Voltammetric analysis of weak acids with microelectrodes

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Abstract

The role of H^+ on the steady-state voltammetric limiting current (I_L) of weak acids (HA) reduction was studied considering results from either lactic acid or acetic acid solutions at constant pH. For solutions with pH > pK_a or pH $\cong pK_a$ the [H^+] effect on the I_L vs c_{HA} slope was important even when the H^+ current contribution was minor. In opposition, when pH << pK_a high H^+ current contributions were found nevertheless the I_L vs c_{HA} slope was almost insensitive to pH. A general relationship between I_L and c_{HA} was derived considering both the H^+ current contribution and the dissociation extent. This equation allows the analytical determination of weak acids, alone or in the presence of strong acids, from experimental I_L and pH. Acids identification can also be performed through the presented expression, following the I_L susceptibility to pH at constant c_{HA}.

Keywords: Weak acids analysis; Microelectrodes; Voltammetry

1. Introduction

Recently some research groups have studied the voltammetric reduction of hydrogen using microelectrodes [1-14]. The voltammetric steady-state limiting current of strong acids was found to be linearly related to the microelectrode dimension and to the hydrogen ion concentration [2,7], demonstrating thus that the process is mass-transport controlled. Studies in weak acid solutions have demonstrated that the reduction of both free hydrogen ion and undissociated hydrogen can occur [7,8]. While the first process is a direct electrochemical reaction, the second occurs *via* a CE mechanism [15]:

$$HA \rightleftharpoons H^+ + A^- \qquad (1)$$

$$2H^+ + 2e \rightleftharpoons H_2 \qquad (2)$$

For most of the weak acids the dissociation step is very rapid, taking place at a short distance from the electrode surface as compared to the diffusion layer thickness. Therefore, the undissociated form (HA) diffuses to the electrode and the current depends on the acid bulk equilibrium concentration [HA] and on the diffusion coefficient, D_{HA}.

Daniele *et al* [7] analysed the voltammetric response of several monoprotic acids and reported a unique wave which position was related to the acid strength, tending to more cathodic potentials as the pK_a increased. The visibility of the reduction wave was possible for acids with pK_a lower than 7 and was limited by the background discharge. The correlation between the limiting current (I_L) and the total acid concentration (c_{HA}) was found to be not always linear and to depend on the acid strength. This plots curvature was attributed to the variation of the relative [H^+], as well as to the large difference between the diffusion coefficients of H^+

and HA. For a weak monoprotic acid, whose dissociation step is fast, the overall limiting current of a microdisk has been described by [7]:

$$I_L = -4Fr(D_{H^+}[H^+] + D_{HA}[HA]) \qquad (3)$$

Studies in buffer solutions (of mono and polyprotic acids) in which the concentration of the conjugated base was at least equal to that of the acid have been performed [11]. Under the studied conditions, current was linear dependent on the acid concentration in the buffer $(c_{HA})_b$; slopes were independent of the conjugated base concentration and were related to the acid diffusion coefficient and to the electrode radius, whereas intercepts were ascribed to the constant contribution of H^+ to the overall current [11]. Based on this approach, an analytical method was proposed where an excess of conjugated base should be added to the sample. This procedure imposes limitations to the method once the added base can interfere with the analytical system, *e.g.* in the presence of multiple chemical equilibria.

In this work we analyse the voltammetric response of weak acids in media of different pH, where the contribution of H^+ can be relevant (either constant or variable). The role of H^+ is considered for the definition of calibration plots under a wide range of experimental conditions. In this way the evaluation of the analytical concentration of weak acids (c_{HA}) can be accessed directly, which is particularly interesting for *in situ* measurements, such as in the monitorization of a living cell population.

2. Experimental

All the chemicals employed were of analytical-reagent grade and were used as received. Hydrochloric, lactic and acetic acids solutions were standardised by potentiometric titration with a standard solution of NaOH (Titrisol®, Merck). Solutions were prepared with deionised water and potassium chloride was used as the supporting electrolyte (0.1 M). Buffer solutions were prepared by mixing adequate volumes of the acid solution and the standard NaOH solution. The acid concentration in the buffer, $(c_{HA})_b$, was determined from stoichiometric calculations. Constant pH solutions were obtained by adding HCl or NaOH solutions to the weak acid solution up to the required pH. Solutions were deoxygenated with argon (pure 99.999%).

