

## Electrochemical sensor in situ control of acidity level of concentrated HCl solutions

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### Abstract

The experimental device consisting of two paste electrodes: ferrocene and quinone at fixed current potentiometry was studied for the in-situ control of the acidity level of hydrochloric acid solutions at moderate concentrations between 0.6 and 8.0 M. The influence of different factors affecting the variation of potential at imposed current were already studied in previous papers published on H<sub>3</sub>PO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> and HClO<sub>4</sub>. Also, the measured potential variations  $\Delta E_i$  between ferrocene and orthochloranil (oQ) or parachloranil (pQ) electrodes were equal the values as those  $\Delta E$  obtained by the voltamperometric curves at a fixed current. The acidity function  $R_i(H)$  proposed previously was similar to that proposed by Strehlow and named  $R_o(H)$ ;  $R(H)$  representing the  $H^+$  activity is the extended pH towards concentrated acid solutions. The variation of potential determined at imposed current obeyed the Nernst equation and the slope close 0.058 mV.

**Keywords:** Sensor, Ferrocene, Quinone, Concentrated Hydrochloric Acid, Acidity Function.

## 1. Introduction

First introduced by S. Sorenson at Carlsberg Laboratory of the Carlsberg Research Center in 1909 [1], pH (per hydrogen) has been defined as a measure of the acidity or alkalinity of an aqueous solution based on the acidity of hydronium ions in the solution. The potential of Hydrogen ion ( $\text{H}_3\text{O}^+$  or simply  $\text{H}^+$ ) named pH using the formulae  $\text{pH} = -\log [\text{H}_3\text{O}^+]$  where is the concentration of hydrogen ion, to control the enzymatic process in all biochemical processes.

Numerous researches pointed out that the quantitative comparison of the acidities of non-aqueous or partially aqueous solutions is a problem of far greater complexity than the measurement of pH values in aqueous solutions. The term “non-aqueous” includes strong aqueous solutions of acid. So the use of the direct determination of acidity level in concentrated acid solutions was an important role in the control in situ of many processes such as acid pickling, industrial acid cleaning and oil well acidizing [2].

The basic thermodynamic quantity that is assigned to an electrode process is the standard or formal reduction potential ( $E_0$  or  $E_f$ ). In aqueous solution, the measurement of reduction potentials is facilitated by the use of reliable and universally accepted reference electrodes such as the normal hydrogen electrode (NHE) or the saturated calomel electrode (SCE) [3]. In many instances electrochemical measurements in water are impossible due to insolubility or instability of the compound. Unfortunately, no universal reference electrode exists for non-aqueous solvent [4,5]. SCE is one reference electrode commonly used in non-aqueous or concentrated acid solutions. Electrode potentials prepared in moderate or neutral solutions, when determined includes inevitably unknown liquid junction potentials [4,5].

pH reliability is limited to relatively acid solutions, i.e. when ionic strength and/or solvent composition vary; pH measurements lose its validity. Several researchers attempt to introduce other generalised pH as Hammett's and Strehlow's acidity functions [7-11]. Hammett studied the change of color of an indicator involves a transfer of protons :

$$\text{H}^+ + \text{In} \rightleftharpoons \text{InH}^+ \\ pK_{\text{HIn}^+} = -\log a_{\text{H}^+} \frac{C_{\text{In}}\gamma_{\text{In}}}{C_{\text{HIn}^+}\gamma_{\text{HIn}^+}} = H_0 - \log \frac{C_{\text{In}}}{C_{\text{HIn}^+}} \quad (1)$$

Where C is the concentration and  $\gamma$  is the activity coefficient related to  $\text{InH}^+$  and I. It is clear that :

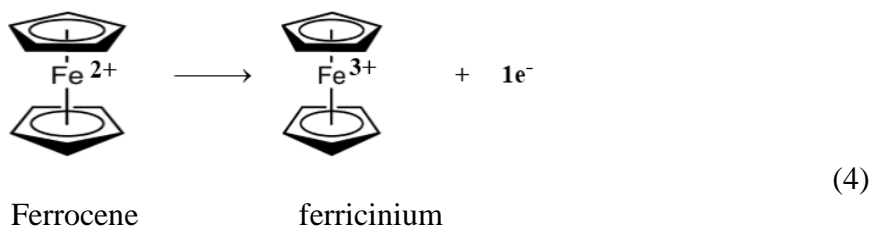
$$H_0 = -\log a_{\text{H}^+} - \log \frac{\gamma_{\text{In}}}{\gamma_{\text{HIn}^+}} \quad (2)$$

