

Electrooxidation of Ferrocene in Nano-emulsion

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Abstract: Nano-emulsion, a kinetically stable system of nanosized oil droplets in water has been numerously used as a medium for biological and medicinal processes. It is also used as a solubilizing medium for compounds or molecules that are insoluble or poorly soluble in aqueous medium in addition to its use as a penetration enhancer in dermatological processes. Ferrocene, a metallocene that is known to be quite insoluble in aqueous medium is liberally soluble in the prepared oil-in-water nano-emulsion. In this medium, ferrocene undergoes a quasi-reversible reaction process and its relevant electrochemical kinetic parameters such as the heterogeneous rate constant, k_s , the formal redox potential, E^o , the half-wave potential, $E^{1/2}$, the electron transfer coefficient, α , and its diffusion coefficient, D , are determined in this medium. These important electrochemical parameters including the observed current function have been used to formulate a plausible mechanism for the oxidation of ferrocene in the formulated nano-emulsion.

Key words: Nano-emulsion, ferrocene, half-wave potential, metallocene, electrochemical.

1. Introduction

Nano-emulsion, a heterogeneous solvent system formed by water-oil-surfactant and co-surfactant exhibits unique chemical properties including solubilization of both ionic and non-ionic solutes. As a result of these unique properties, it has been used in most water-insoluble molecules [1-4], in drug delivery [1, 5-7], in medicine [6, 8], in pharmaceutical formulations [9, 10], in dermatology [11, 12], as penetration enhancer [12, 13] and a host of other applications. The literature is replete of review [13-16] detailing the formulations and applications of this unique system. Ferrocene, a well-known compound that belongs to the metallocene family is insoluble in water [17-19] but is liberally soluble in nano-emulsion. In addition to its myriad of utilities, especially in electrochemistry, it has been found useful in cancer research [20]. A review of its chemistry and its utility in bioorganic chemistry has been carried out by Van Staveren and Metzler-Nolte [21]. In normal non-aqueous solutions, ferrocene is known to undergo a one-electron reversible oxidation process to produce ferrocenium ion. However, in most heterogeneous

systems, such as ionic liquids and microemulsions, ferrocene is observed to undergo a diffusion-controlled quasi-reversible reaction [22, 23]. In nano-emulsion also, as evidenced by the data in this work, ferrocene, in the absence of supporting electrolyte, is observed to undergo a quasi-reversible one-electron oxidation reaction process. We observed that addition of some supporting electrolyte to the prepared nano-emulsion leads to instability and phase separation. However, in order to fully characterize the behavior of this versatile compound (ferrocene) we proceeded to determine some of its relevant electrochemical kinetic parameters in nano-emulsion medium without an added electrolyte. The parameters determined include the formal redox potential, E^o ; the electron transfer coefficient, α ; the heterogeneous rate constant, k_s ; the half-wave potential, $E^{1/2}$ and the diffusion coefficient, D . The chemical structure of ferrocene and the SEM (scanning electron microscope) image of the prepared nano-emulsion are shown in Figs. 1 and 2, respectively.

2. Experimental

2.1 Chemicals

Water used throughout the experiment was a triply distilled and de-ionized using Photronix Reagent Water

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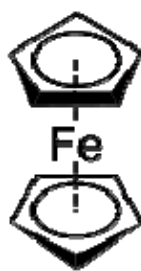


Fig. 1 The chemical structure of ferrocene.