Measurements were performed using a potentiostat (Autolab type PGSTAT30, Ecochemie) controlled by the GPES 4.8 software. Steady-state voltammograms from linear sweep voltammetry were obtained using a 50 mV s^{-1} scan rate. Voltammetric experiments were carried out, at room temperature, in a two-electrode cell placed in a Faraday cage. The reference / counter electrode was a Ag|AgCl|KCl (3 M). The working electrode was a platinum microdisk of 17.68 μm radius, made of cross section of Pt wire (Goodfellows) sealed into soft glass. The electrode was polished with alumina (1 and 0.3 μm) on a polishing microcloth. Electrode diameter was calibrated by measuring the limiting voltammetric current for a known concentration of ferricyanide in water, using the equation [16]:

$$I_L = 4nFDcr \qquad (4)$$

with D = 7.2×10^{-6} cm^2 s^{-1} [17].

Prior each experiment the electrode surface was activated electrochemically by cycling the potential three times over the range -0.1 to 2 V at 200 mV s^{-1} and then keeping the electrode at -0.1 V for 10 s [7]. pH measurements were performed by means of a Metrohm 654 pH-meter, using a glass electrode (Metrohm, 6.0202.000). Current data correspond to the average of three to five determinations.

3. Results and discussion

Voltammetric experiments in lactic and acetic acids solutions were performed with platinum microelectrodes for a range of acid concentration wider than those reported in similar studies (up to 10 mM [7,11,12] or 100 mM [2]). While voltammograms recorded for acid concentrations lower or equal to 300 mM were well defined, those from higher concentrations were frequently spoiled by the hydrogen evolution. The limiting current obtained from the steady-state voltammograms presented in Fig. 1(A) did not follow a linear correlation with the analytical acid concentration, c_{HA}, for both studied acids as presented in Fig. 1(B) for lactic acid.

Voltammetric experiments in buffer solutions, where the acid to base concentration ratios were 10:1, 10:3, 1:1 and 1:10, were also performed.
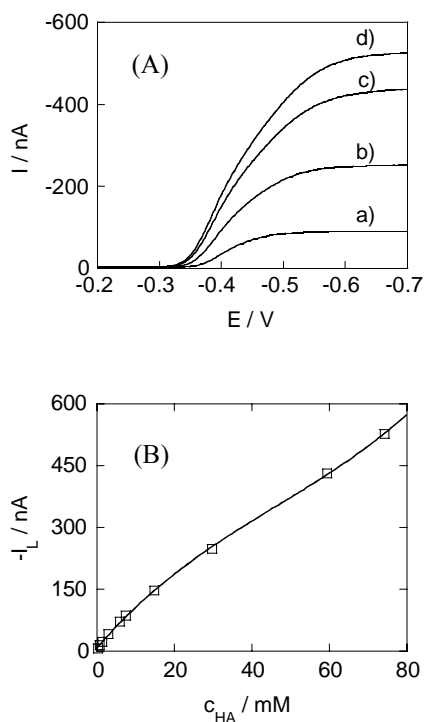

Fig. 1. (A) Steady-state voltammograms recorded with a 17.68 μm radius platinum microelectrode in lactic acid solutions of: a) 7.42, b) 29.7, c) 59.4 and d) 74.2 mM; (B) Calibration curve of limiting current of lactic acid versus c_{HA}. The plotted curve was obtained by a spline fitting.

Limiting currents were distributed along four curves, each one corresponding to a different buffer composition, as it is illustrated in Fig. 2 for lactic acid. For each acid concentration, higher limiting currents were obtained in the buffer solutions of lower conjugated base concentration. The same trend is tracked by the curves intercept. These results are in apparent contradiction with those reported by Daniele *et al* [11] (where a linear dependence was observed independently of the buffer composition) owing to the limited range of buffer composition and acid concentration considered in their studies. Although the acid to base concentration ratios of the analysed solutions where the commonly used for the preparation of buffer solutions, the pH variation was not always negligible, particularly in the more acidic solutions. The H^+ role on the limiting current must therefore be taken into account, considering both its current contribution (equation 5) and its effect on the acid dissociation extent (equation 6):

