

ELECTROCHEMICAL STUDY OF THE OXIDATION OF BROMIDE BY ROTATING DISC VOLTAMMETRY IN AN HYDROUS ACETIC ACID

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Abstract:

The voltammetric behavior of bromide has been examined at rotating disc electrodes of platinum and carbon paste in anhydrous acetic acid (HOAC). Anodic oxidation of bromide displayed well-defined anodic wave and obeyed the Levich plots at both electrodes. The limiting current is linearly proportional to concentration affording an excellent and rapid determination of bromide ion. The electrode kinetic parameters, conditional potentials have been determined and mechanisms are suggested.

Introduction

Electrogenerated bromide has been widely used in conlometric titration of many inorganic compounds, organic substances, and product of the pharmaceutical industry in non- aqueous media⁽¹⁻⁵⁾. A number of papers have been published on the electrochemical behavior of bromine /bromide systems in aqueous and non- aqueous solvents⁽⁶⁻⁹⁾. Aqueous solutions of bromine are unstable and rarely used as titration agents in quantitative analysis⁽¹⁰⁻¹¹⁾. Moreover, many authers report the adsorption of bromide at platinum electrode in aqueous medium⁽¹²⁾ for the above reasons it was decided to study the electrochemical behavior of bromide in acetic acid in the presence of perchlorate as supporting electrolyte.

Experimental

The purification of anhydrous acetic acid has been described in the literature⁽¹³⁻¹⁴⁾. Anhydrous lithium bromide and anhydrous lithium perchlorate were obtained from Fluka. Stock solution of the substance studied was prepared by dissolving the required amount in anhydrous acetic acid . All electrochemical measurement was carried out using a potentiostat (Gerhard Bank Electronic, Model ST72).

A type R.3.2 wave from generator, supplied by chemical electronics was used. The voltammograms were recorded using a Baryons 2900 A X-Y recorder. A three-electrode cell was used. The working electrode was Bruckner ERS, rotating disc with the platinum and carbon paste electrodes. The reference electrode was a saturated calomel electrode (SCE) and the counter electrode was platinum plate. The normal voltammetric scan rate was 5 mVs^{-1} and the geometric area of the disc electrodes was 0.28 cm^2 .

All measurements were carried out at room temperature (20°C).

Results and Discussion:

Voltammetry

The current-potential curves for the oxidation of bromide were recorded at platinum and carbon paste electrodes rotating at 50 Hz. As can be seen a much more defined limiting current was obtained at platinum than of carbon paste that carbon paste Fig (1) and this may be due to some specific absorption at this electrode. Fig (2) Exemplifies the curves obtained for platinum electrode at different rotation speeds. The observed currents are mass transfer dependent. The Levich plot of $I_{L,a} \text{Vs} \omega^{1/2}$ is shown in Fig (3). This plot is a straight line passing through the origin for both electrodes. A similar behavior is found for the dependence of the limiting current on bromide concentration from $6 \times 10^{-4} \text{ M}$ to $3 \times 10^{-3} \text{ M}$, this is also another supporting evidence that the observed limiting is a diffusion controlled process. The diffusion coefficient values were evaluated from the slopes of the straight-line Fig (4). The values obtained are given in table (1). The lower diffusion coefficient in acetic acid than in aqueous solutions can be attributed to the higher viscosity of acetic acid.

Table (1): Diffusion coefficients for 0.004M

Electrode	D ($\text{cm}^2 \text{ s}^{-1}$)	Reported value in 0.1M of H_2SO_4 ⁽¹⁶⁾
Pt	0.46×10^{-5}	1.58×10^{-5}
C	0.45×10^{-5}	-----

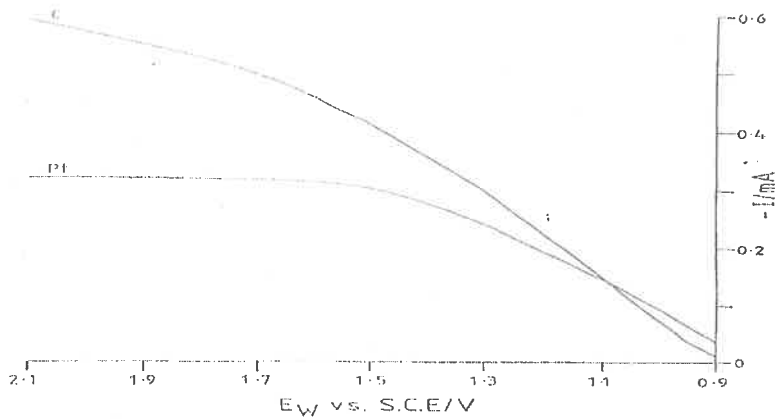


Fig (1) :Anodic oxidation 0.04M Lithium bromide in anhydrous acetic acid ,LiClO₄(0.5M) ,rotation speed 50Hz, scan speed 5mVs⁻¹ , electrode area 0.275 cm²