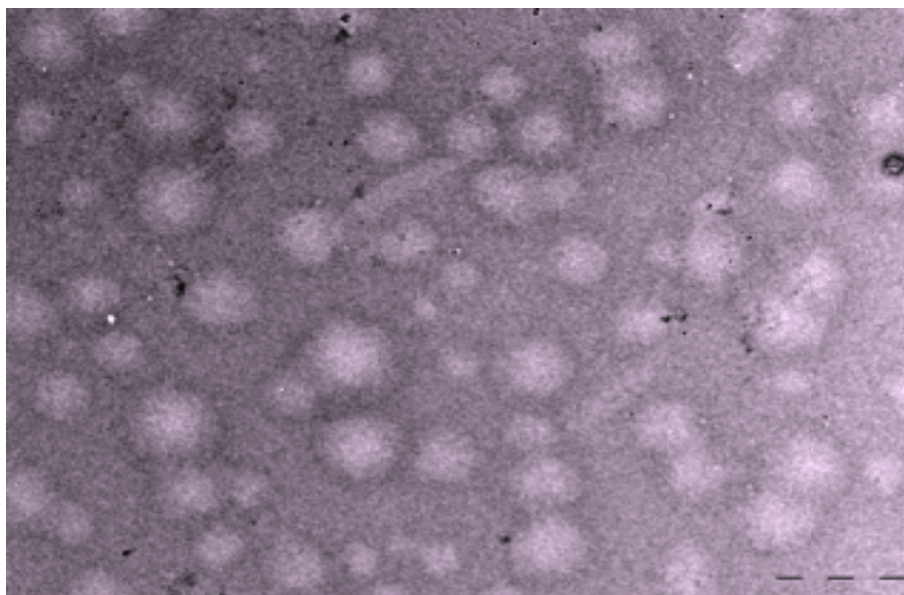


Fig. 2 SEM image of ferrocene in nano-emulsion.

System. 1-pentanol, as co-surfactant, 1-tetradecane and cetyltrimethylammonium bromide (CTAB) were obtained from Acros Chemical in 99% purity. All chemicals were used as received.

2.2 Instrument

All the electrochemical measurements were made in a 1-compartment electrochemical cell using a three-electrode system comprising of the working electrode (1.0 mm diameter), glassy carbon electrode (GCE) obtained from Cypress Systems, a wound platinum wire as the counter electrode and a commercial calomel electrode as the reference electrode, which was obtained from Fisher Scientific. A computer-controlled electrochemical analyzer system supplied by Cypress Systems, Model CS-10190 was used to obtain the requisite voltammograms. The

polisher, Metaserve®200, a brown polishing cloth, to resurface the electrode surface and 0.05 γ -aluminum powder, used in conjunction with the polishing cloth were obtained from Buehler Ltd.

2.3 Nano-emulsion Preparation

Appropriate weight of CTAB and a measured volume of water were mixed together. 1-tetradecane as oil was added to it. Co-surfactant (1-pentanol) was added drop-wise to this mixture and the mixture was mechanically stirred, very vigorously, after each drop until isotopic translucent solution was obtained after which the solution was vigorously stirred for about 5 min before transferring it to the ultrasonic sonicator for about 7-10 min. The solution so prepared was clear and translucent. It was stable for a considerable length of time. The chemical components and their composition

Table 1 Nano-emulsion composition.

Component	Wt., g	Percentage, %	Volume, mL	Volume fraction, ϕ
Water ¹	174.0	76.0	174.0	0.735
CTAB (surfactant) ²	12.0	5.0	12.63	0.053
Oil (tetradecane) ³	14.0	6.0	18.25	0.077
1-pentanol ⁴	29.9	13.0	31.8	0.134

¹ Density = 1.0 g/cm³; ² Density = 0.995 g/cm³; ³ Density = 0.767 g/cm³; ⁴ Density = 0.814 g/cm³.

used in the preparation of nano-emulsion are shown in Table 1.

2.4 Methodology

A total of 10.0 mL of 5.4 mM ferrocene in nano-emulsion was introduced into the electrochemical cell and scanned from -100.0 to 1,000 mV at scan rate ν that varied from 20 to 1,000 mV/s. After each scan the working electrode surface was renewed by polishing as described above.

3. Results and Discussion

We show in Fig. 3 the voltammograms of ferrocene obtained at different scan rates.

It can be seen that the current obtained is increased with an increase in scan rate. This observation is normal with all electrochemical processes. Also, it can be noticed that while the anodic peak potentials are not constant but shift positively the cathodic peak potentials shift negatively resulting in a wider peak separation as can be seen in Table 2.

This large variation in ΔE_p , ($E_{pa} - E_{pc}$), indicates a quasi-reversible reaction and the voltammograms observed are interpreted in that way.

3.1 Determination of Redox Potential, E^0

In accordance with the Nicholson formalism [24] the following equation was used to determine the value of E^0 :

$$E_p = E^0 - (RT/3nF)\ln(F\nu/RT/k_s C_0) \quad (1)$$

In this equation, E_p is the peak potential in volts, ν , and C^0 is the bulk solution concentration which is 5.4×10^{-3} M. A plot (Fig. 4) of E_p versus $\ln \nu$ gives an intercept of E^0 which is 0.33 V.

This value is in reasonable agreement with the literature value [25, 26].