$$I_L = I_L^{H^+} + I_L^{HA} \qquad (5)$$

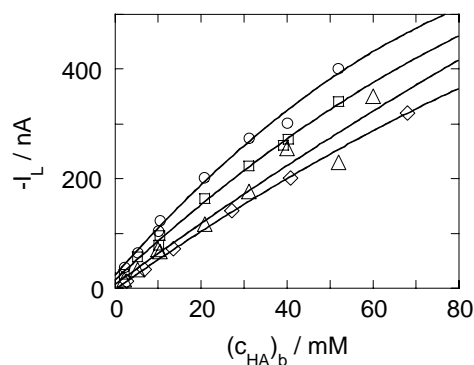$$[HA] = \frac{[H^+]}{K_a + [H^+]} c_{HA} \qquad (6)$$

Fig. 2. Representation of the limiting current as a function of the concentration of lactic acid in the buffer, $(c_{HA})_b$, for different buffer compositions ([HA]:[A⁻]): ○) 10:1; □) 10:3; Δ) 1:1 and ◊) 1:10. Lines represent the general trend followed by current in each buffer composition.

where $I_L^{H^+}$ and I_L^{HA} are the limiting current contributions from H^+ and HA, respectively. From equations 4, 5 and 6 a relationship between the limiting current and the weak acid analytical concentration is established for a microdisk electrode:

$$I_L = -4Fr\left(D_{H^+}[H^+] + D_{HA}\frac{[H^+]}{K_a + [H^+]}c_{HA} \right) \quad (7)$$

According to equation 7 the magnitude of $[H^+]$ as well as its variation determines the I_L vs c_{HA} correlation. Thus, non-linear dependences are expected for significant $[H^+]$ variations and linear correlations for negligible $[H^+]$ variations. Under this last condition, the intercept should be a measure of the H^+ current contribution and the slope should be related to the dissociation extent and to the acid diffusion coefficient.

The validity of equation 7 was tested using results from either lactic acid or acetic acid solutions of constant pH, adjusted by the addition of HCl or NaOH solutions. The I_L vs c_{HA} plots displayed linear trends despite of the solution pH as it is presented in Fig. 3(A) for lactic acid. Straight-lines from the more acidic solutions exhibited larger

intercepts, which values matched the limiting currents measured in solutions of a fully dissociated acid (HCl) at the same pH. Slopes also varied according to the solution acidity, becoming larger as pH decreased, in agreement with the predicted from equation 7. A quantitative analysis of the $[H^+]$ effect on intercepts is presented in Fig. 3(B). Either intercepts or experimental I_L from HCl solutions were proportional to $[H^+]$. The H^+ diffusion coefficient (9.39×10^{-5} cm^2 s^{-1}) estimated from the slope (equation 4) was in agreement with the literature value (9.311×10^{-5} cm^2 s^{-1}) [18], corroborating the meaning ascribed to the intercept in equation 7. The representation of the experimental slopes (from plots in Fig. 3(A)) as a function of pH is exhibited in Fig. 3(C). The observed correlation, described by a sigmoid type curve, is consistent with the predicted variation for the term used to describe the slope in equation 7. The slope absolute value increased as the solution pH decreased from 4.88 to 2.86 and a constant value was achieved for pH $\leq$ 2.86. This variation is in agreement with the second term description in equation 7, which is predicted to vary for $[H^+]$ less than or comparable to K_a and to remain constant for $[H^+]$ larger than K_a.
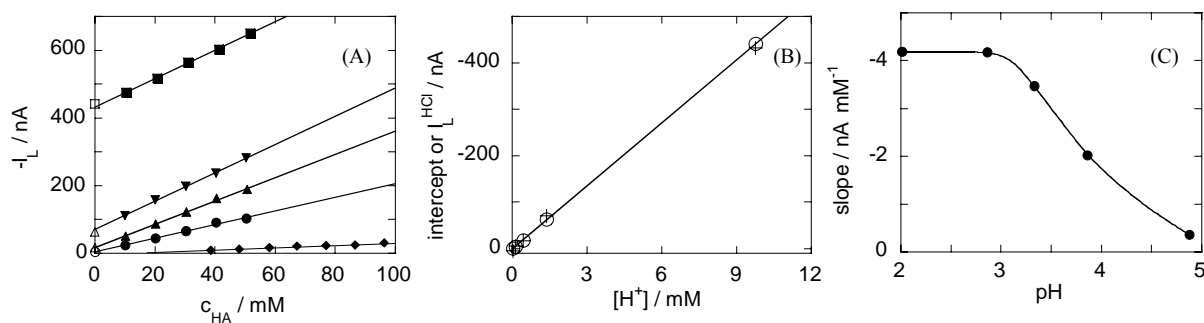