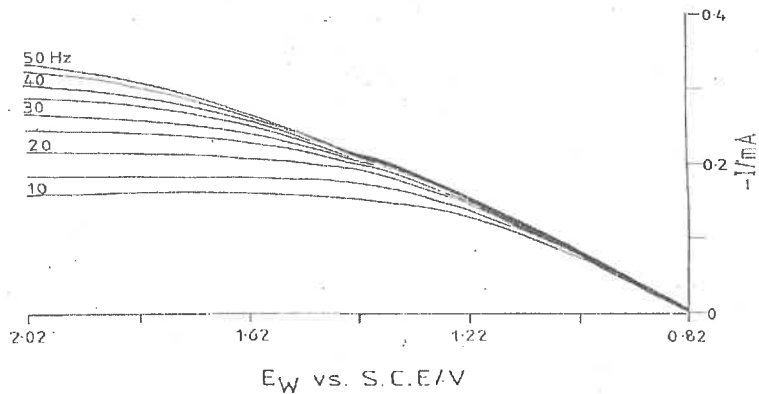
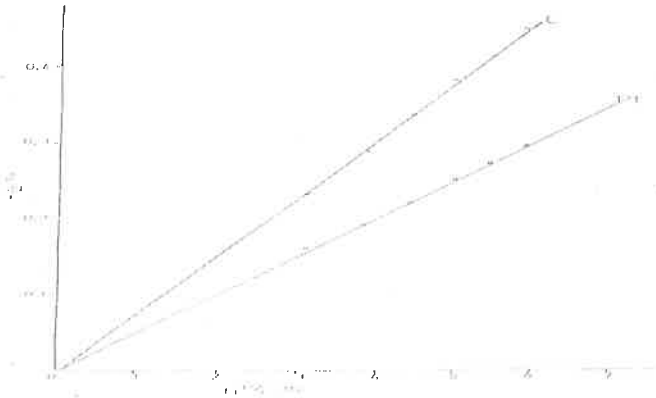


Fig (2) :Anodic oxidation 0.004 M Lithium bromide at platinum at different rotation speeds in anhydrous acetic acid, LiClO₄(0.5M) ,rotation speed 50Hz, scan speed 5mVs⁻¹ , electrode area 0.275 cm²



Fig(3) :Levich plots for oxidation of lithium bromide in anhydrous acetic acid

Kinetic parameters

The charge transfer rate constants (K^0) and the charge transfer coefficients β (anodic) were determined by the mass extrapolation method using the relationship⁽¹⁵⁾.

$$1/i_{(A)} = 1/I_{(A)} + K/W^{1/2} \dots\dots\dots(1)$$

Where $i_{(A)}$ is the current for particular reaction, W (red S^{-1}) is electrode rotation frequency, K is a potential dependent constant and $I_{(A)}$ is the current corrected for diffusion.

The intercept of the graph of $1/i$ versus $1/W^{1/2}$ gives I which is measured as a function of potential gives a total plot and β and K^0 can be obtained from the slope and the intercept, respectively:

$$\log I = \log nFAcK^0 + \beta nF/RT (E - E^0) \dots\dots\dots(2)$$

Where n , F , R and T are as in the Nernst equation.

The kinetic parameters obtained are given in table (2). The charge transfer rate constant and charge transfer coefficient on platinum have a somewhat higher value than that on carbon paste, this might be due to some adsorption on this material. The kinetic parameters were evaluated at 0.1 M sulphuric acid in order to compare with those obtained in acetic acid, the values also included in table (2). As can be seen, charge transfer proceeds faster in aqueous sulphuric than in anhydrous acetic acid. At present no quantitative explanation can be offered but the lower reaction rate in acetic acid suggest a high free energy of activation of the transition state in this medium.