The acidity function,  $H_0$ , is equal the thermodynamic pH if the  $\frac{\gamma_{\text{In}}}{\gamma_{\text{HIn}^+}}$  ratio is unity. This approach is valuable only at diluted solutions. Hammett's great contribution (in 1928) to chemistry was the concept of superacidity and his acidity function; and may be useful when the two species  $\text{InH}^+$  and I have the same degree of solvation in non-aqueous or hyperacid solutions. However, all these and other acidity functions are based on Hammett's principle and can be expressed by Eq. (3), in which B and A are the basic and the conjugate acidic form of the indicator, respectively.

$$H_x = pK_a - \log \frac{A}{B} \quad (3)$$

They become identical with the pH scale in highly dilute acid solutions. The relative and absolute validity of the different acidity functions have been the subject of much controversy and the subject has been extensively reviewed. [12-16].

Strehlow and Wendt in the early of 1960, [9] proposed a new acidity function based on electrochemistry measurement. They suggested a method to measure the potential variation of a pH-dependent system with respect to a reference system whose potential was solvent-independent [17,18]. The measurement was made with a cell using Pt/H<sub>2</sub>/H<sub>2</sub>O–H<sub>2</sub>SO<sub>4</sub>, ferrocene–ferricinium /Pt:



The choice is based on an extrathermodynamic hypothesis which admits the normal potential of ferricinium / ferrocene reference system independent on the acid content [19].

$$R_0(H) = \frac{F}{2.303RT} (E^X - E^S) \quad (5)$$

which  $E^X$  and  $E^S$  are the electromotive forces of the cell at proton activities  $x$  and standard, respectively.

Like all the Hammett acidity functions,  $R_0(H)$  equals pH in dilute aqueous solution. In strong acids, this function should be a logarithmic measure of the proton activity as long as the normal potential of the redox system, ferrocene–ferricinium, is constant [18]. In non-aqueous solvent, system potentials are referred to the half-wave potential of the ferrocene–ferricinium ( $\text{Fc}/\text{Fc}^+$ ) system determined by polarography as the normal potential  $E^\circ$  system.

In previous works, the ferrocene–ferricinium ( $\text{Fc}/\text{Fc}^+$ ) used we have shown that it is possible to realise a reference electrode by using ferrocene in paste electrode ( $\text{Fc}\downarrow$ ). The ferricinium ion is easily prepared in biphasic toluene-acid media at various concentrations. The reference electrode  $\text{Fc}^+/\text{Fc}\downarrow$  has been prepared in concentrated mineral acid as  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$  [18-26] to avoid junction potential in a given medium. We have shown that the transfer activity coefficient of ferricinium ion equals to unity in each medium studied. This application ceases when the acid concentration varies within a wide range due to the variation of the potential of junction. This limitation incited to propose the device  $\text{Q}\downarrow / \text{Acid} (xM) / \text{Fc}\downarrow$  for the in situ determination of acidity level in concentrated acid. Encouraging results [24-26] were obtained in concentrated  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$  solutions. Also, the varying of  $\Delta E$  of the device with the acid concentration permitted to introduce a new acidity function  $R_i(H)$ . The device  $\text{Q}\downarrow/\text{acid} (xM) / \text{Fc}\downarrow$  is then studied and the potential taken by the quinone electrode is:

$$E^X = E^W + \frac{2.303RT}{F} \log(a_{H^+}) \quad (6)$$

$E^X$  and  $E^W$  are the measured potentials with respect to the ferrocene-ferricinium system in the acid media and the water respectively.  $a_{H^+}$  is the proton activity.  $R$ ,  $T$ ,  $F$  and  $n$  have their usual meaning.