Fig. 3. (A) Calibration plots of the limiting current of lactic acid versus c_{HA} obtained in constant pH solutions: ■) 2.01, ▼) 2.86, ▲) 3.36, ●) 3.86 and ♦) 4.88; open symbols are the limiting currents from HCl solution at the pH assigned with the same shape solid symbols; (B) Representation of the limiting current obtained in HCl solutions (○) and the intercepts of the plots in Fig. 3(A) (+) as function of $[H^+]$; (C) Representation of the straight-line slope in Fig. 3(A) as function of pH.

A comprehensive validation of the second term of equation 7 is performed through the corrected limiting current $(I_L)_{corr}$, calculated subtracting to each experimental point (from Fig. 3(A)) the value of the corresponding straight-line intercept. The $(I_L)_{corr}$ is an estimative of the current contribution due to the undissociated acid, I_L^{HA}, that according to equation 7 is expressed by:

$$(I_L)_{corr} = -4FrD_{HA}\frac{[H^+]}{K_a+[H^+]}c_{HA} \qquad (8)$$

The effect of pH on I_L^{HA} can be checked through the representation of $1/(I_L)_{corr}$ vs $1/[H^+]$ at constant c_{HA} (Fig. 4), according to equation 9 (equivalent to equation 8):

$$-\frac{1}{(I_L)_{corr}} = \frac{1}{4FrD_{HA}c_{HA}} + \frac{K_a}{4FrD_{HA}c_{HA}}\frac{1}{[H^+]} \qquad (9)$$

The intercept and slope of each straight-line (from different c_{HA}) correspond to $1/4FrD_{HA}c_{HA}$ and to $K_a/4FrD_{HA}c_{HA}$, respectively. Thus, from the ratio slope/intercept K_a is directly computed. The estimated pK_a values from all straight-lines are identical (3.74±0.04) and similar to the literature
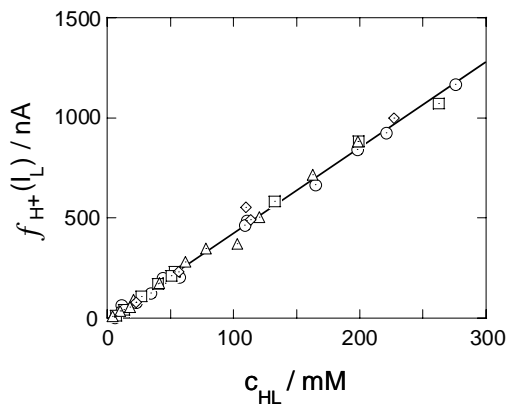

Fig. 4. Representation of the reciprocal of $(I_L)_{corr}$ as a function of the reciprocal of $[H^+]$ (measured by potentiometry) from lactic acid solutions of different concentration: ▽) 10, ○) 20, □) 30, ◇) 40 and △) 50 mM. The inset shows the same plot in a wider pH range. Solid symbols are extrapoled values from the regression equation of the straight-lines presented in Fig. 3(A).

value (3.66, I = 0.1 M) [19]. The estimated pK_a for acetic acid of 4.58±0.02 was also similar to the literature value of 4.56 (I = 0.1 M) [19]. The uncertainty presented for the pK_a values were estimated using the standard deviation of slopes and intercepts. The similarity of experimental and literature values validates the rationalization described by equation 7.

Based on equation 7 a transformed limiting current ($f_{H^+}(I_L) = (I_L + 4FrD_{H^+}[H^+])(K_a+[H^+])/[H^+]$) linearly related with c_{HA} can be defined using data acquired at different pH. This approach relies on the evaluation of the $[H^+]$, that can be performed by potentiometry. In Fig. 5(A) are presented the $f_{H^+}(I_L)$ values for lactic acid calculated using results of Fig. 2. In Fig. 5(B) are exhibited the corresponding results from acetic acid solutions. A unique linear correlation with c_{HA} is observed for each acid, in opposition to the trend before current corrections. From the slope of each regression line lactic and acetic acids diffusion coefficients of 8.65×10^{-6} and 1.18×10^{-5} cm^2 s^{-1} were estimated, which are in agreement with the literature values of 8.59×10^{-6} and 1.07×10^{-5} cm^2 s^{-1} [8], respectively.

