the first and the third waves were related to the interaction of the reagent with the electrodic material.

In the present work, the electrochemical behaviour of 4-chloro-*N*-8-quinolinybenzenesulfonamide by differential pulse and cyclic voltamperometry is studied. The influence of the presence of Cu(II) in the electrochemical reduction of the reagent looking for complex formation in the hydroalcoholic solution is also studied.

2. Experimental

2.1. Reagents and solutions

4-chloro-*N*-8-quinolinybenzenesulfonamide (HL) was synthesized and purified as described elsewhere [14]. Solutions of the reagent ($C_{HL} = 6.28 \cdot 10^{-5}$ M) in 0.1 M KCl and 25 % methanol were used. Previously the composition of the medium was optimized in order to maintain a constant ionic strength and to assure the solubility of the extractant in the hydroalcoholic medium in all the experimental conditions used. The acidity was adjusted using Britton-Robinson buffer solutions (mixture of phosphoric, acetic and boric acids, 0.04 M each). Phosphoric acid/potassium dihydrogenphosphate buffer was used in the study of the extractant in the presence of Cu(II). Copper solutions were prepared from $CuSO_4$ (Merck, p.a.). All the chemicals used were of analytical reagent grade.

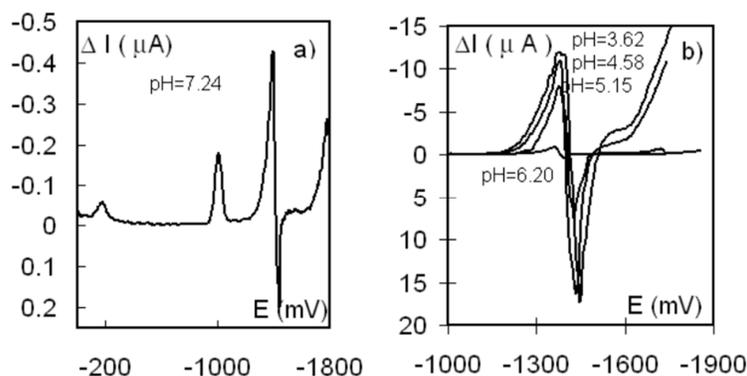


Figure 1. Differential pulse polarograms of 4-chloro-*N*-8-quinolinylbenzenesulfonamide a) at pH = 7.24 and b) the third peak at different pH values.

2.2. Experimental procedure

The electrochemical measurements were carried out using an Inelecsa voltamperometric analyzer. A three-electrode cell (25 mL capacity) was used. The cell consists of a glass cylinder with a cap having holes for introducing electrodes and tubing for nitrogen gas. A platinum auxiliary electrode and a saturated calomel electrode [Hg/Hg₂Cl₂/KCl] as reference electrode were used for all measurements.

The working electrode was either a dropping mercury electrode (DME), a hanging mercury drop (HMDE) or a glassy carbon electrode. The electrodes were washed with doubly distilled water/methanol and tested prior to each experiment.

Polarography in sampled dc (5 mV/s and 1 s drop-time) and differential pulse modes (5 mV/s and 1 s drop-time) was applied. Cyclic voltammograms were recorded at scan rate ranging from 0.2 up to 10 V/s.

All the experiments were performed at 298 ± 0.5 K. Oxygen was removed from the solutions by passing nitrogen gas through the solution for about 10 min.

The pH of the solutions was measured using a Radiometer pHM64 fitted with an Ingold combined Ag/AgCl glass electrode.

For each experiment the corresponding blank solution was also registered and taken into account when necessary.

3. Results and discussion

3.1. Effect of pH on the current-voltage function

The current-voltage function in sampled dc polarography, differential pulse polarography and cyclic voltamperometry was investigated by recording voltammograms of the reagent at different pH values. In all cases several waves were observed suggesting three different processes.

The use of sampled dc polarography technique showed that the first reduction wave dropped into positive intensity at the beginning of the wave, whereas the third wave showed a maximum. Only the second wave followed the standard pattern.