Table (2): Kinetic parameters for the oxidation of 0.004 M Lithium bromide

Electrode	In Acetic acid		In 0.1M H ₂ SO ₄	
	K (cm s ⁻¹)	B	K (cm s ⁻¹)	β
Pt	2.6x10 ⁻⁴	0.38	4.8x10 ⁻³	0.43
C	1.3x10 ⁻⁴	0.33	4.3x10 ⁻³	0.35

Determination of The Number of Electrons

The half electrolysis method was employed. The limiting current was measured for the Oxidation of 0.005M and 0.0025M of lithium bromide and 250 cm³ of 0.005M solution of lithium bromide was coulometrically oxidized with a current of 20 mA for 100 minutes. The limiting current fell to the value found for 0.0025M solutions, hence n: 1. This indicates a direct Oxidation of bromide atoms in acetic acid.

The conditional potentials

The conditional potential for the system Br₂/Br⁻ was determined as follows. The equilibrium zero current potential was measured for a solution of fixed concentration of bromine and different concentration of bromide. The experimental results are shown in Fig:(4) and the values of the conditional potentials and slopes found at both electroded are summarized in table: (3) .

It can be seen that the values obtained at platinum electrode is slightly higher than that at carbon. Furthermore, the higher values for bromine/bromide in anhydrous acid then in water indicates that the salvation energy of this couple is lower in acetic acid.

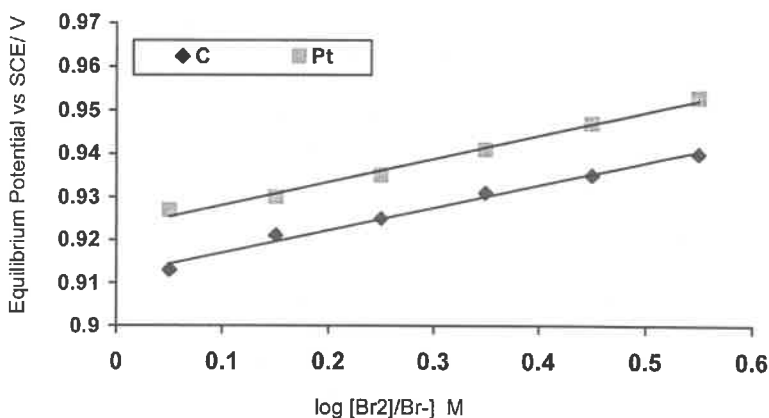


Fig (4): The dependence of the equilibrium potential Br₂/Br⁻ on the logarithm of the rat of bromine to bromide concentration

It was also observed that the slope of the straight lines Fig:(4) is 53.6, 52.4mV for platinum and carbon respectively, which correspond to one –electron transition. This confirms our coulometric results about the number of electrons involved in the electrochemical reaction.

Table (3): The conditional potential in 0.5M Lithium perchlorate in anhydrous acetic acid.

Electrode	Slope	Ew vs SCE/V	Reported value in 0.1M of H ₂ SO ₄ ⁽¹⁶⁾
Pt	53.6	0.924	0.841 vs SCE/V
C	52.4	0.914	-----

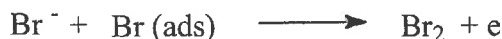
Reaction mechanism

The presence of species such as Br₃⁻ (13) is not detected in the present investigation since anodic voltammograms for the oxidation of bromide showed only one anodic wave moreover the number of electrons taking part in the reaction was found to be one; this indicates the direct Oxidation of bromide to bromine atoms.

Consequently the following two reaction mechanism can be proposed. The first step is the discharge of bromide ions on the electrode surface.



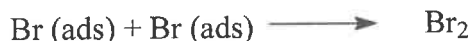
The second step is the discharge of another bromide ion on the adsorbed bromine atom to form bromine molecule.



This step could be the rate determined step .



and



Analytical validity:

The good concentration plot encouraged us to examine the analytical application of rotating disc voltammetry. To appraise the reliability of rapid determination, a series of five solutions of lithium bromide standards was prepared and a single measurements of the limiting currents was made at each of the five rotation speeds. The concentration was calculated from the slope, and the intercept the results are satisfactory considering the propagation of errors from five calibrations; the mean relative standard deviation is 1.15%.

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دراسة كهر وكيميائية لأكسدة البروميد باستخدام تقنية فولتامetri القطب الدوار في حامض الخليك الجاف

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الملخص :

تم دراسة السلوك الفولتامetri للبروميد باستخدام تقنية فولتامetri القطب الدوار على أقطاب من البلاتين والكربون في حامض الخليك الجاف . أعطت الأكسدة الانودية للبروميد موجات واضحة تنطبق عليها رسوم ليفنج . كان التيار الحدي يتناسب طرديا مع التركيز ، تم إيجاد المعاملات الحركية والجهود الظرفية كما تم اقتراح ميكانيكية للتفاعل .