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A sensor for in situ control of acidity level of concentrated HF solutions

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Abstract

Two paste electrodes: ferrocene and quinone at fixed current potentiometry composes the device and are used for the in-situ control of the acidity level of hydrofluoric acid solutions at moderate concentrations between 3.0 and 12.0 M. The influence of different factors affecting the variation of potential at imposed current were studied in previous papers published on HCl, H_3PO_4, H_3PO_4 and $HClO_4$ as well as their mixtures. Also, the measured potential variations ΔE_i between ferrocene and orthochloranil (oQ) electrodes are equal the values as those ΔE obtained by the voltamperometric curves at a fixed current. The acidity function $R_i(H)$ proposed previously is 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 follows the Nernst equation and the slope of 0.058 mV is obtained.

Key words: Ferrocene; Acidity function, Strehlow, Concentrated acid, HF.

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1. Introduction

The potential of Hydrogen ion (H_3O^+ or simply H^+) named pH is first by the famous Danish Chemist, Sorenson, in 1909 [1] using the formulae:

$pH = -\log [H_3O^+]$ where is the concentration of hydrogen ion.

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In other words, Sørensen introduced the pH scale during his pioneering research into proteins, amino acids and enzymes - the basis of today's protein chemistry. Basically meaning 'the power of hydrogen', the scale provides a simple and universal measurement of the amount of hydrogen ions in a solution, which affects its acidity and how it reacts chemically.

However, 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 [2-6].

Hammett studied the change of color of an indicator involves a transfer of protons :

$$H^+ + In \Leftrightarrow InH+$$

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

Where C is the concentration and γ is the activity coefficient related to InH^+ and I. It is clear that :

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

The acidity function, H_0, is equal the thermodynamic pH if the $\frac{\gamma_{In}}{\gamma_{HIn+}}$ 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 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. (1.19), 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. [7-11].

Strehlow and Wendht in the early of 1960, [4] 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 [12,13]. The measurement was made with a cell using $Pt/H_2/H_2O–H_2SO_4$, 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 [14].

$$R_0\,(H) = \frac{F}{2.303RT}(E^X - E^S) \quad (4)$$

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 [13].

In non-aqueous solvent, system potentials are referred to the half-wave potential of the ferrocene–ferricinium (Fc/Fc^+) system determined by polarography as the normal potential E° system.

In previous works, the ferrocene–ferricinium (Fc/Fc^+) used we have shown that it is possible to realise a reference electrode by using ferrocene in paste electrode (Fc↓). The ferricinium ion is easy prepared in biphasic toluene-acid media at various concentrations. The reference electrode Fc^+/Fc↓ has been prepared in concentrated mineral acid as H_3PO_4, HCl, H_2SO_4, $HClO_4$ and in their mixtures [14-19] 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 Q↓ / Acid (xM) / Fc↓ for the in situ determination of acidity level in concentrated acid. Encouraging results [20-23] were obtained in concentrated H_3PO_4, H_2SO_4, HCl and $HClO_4$ solutions. Also, the varying of ΔE of the device with the acid concentration permitted to introduce a new acidity function $R_i(H)$.

The device Q↓/acid (xM) /Fc↓ is then studied and the potential taken by the quinone electrode is:

$$E^X = E^W + \frac{2.303RT}{F} log(a_{H^+}) \tag{5}$$

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 $R_o(H)$ acidity function is defined by [24]:

$$R_o(H) = - \log (a_H^+) \tag{6}$$

$$R_i^x(X) = R_i^S(X) + \frac{F}{2.3RT}(\Delta E_i^S - \Delta E_i^x) \tag{7}$$

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

The "i" subscript indicates that electrochemical chain oTQ↓ / HF / Fc↓ is crossed by a current of low intensity (0.5µA). $\Delta E_i^x and\ \Delta E_i^S$ 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 [24] as standard solution. $R_i^a(H)$ is then calculated by:

$$R_i^x(X) = R_0^S(X) + \frac{F}{2.3RT}(\Delta E_i^S - \Delta E_i^x) \tag{8}$$

The choice of H3PO4 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↓ / acid (xM) / Fc↓ for the in situ determination of acidity level in concentrated hydrofluoric acid. The determined acidity function, $R_i(H)$, has been compared to the Strehlow $R_o(H)$ function.