On the other hand, and using differential pulse polarography, the chelating reagent exhibited three reduction peaks at the studied pH range (1.0 – 11.0). The extractant solutions showed only one reduction peak at potential values close to –800 mV at acidic conditions, whereas at neutral pH values two new reduction peaks (around –150 mV and –1400 mV) appeared. A typical polarogram is shown in Figure 1a, whereas Figure 1b shows the peculiar shape of the third peak, which seems to be due to the presence of some catalytic process.

The variation of the potential of the three peaks with pH is illustrated in Figure 2a. The first reduction peak shows two

differentiated linear parts which break at pH = 8.8. The representation for the second reduction peak reveals three linear parts that break at pH = 2.6 and pH = 8.8. Thus the value of pK_a = 8.8 can be estimated and log K = 2.6 can be attributed to the protonation of the amino group in the reagent. Finally, the potential of the third peak, which only appears when the reagent is present as the neutral protolytic form, does not vary with pH.

Comparing these pK_a values with those obtained for 4-methyl-*N*-8-quinolinylbenzenesulfonamide in the same conditions (3.0 and 9.2, respectively), [13] it can be noticed that the acidity constant value due to the protonation of the quinoline group is slightly higher for the methyl homologue whereas the substitution of methyl by chloro increases the acidity of the compound in 0.6 unities. Moreover, this pK_a can be predicted considering the mentioned substitution according to the procedure described by Perrin *et al.* [15] which takes into account Hammett equation and the constant values due to the contribution of each substituent.

On the other hand, the variation of the current as a function of pH for the first and second peaks is shown in Figure 2b. It can be appreciated that the intensity of the first peak is practically constant with pH whereas the second peak intensity decreases with this magnitude. However, the sum of the intensities of both peaks is practically constant until pH ~ 8.5. These results seem to indicate that the extractant participates in two different processes. Finally, the intensity of the third peak (not shown) strongly decreases with pH.

Cyclic voltammograms for 4-chloro-*N*-8-quinolinylbenzenesulfonamide solutions showed only one reduction peak at potential values close to –800 mV at acidic conditions. When pH increased up to 6.2 two new reduction peaks (around –150 mV and –1400 mV) appeared together with anodic waves. At higher values (pH > 8.5) the first reduction peak splitted in two, as seen in Figure 3. The dependence of the potential peak with pH in cyclic voltammograms was quite similar to that shown in differential pulse polarography measurements.

3.2. Reversibility of the electrodic processes

The reversibility of the electrodic processes was studied using sampled dc polarography and cyclic voltamperometry.

The logarithmic analysis of the waves obtained in sampled dc mode gave rise to αn values for the second reduction process which ranged from 1 to 2 (mean value 1.3) at different pH values. Assuming that the reduction process involves two electrons [16] it seems to be an irreversible process. Two straight lines were obtained for the third reduction wave thus indicating a complex process.