In concentrated media, the  $R_0(H)$  acidity function is defined by [27]:

$$R_0(H) = -\log(a_{H^+}) \quad (7)$$

$$R_i^X(X) = R_i^S(X) + \frac{F}{2.3RT} (\Delta E_i^S - \Delta E_i^X) \quad (8)$$

$R_i(H)$  is proposed as an important tool for the direct determination of  $H^+$  activity in the solution.

The "i" subscript indicates that electrochemical chain  $\text{oTQ}\downarrow / \text{HCl} / \text{Fc}\downarrow$  is crossed by a current of low intensity (0.5  $\mu\text{A}$ ).  $\Delta E_i^X$  and  $\Delta E_i^S$  are the potential variations measured by electrochemical chain in the

solution to be analyzed and in the standard solution, respectively.  $R_i^x(H)$  and  $R_i^s(H)$  are the acidity function values of the acid media of unknown and standard solutions, respectively.

By convention, 2.0 M  $H_3PO_4$  with  $R_i^s(H) = R_o^s(H) = -0.2$  [27] as standard solution.  $R_i^a(H)$  is then calculated by:

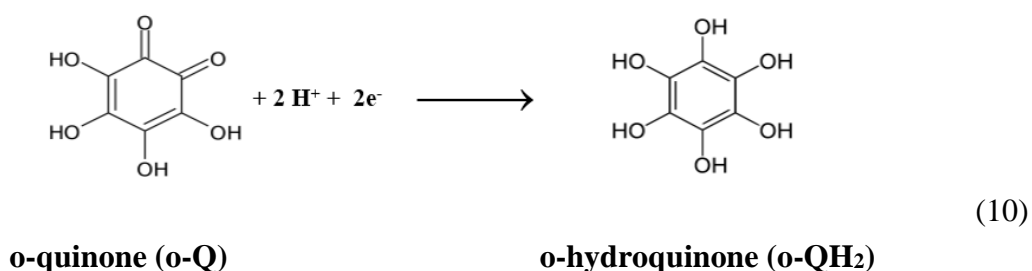
$$R_i^x(X) = R_o^s(X) + \frac{F}{2.3RT} (\Delta E_i^s - \Delta E_i^x) \quad (9)$$

The choice of  $H_3PO_4$  medium is maintained for all the different acids to level on the same scale.

This paper is aimed to extend the study this device  $Q\downarrow / \text{acid (xM)} / Fc\downarrow$  for the in situ determination of acidity level in concentrated hydrochloric acid. The determined acidity function,  $R_i(H)$ , has been compared to the Strehlow  $R_o(H)$  function.

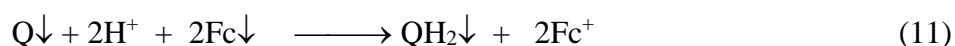
## 2. Experimental Section

The electrodes made of these two compounds are prepared according to the technique of the carbon paste electrodes with a non conductive link [28] as described elsewhere [24]. The electric contact is assured by platinum wire. The orthochloranil (o-Q) and parachloranil (p-Q) are Fluka products and ferrocene (Fc) is Merck product. Freshly prepared paste electrodes were usually conditioned in 2.0 M  $H_3PO_4$  solution for 1 h. Cell used in Teflon to avoid glass attack. The current is obtained by a potential generator in series with  $R(M\Omega)$  ohmic resistor. Potentiometric measurements of potential variation  $\Delta E_i$  were performed with a digital voltmeter with high input impedance (Orion Research 601A). All experiments are made at  $25 \pm 1^\circ C$ .



## 3. Results and discussion

Quinone–hydroquinone systems are widely used as electrochemical pH indicators. There have been used with success by Tremillon and co-workers [29-31] for acidity measurements in concentrated acids. We proceed to use the orthoquinone or paraquinone as  $H^+$  indicator and ferrocene as reference in carbon paste electrodes. The determination of acidity level is based on the use of potentiometric method at imposed weak current. The measure of the potential variation  $\Delta E_i = E_Q - E_{Fc}$ , has a double role: working without polluting the solution with an addition of ferricinium ions for the stabilisation of  $Fc\downarrow$  electrode and also avoid the junction potential. The global reaction may be abbreviated in eq.11:



$Q\downarrow$ ,  $QH_2\downarrow$  and  $Fc\downarrow$  represent the insoluble compounds of ortho-chloranil, hydro-ortho-chloranil and ferrocene in the paste electrode respectively.