2. Material and methods

The electrodes made of these two compounds are prepared according to the technique of the carbon paste electrodes with a non conductive link [25] as described elsewhere [20]. The electric contact is assured by platinum wire. The orthochloranil (oTQ) and parachloranil (pTQ) are Fluka products and ferrocene (Fc) is Merck product. Freshly prepared paste electrodes were usually conditioned in 2.0 M HF solution for 1 h. Cell used in Teflon to avoid glass attack. The current is obtained by a potential generator in series with R(MΩ) ohmic resistor. Potentiometric measurements of potential variation ΔE_i were performed with a digital voltmeter with high input impedance (Orion Research 601A). All experiments are made at 25 ± 1°C.

3. Results

Quinone–hydroquinone systems are widely used as electrochemical pH indicators. There have been used with success by Tremillon and co-workers [26-28] for acidity measurements in anhydrous HF and HF containing superacids. We proceed to use the orthoquinone 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 doble role: working without polluting the solution with an addition of ferricinium ions for the stabilisation of Fc↓ electrode and also avoid the junction potential. The global reaction may be abbreviated in eq.9:

$$oQ\downarrow + 2H^+ + 2Fc\downarrow \longrightarrow oQH_2\downarrow + 2Fc^+ \quad (9)$$

$oQ\downarrow$, $oQH_2\downarrow$ and $Fc\downarrow$ represent the insoluble compounds of ortho-chloranil, hydro-ortho-chloranil and ferrocene in the paste electrode respectively.

We not that the potential at null intensity between oQ (cathode) and Fc (anode) is not stable because of the absence of the oQH_2 and Fc^+ compounds at the electrode surfaces, respectively.

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

The evolution of ΔE_i function with the acid concentration (3.0-12.0M) is resumed in Table 1. ΔE_i reaches its final potential rapidly less than 2 minutes. More and more the HF concentration increases, ΔE_i increases.

Table 1. ΔE_i obtained by ortho-chloranile electrode at I = 0.5µA.

HF (M)	2.0	6.0	9.0	12.0
ΔE_i (mV)	513	554	615	729

This variation may be used as calibration curve for the in situ determination of the pure HF concentration of any solution studied (Figure 2). The device is also sensible with addition of concentred acid or distilled water.

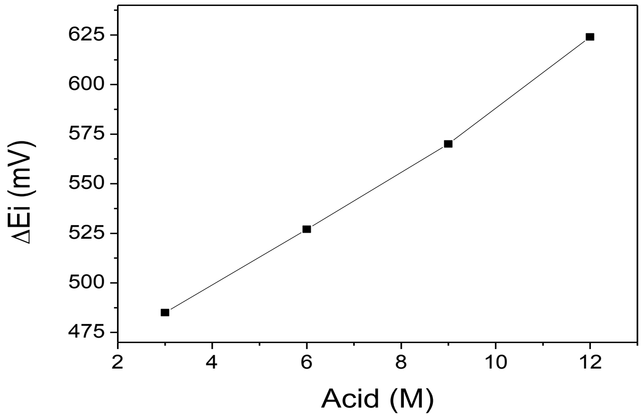

Fig. 1. Variation of ΔE_i measured with HF concentration

The new acidity $R_i(H)$ function

The device proposed Q↓/HF (xM) /Fc↓ crossed by 0.5µA is then studied; the variation of ΔE_i is more than 300 mV when the acid concentration varies from from 3.0 to 12.0 M. These finding permit to calculate the values of $R_i(H)$ by the equation (8). Figure 2 represents a linear plot of ΔE_i versus $R_i(H)$ satisfying the following relationship:

$$\Delta E_i = 0.488 - 0.054\, R_i(H) \tag{10}$$

The plot is numerically (0.054 mV-dec.) close to the ideal Nerstian response (2.303 RT/F (59.16 mV per decade at 298.15 K)) with the correlation coefficient equal to 0.9964. 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 ΔE_i^X and ΔE_i^S are sufficient for the determination of the $R_i(H)$ value for a given acid medium.