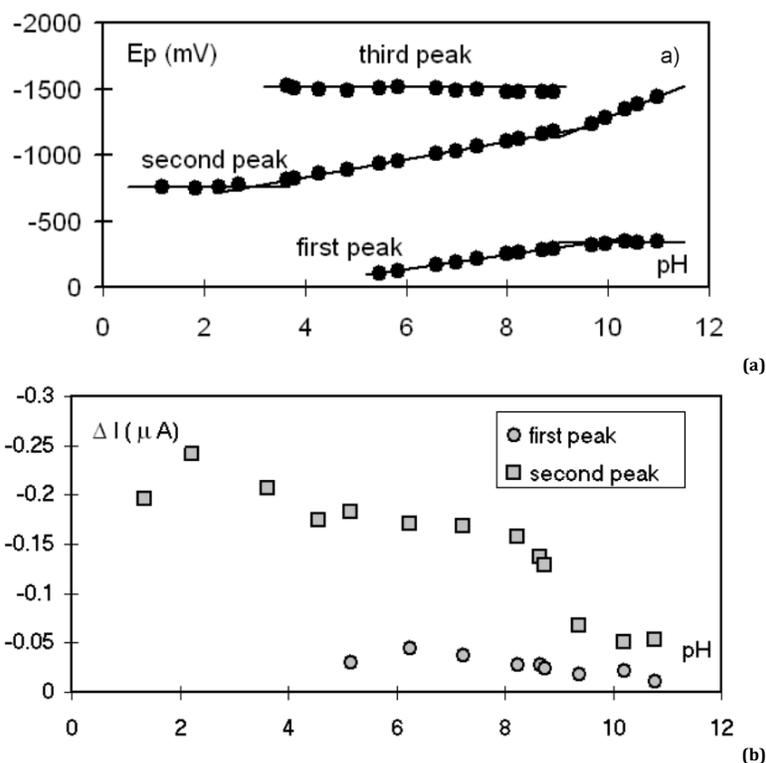


Figure 2. Variation of (a) potential and (b) intensity of the reduction peaks of 4-chloro-*N*-8-quinolinylbenzenesulfonamide with pH.

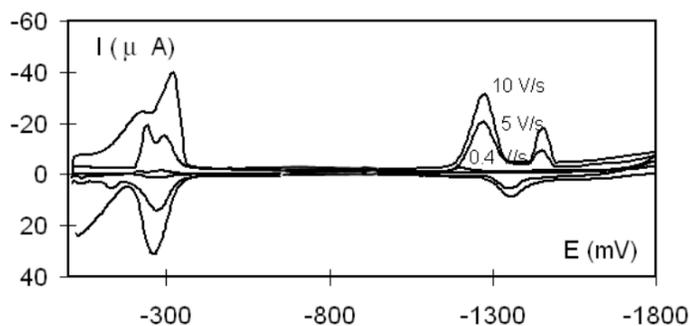


Figure 3. Cyclic voltammograms of 4-chloro-*N*-8-quinolinylbenzenesulfonamide at different scan rates (pH = 8.5).

Finally, the positive intensity observed in the polarogram of the first reduction wave did not allow the calculation of the corresponding αn values.

The results obtained using cyclic voltamperometry showed the presence of anodic waves for the first process in the whole pH range studied. The same was observed for the third process in neutral and alkaline conditions. No anodic wave could be appreciated for the second process.

From the plots of the intensities of cathodic and anodic peaks as a function of the scan rate it could be deduced that the ratio of both magnitudes was close to 1.0 for the first process, except at low pH values. In the case of the third process the ratio was different to 1.0 in acidic conditions.

Furthermore, the study of the reversibility of the reduction processes of 4-chloro-*N*-8-quinolinylbenzenesulfonamide was carried out through the relationship between peak potential (E_p) and scan rate ($\log v$) in cyclic voltammograms of the

reagent solutions. The function $E_p = f(\log v)$ was represented for all the anodic and cathodic peaks at several pH values.

The potential remained nearly constant for the first anodic and cathodic peaks, which seems to indicate a reversible behaviour of the electrodic process. On the other hand, the plot of the function $E_p = f(\log v)$ for the third peak revealed the reversible behaviour of the process in neutral and alkaline conditions, whereas small deviations in acidic conditions and high scan rate values were observed.

However, both reduction processes seem not to be completely reversible attending to the values of the differences between the cathodic and anodic peak potentials at the different scan rates as well as considering peak widths.

Finally, Figure 4 illustrates the function $E_p = f(\log v)$ for the second peak. The peak potential shifts to more negative values when increasing the scan rate.