We note that the potential at null intensity between Q (cathode) and Fc (anode) is not stable because of the absence of the  $QH_2$  and  $Fc^+$  compounds at the electrode surfaces, respectively.

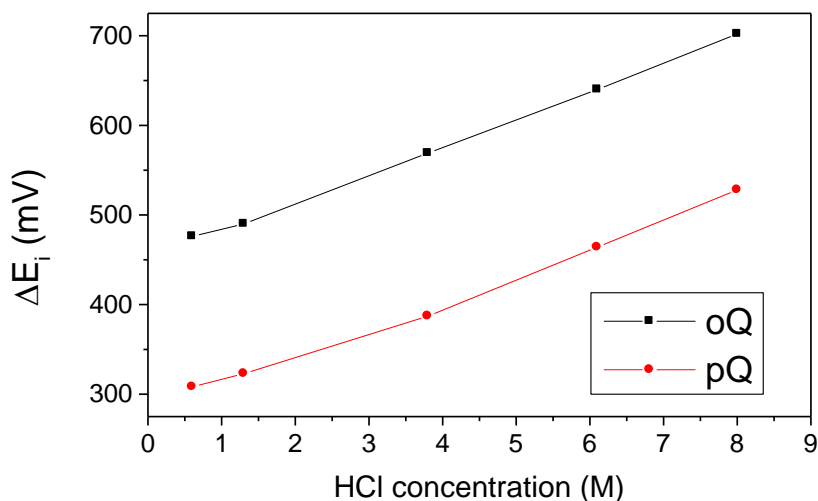
We have shown in previous works that several factors affect the potential variation  $\Delta E_i$  as current intensity, response time, temperature, stirring rate of solution and  $H^+$  ion concentrations. Results obtained show that at  $0.5\mu A$ ,  $\Delta E_i$  values are more stable in record time. The stirring rate of solution is kept constant during all measurements.

The evolution of  $\Delta E_i$  function with the acid concentration (0.6-8.0M) was summarised in Table 1.  $\Delta E_i$  reached its final potential rapidly less than 2 minutes. More and more the acid concentration increases,  $\Delta E_i$  increased.

**Table 1.**  $\Delta E_i$  obtained by ortho-chloranile and para-chloranile electrodes at  $I = 0.5\mu A$ .

HCl (M)	0.6	1.3	3.8	6.1	8.0
$\Delta E_i(oQ)$ (mV)	476	480	569	640	702
$\Delta E_i(pQ)$ (mV)	308	323	387	464	528

This variation may be used as calibration curve for the in situ determination of the pure HCl concentration of any solution studied. The device was also sensible with addition of concentrated acid or distilled water.



**Fig. 1.** Variation of  $\Delta E_i$  measured with HCl concentration

#### *The new acidity $R_i(H)$ function*

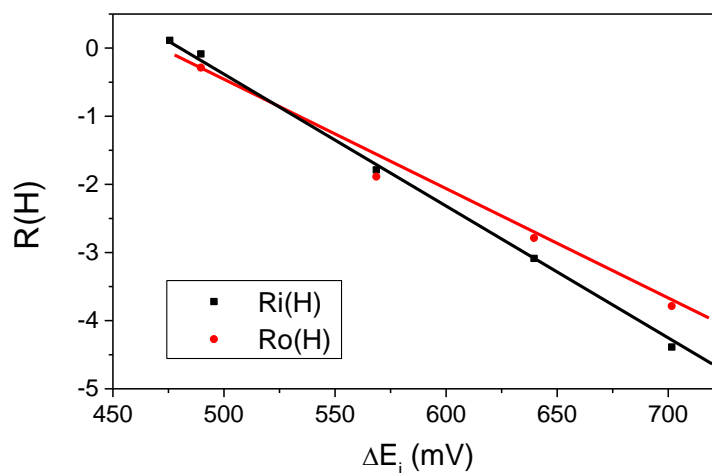
The electrochemical chain  $Q\downarrow/HCl(xM)/Fc\downarrow$  crossed by  $0.5\mu A$  was investigated; the variation of  $\Delta E_i$  obtained was significant (more than 220 mV) when the acid concentration increased from 0.6 to 8.0 M. These finding permit to calculate the values of  $R_i(H)$  by the equation (8). Fig. 2 represents a linear plot of  $\Delta E_i$  versus  $R_i(H)$  satisfying the following relationship:

$$\Delta E_i(oQ) = 0.484 - 0.055 R_i(H) \quad (12)$$

$$\Delta E_i(pQ) = 0.283 - 0.058 R_i(H) \quad (13)$$

The plot is numerically (0.055 and 0.058 mV/dec.) close to the ideal Nernstian response ( $2.303 RT/F$  (59.16 mV per decade at 298 K)) with the correlation coefficient equal to 0.984. This new acidity function  $R_i(H)$  can be used to level each acid separately and has als the advantage of being easy to

establish a new scale of mineral acids, since two potentiometric measurements  $\Delta E_i^X$  and  $\Delta E_i^S$  are sufficient for the determination of the  $R_i(H)$  value for a given acid medium.

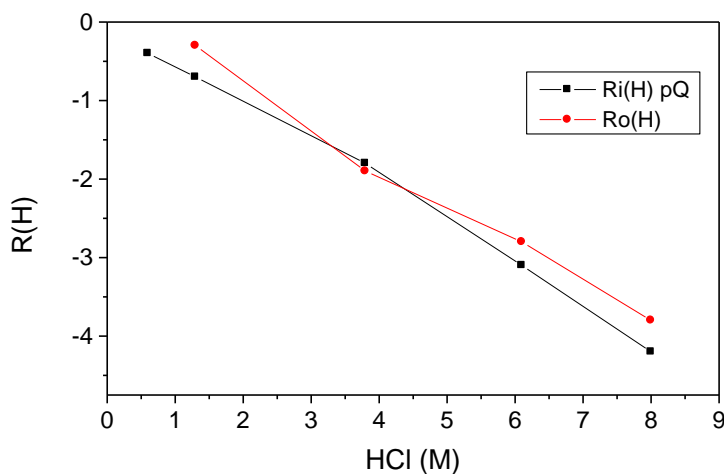


**Fig. 2.** Variation of  $\Delta E_i$  measured with  $R_i(H)$  in HCl solution

Furthermore, there is a high correlation between  $R_i(H)$  and  $R_o(H)$  functions, may be obtained by the limit of  $R_i(H)$  when the current is null, then we can write:

$$\lim_{i \rightarrow 0} R_i(H) = R_o(H) \quad \text{and} \quad \lim_{i \rightarrow 0} \Delta E_i = \Delta E_{i=0} \quad (14)$$

In order to situate the  $R_i(H)$  function recently introduced, it is better to be compared to other acidity functions such as  $R_o(H)$  [32] (Fig.3).



**Fig. 3.** Comparison of  $R_i(H)$  to  $R_o(H)$  (pQ data)

Similar results were also obtained by para-chloranil (p-quinone). We remark that  $R_i(H)$  and  $R_o(H)$  operate in the same way. The principal advantage of our  $R_i(H)$  against  $R_o(H)$  is the in situ determination of the proposed device while  $R_o(H)$  is calculated using the half wave potential of oxidation of ferrocene

at dropping mercury electrode in various media [11]. The  $R_i(H)$  function varies in the same way as the  $R_o(H)$  function for a large range of acidity.

## Conclusion

According to the study of the electrochemical device for the chain:  $Q\downarrow/HCl/Fc\downarrow$  at imposed current ( $i=0.5\mu A$ ), the following conclusions can be drawn:

- The device has both a fast response time less than 2 minutes and a long lifetime.
- The in-situ determination of the concentration of the HCl acid by our device is now possible, simple and reproducible.
- The device may be used in the industrial control of acidity.
- The practical acidity  $R_i(H)$  function was determined in HCl solutions and played the same properties as the thermodynamic  $R_o(H)$  function.

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