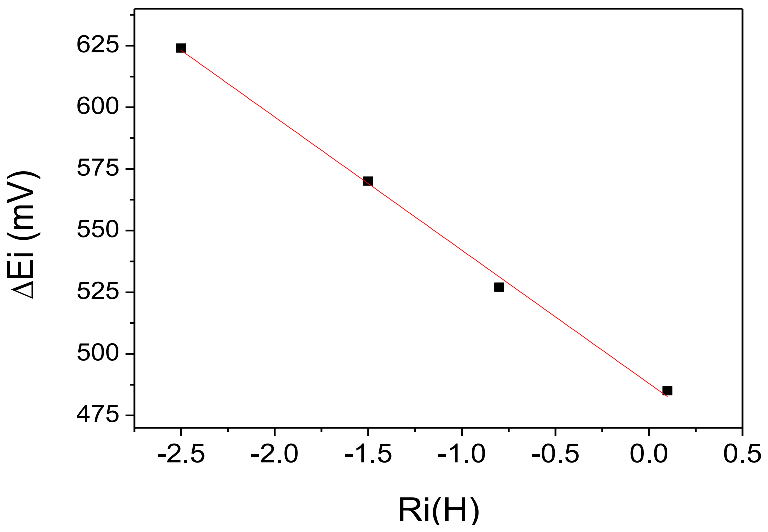

Fig. 2. Variation of ΔE_i measured with $R_i(H)$ in HF solution

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

$$\lim_{i \to 0} R_i(H) = R_o(H) \quad \text{and} \quad \lim_{i \to 0} \Delta E_i = \Delta E_{i=0} \tag{11}$$

In order to situate the $R_i(H)$ function recently introduced, it is better to be compared to other acidity functions such as $R_o(H)$ [29] (Figure 3).

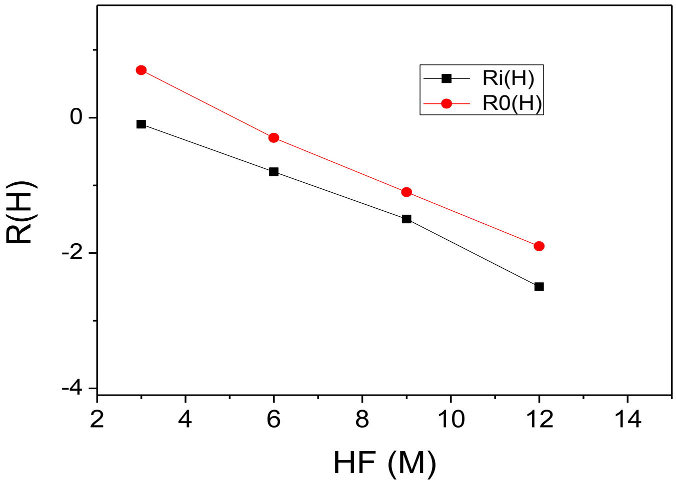

Fig. 3. Comparison of $R_i(H)$ to $R_O(H)$

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 [30]. The $R_i(H)$ function varies in the same way as the $R_o(H)$ function for a large range of acidity. The difference observed between $R_i(H)$, Ro(H).

Conclusion

Based on the study of the electrochemical device for the chain: Q↓/ HF / Fc↓ at imposed current (i=0.5µA), the following conclusions can be enounced:

- The device has a fast response time less than 2 minutes and has also a long lifetime.
- The in-situ determination of the concentration of the HF 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 HF solutions. It has the same properties as the thermodynamic $R_o(H)$ function.

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