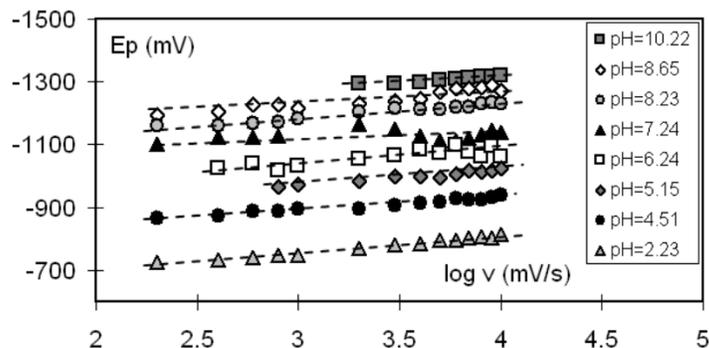


Figure 4. Plot of the function $E_p = f(\log v)$ for the second reduction peak of 4-chloro-*N*-8-quinolinylbenzenesulfonamide at different pH values.

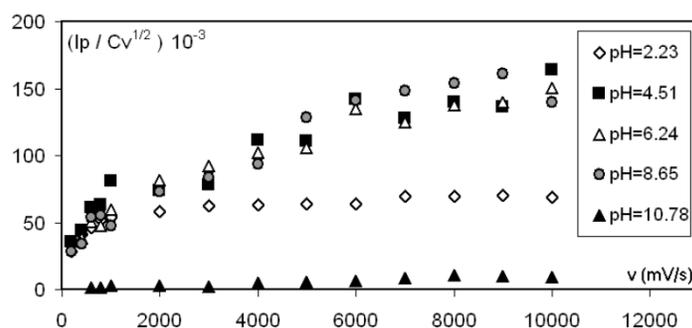


Figure 5. Variation of the peak current function with the scan rate for the second wave of 4-chloro-*N*-8-quinolinylbenzenesulfonamide.

From the slopes of this function at different pH values, the values of αn were estimated ($\alpha n = 1.1$ at $\text{pH} < \text{pK}_{a1}$, $\alpha n = 1.4$ at $\text{pK}_{a1} < \text{pH} < \text{pK}_{a2}$ and $\alpha n = 1.0$ at $\text{pH} > \text{pK}_{a2}$), confirming thus the irreversible behaviour of the second electroic process.

On the other hand, the function $I_p = f(v^{1/2})$ for the three cathodic peaks showed that none of them fitted to a linear function in all the acidity conditions. This fact seems to indicate that the corresponding reduction processes are complicated with some kinetic aspects. For this reason, the variation of the peak current function with the scan rate for the three waves was studied. The results showed that both first and third reduction processes could be associated with chemical reactions, the first being electrochemical-chemical process and the third one a catalytic process. Concerning the second reduction peak the function was not affected by the scan rate in the acidity conditions where the third process did not appear. However, in neutral and alkaline conditions the peak current function increased with the scan rate, as shown in Figure 5, and consequently, an electrochemical-chemical mechanism could be derived [17].

3.3. Nature of the electrode process

The first reduction wave of the compound is sometimes accompanied by another wave, indicating that the process is not only diffusion controlled. The second wave exhibits symmetry only in acidic conditions in which the third peak does not appear, indicating that the process is diffusion controlled. Finally, the third process and the second one in neutral and alkaline conditions are adsorption controlled.

The shape of the first and third waves in sampled dc and DPP polarography seems to indicate that they are not simple diffusion processes. In fact, the first process seems to be complicated with adsorption processes or chemical reactions.

Concerning the third peak it has the typical shape of catalytic wave in DPP.

The intensity of the second peak varies linearly with the extractant concentration in the range 2.21×10^{-5} - 8.39×10^{-5} M at acidic and neutral pH conditions thus indicating that the reduction process is diffusion controlled. On the other hand, the intensities of the first and third peaks do not follow a linear pattern but they reach limit values which seems to indicate that adsorptive and/or catalytic processes are involved.

In order to confirm these hypothesis the function $\log I_p = f(\log v)$ has been represented for both cathodic and anodic peaks. In the case of the first peak (cathodic and anodic) and the third anodic peak the functions fit to straight lines with slope 1, indicating adsorption controlled processes. However, no conclusion can be derived for the third peak since the corresponding function does not fit to straight lines of 0.5 or 1.0 slope values.