In the two approaches presented for the determination of c_{HA} potentiometric measurements were carried out. When constant pH calibration plots were used, the solutions pH was measured in order to settle an identical value in all standards and sample solutions; nevertheless the value of pH was not used in subsequent calculations. This method accuracy and precision depends on the likeness of all the solutions pH. In the second approach, where the solutions pH was not adjusted, the $[H^+]$ must be known in order to calculate the transformed limiting current $f_{H^+}(I_L)$ from which c_{HA} was estimated. Thus, the method accuracy is highly dependent on the significance of the pH measurement. The equivalence between $[H^+]$ and
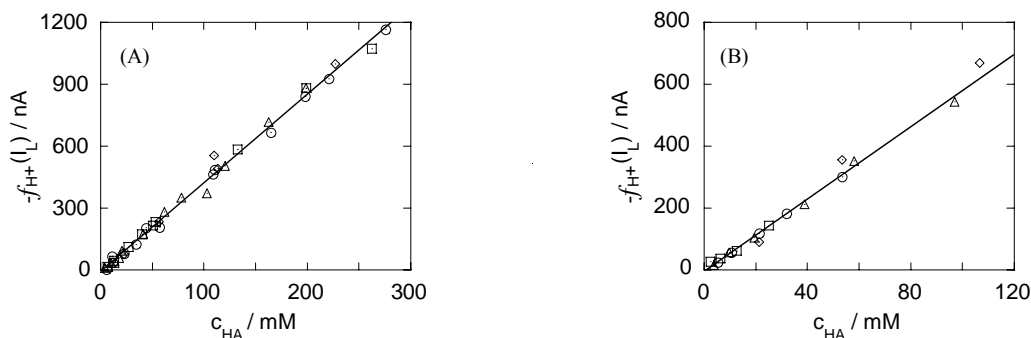
Fig. 5. Representation of the transformed limiting currents, $f_{H^+}(I_L) = (I_L + 4FrD_{H^+}[H^+])\dfrac{K_a + [H^+]}{[H^+]}$, as a function of the analytical acid concentration, c_{HA}, from (A) lactic acid and (B) acetic acid solutions in different buffer compositions ([HA]:[A⁻]): ○) 10:1; □) 10:3; Δ) 1:1 and ◊) 1:10.

10^{-pH} relies on the validity of the calibration procedure, which depends on the composition similitude of standard solutions and samples. This is related to the dependence of the potentiometric pH on the H⁺ activity and on the liquid junction potentials. In terms of precision, the estimation of [H⁺] has a relative uncertainty of about 2% (for an precision of ±0.01 pH unity), which is about the same order of magnitude of the other variables uncertainty used in the evaluation of $f_{H^+}(I_L)$.

We believe that a similar approach, combining voltammetry and potentiometry (or other techniques), can also be applied in the study of other reactions following a CE mechanism, as it is the case of the reduction of labile complexes in metal speciation studies.

4. Conclusions

Although linear correlations I_L vs c_{HA} can be defined when a narrow range of acid concentration is considered, either in weak acid solutions [2] or in buffer solutions where an excess of conjugated base is present [11], non-linear correlations were found under a wide concentration range. The plots curvature was related to the pH variation associated with the acid dissociation. Experiments performed in solutions where the pH was settled constant led to the definition of calibration straight-lines from which the [H⁺] effect was split in two contributions, evaluated from intercepts and slopes. These contributions where used to define an expression that relates I_L with c_{HA} and [H⁺]. This correlation was used in the definition of transformed limiting currents, free of the H⁺ current contribution and normalized for the dissociation extent. The presented analytical treatment allows the correction of limiting current data from samples having different pH of that of the standard solutions. Moreover, a straight calibration plot can be defined using standard solutions of different pH.

The determination of pK_a values was performed through the dependence of I_L-$I_L^{H^+}$ on pH. The pK_a uncertainties of ± 0,04 and ± 0,02 from lactic and acetic acids, respectively, were calculated. These values can be used as a measure of the method sensitivity for the identification of acids through their pK_a.

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