Finally, as it can be seen in Figure 6, the second peak seems to be adsorptive controlled (slope 1.0) except in acidic conditions $\text{pH} = 2.23$ and high scan rates where the function presents a slope value of 0.5 indicating a diffusion controlled process.

3.4. Influence of the presence of metal ions

3.4.1. Influence of the presence of mercury (Reduction at glassy carbon electrode)

In order to check the influence of mercury as electroic material in the experimental reduction behaviour of 4-chloro-*N*-8-quinolinylbenzenesulfonamide, the reduction of reagent solutions using a glassy carbon instead of mercury electrode, in the same experimental conditions, has been tested.

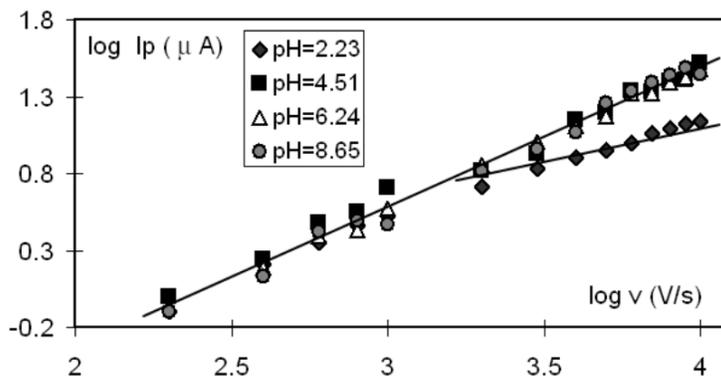


Figure 6. Plot of the function $\log I_p = \log v$ for the second reduction peak of 4-chloro-*N*-8-quinolinylbenzenesulfonamide.

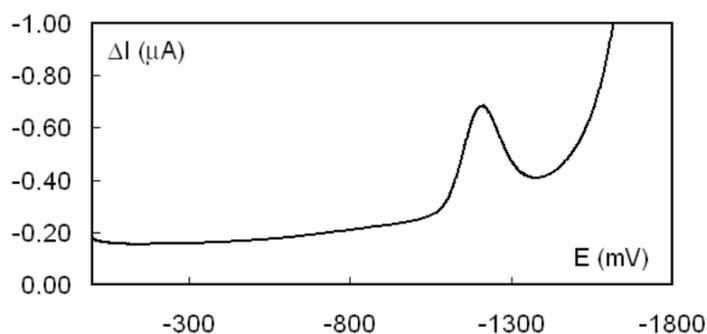


Figure 7. Differential pulse voltammogram of 4-chloro-*N*-8-quinolinylbenzenesulfonamide at a glassy carbon electrode (pH = 6.20).

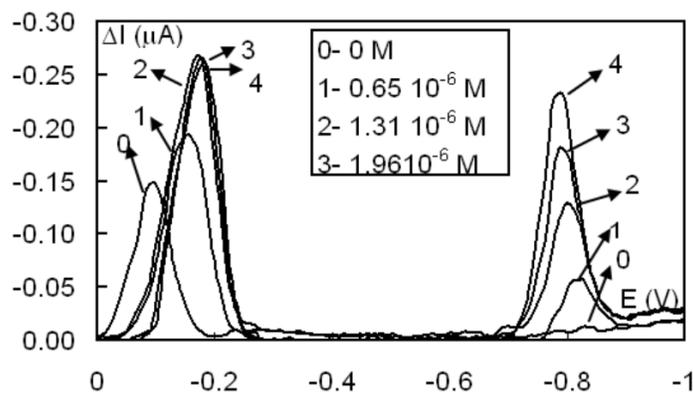


Figure 8. Differential pulse voltammograms of a 5.66×10^{-7} M Cu(II) solution (in KCl 0.1 M, 10% methanol at pH = 3.50) (0) and after the addition of different concentrations of 4-chloro-*N*-8-quinolinylbenzenesulfonamide (1-4).

Figure 7 shows the voltammogram obtained at pH = 6.20. It can be appreciated that a single peak around -1200 mV appears, which indicates that the first and third waves are clearly related to the mercury from the electrode.

3.4.2. Influence of the presence of copper

The ability of 4-chloro-*N*-8-quinolinylbenzenesulfonamide to form complexes with copper ions has been already proved in organic solutions, giving rise to good efficiency in copper extraction from aqueous acidic solutions by the use of the

reagent 4-chloro-*N*-8-quinolinylbenzenesulfonamide dissolved in toluene [14].

The influence of the presence of copper in the reduction of the reagent dissolved in the hydroalcoholic medium used in this work, 25 % methanol and 0.1 M KCl, has been studied at different pH values.

Thus, Figure 8 shows the voltammogram (0) of a solution containing Cu(II) (5.66×10^{-7} M), in the hydroalcoholic medium at pH = 3.50, where only the reduction peak of Cu(II), centered at potential values around -0.1 V is observed.

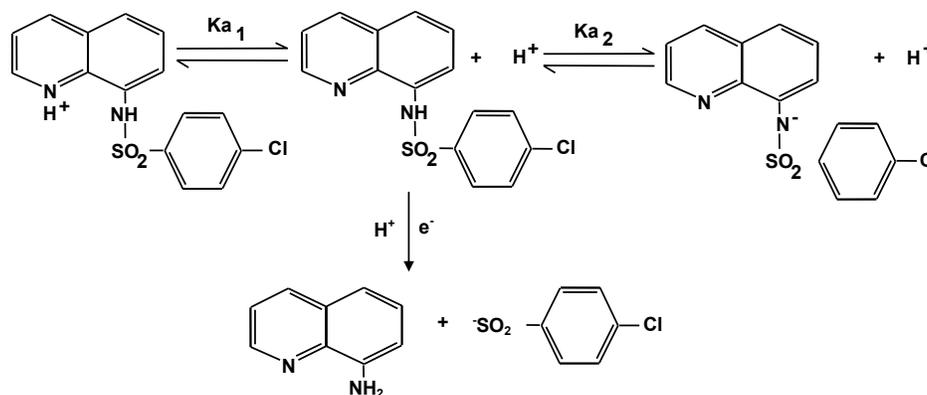


Figure 9. Reduction reactions of 4-chloro-*N*-8-quinolinylbenzenesulfonamide.

The addition of the organic reagent at different concentrations (1-4) gives rise, on one hand, to a shift in the potential value of the Cu(II) reduction peak. On the other hand, the reduction peak of the ligand appears at -0.8 V. These results can be attributed to the formation of copper complexes which can be reduced either through the cation or through the ligand, thus originating reduction peaks at potential values close to those of copper or the reagent, respectively.

The intensity of the extractant reduction peak increases gradually with its concentration. However, the intensity of copper reduction peak increases until the concentration ratio Cu:L is approximately 1:2, which corresponds with the stoichiometric ratio reported for the complex formed in organic solutions [14].

3.5. Scheme of reduction

The electrochemical reduction of 4-chloro-*N*-8-quinolinylbenzenesulfonamide has been studied being similar to that of 4-methyl-*N*-8-quinolinylbenzenesulfonamide and giving rise to three different processes [13]. The more significant differences are in agreement with the more acidic nature of the first compound. The acidity constants of the reagent, $pK_{a1} = 2.6$ and $pK_{a2} = 8.8$ can be attributed to the reactions of the compound shown in Figure 9.

Taking into account the three slope values of the function $E_p = f(\text{pH})$ for the second reduction peak showed in Figure 2a (0.0 , 6.4×10^{-2} and 16.4×10^{-2} mV/pH), the changes of current as a function of pH showed in Figure 2b, as well as the an values obtained from Figure 4, it can be proposed that the reduction process of 4-chloro-*N*-8-quinolinylbenzenesulfonamide is performed through the cleavage of the S-N bond to give 8-aminoquinoline and *p*-chlorobenzenesulfonate, as seen in Figure 9. The net reaction consumes two electrons and 0, 1 or 2 hydrogen ions depending on the acidity conditions, that is, depending on the predominant protolytic species in solution. The corresponding reactions of this process, responsible for the second reduction wave, are included in Figure 9.

On the other hand, first and third processes are more complex, but are clearly related to the mercury from the electrode. Taking into account the potential value and the shape, the first wave can be attributed to the anodic mercury dissolution that compounds with high affinity for mercury undergo [18-21]. Moreover, two cathodic peaks that can be attributed to adsorption and desorption of the products formed can be observed in cyclic voltamperometry, in a similar way that it occurs with 8-hydroxyquinoline [18].

The third reduction process for 4-chloro-*N*-8-quinolinylbenzenesulfonamide is also clearly related with mercury. Taking into account that the wave appears a) in the

acidity conditions where the neutral reagent form is the predominant species, and b) at a potential value more negative than the corresponding to the reduction of the extractant (second wave), it can be deduced that the third wave observed in the voltammograms of 4-chloro-*N*-8-quinolinylbenzenesulfonamide is due to a strong adsorption of the neutral reagent [22].

However, in many cases, other chemical or electrochemical processes are involved in adsorption phenomena. In fact, the existence of maxima and the peculiar shape of the wave observed in DPP have been attributed to kinetic reactions with the mercury electrode, [23] formation of solid species at the electrodic surface [24], or reactions with mercury with hydrogen release due to proton reduction [24,25].

For all these reasons it is probable that the third reduction process of the chelating reagent is originated by the adsorption of the extractant at the electrode surface with subsequent reduction. Moreover, coupled chemical reactions, such as the reaction between the adsorbed compound and mercury yielding a complex can also take place.

Finally, and taking into account the above considerations, the catalytic reduction of hydrogen can be proposed. This behaviour has been described in compounds with N, O and S atoms in the molecule [24]. In fact, the shape of the corresponding wave in DPP is that of a catalytic wave. So, it is possible that 4-chloro-*N*-8-quinolinylbenzenesulfonamide undergoes a chemical reaction with mercury yielding Hg(I) or Hg(II) complexes on the electrode surface, the reduction of the released protons being responsible for the catalytic wave [24].

4. Conclusion

The electrochemical reduction of 4-chloro-*N*-8-quinolinylbenzenesulfonamide in 0.1 M KCl/25% methanol, has been studied at the mercury electrode. Three reduction waves have been obtained, but only the second one, in acid conditions, is diffusion controlled. An adsorption controlled electrochemical-chemical mechanism in neutral and alkaline conditions has been proposed. In these conditions the first and third reduction processes, adsorptive controlled and probably associated with chemical reactions, take place at the same time, the first being an electrochemical-chemical process and the third one a catalytic process.

The influence of the electrodic material in the first and third reduction peaks has been also proved by using a glassy carbon electrode, which only causes the second reduction peak of the reagent.

The acidity constant values of the reagent in 0.1 M KCl/25% methanol have been estimated: the dissociation constant $pK_a = 8.8$ as well as $\log K = 2.6$ attributed to the

protonation of the amino group in the reagent. These values are lower than those of 4-methyl-*N*-8-quinolinylbenzene sulfonamide, in agreement with the more acidic character of the chloro derivative compared with the methyl one.

Finally, the effect of the presence of Cu(II) in the reduction of 4-chloro-*N*-8-quinolinylbenzenesulfonamide has been studied. Complex formation between copper ions and the organic reagent have been observed in hydroalcoholic medium, confirming thus the affinity of the cation for the ligand, which had been demonstrated in previous liquid-liquid extraction experiments.

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