3.2 Determination of Electron Transfer Coefficient, α

The well-known Tafel equation, Eq. (2), was used for the determination of α , for the oxidation of ferrocene in nano-emulsion, that is:

$$\log i = \log i_0 - (1 - \alpha nF/RT)\eta \quad (2)$$

In this equation i and i_0 are the peak current at a given scan rate and the exchange current, respectively. n is the number of electron(s) transferred in the reaction while η is the potential difference at a given potential minus the formal redox potential of ferrocene, that is, $E - E^0$. The rest of the other terms have their usual meaning. Plotting $\log i$ versus η results in a good linear plot as can be seen in Fig. 5.

The slope of this linear plot was used to extract α and the value obtained is 0.6. This value, within limits of an experimental uncertainty, is reasonably in agreement with literature value [27, 28].

3.3 Determination of the Diffusion Coefficient, D

The value of D was calculated using the Randles-Sevcik equation, given in Eq. (3):

$$i_p = 2.69 \times 10^5 A (an)^{3/2} D^{1/2} \nu^{1/2} C^0 \quad (3)$$

In Eq. (3) A is the working electrode surface area, (7.853×10^{-3} cm²), n is the number of electrons transferred in the reaction which is 1, D is the diffusion coefficient of the solute, and ν and C^0 are the scan rate in mV/s and concentration of the solute in the bulk solution in mol/cm³. Plotting the observed current as a function of the square root of the scan rates, that is $di/d\nu^{1/2}$, a linear curve was obtained (Fig. 6)

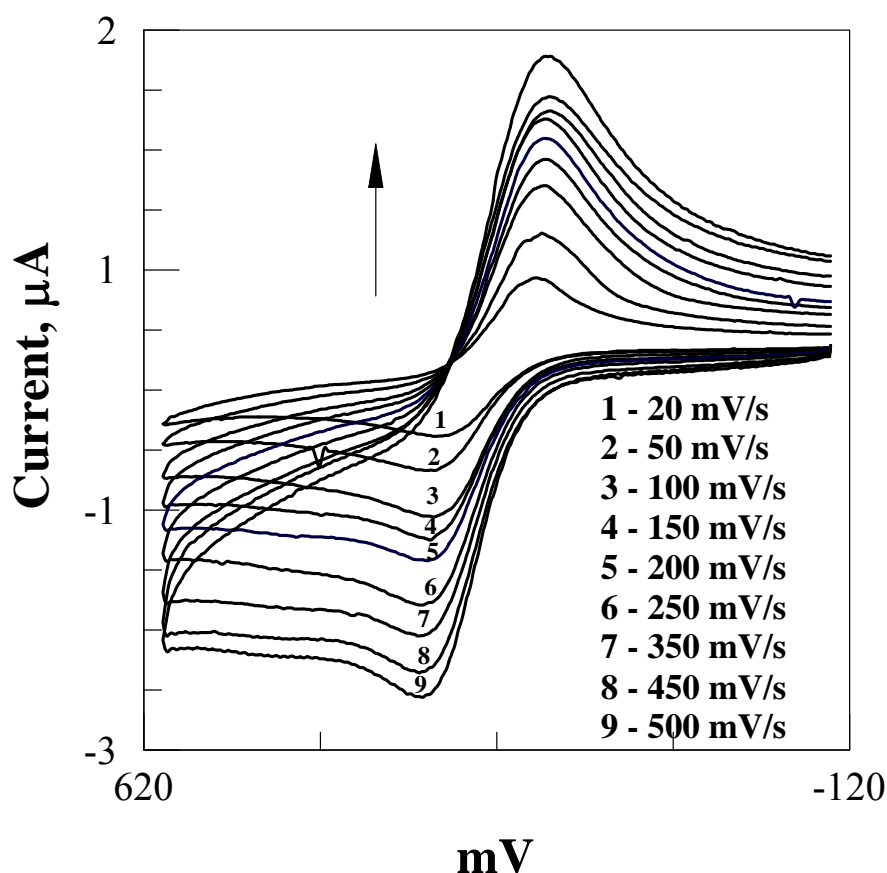


Fig. 3 Voltammograms of 5.4 mM ferrocene at different scan rates.

Table 2 Peak separation with increasing scan rate.

Scan rate, mV/s	ΔE_p , mV
20.0	101
50.0	109
100.0	113
150.0	114
200.0	115
250.0	120
350.0	127
450.0	129
600.0	137
1,000.0	142

from which diffusion coefficient, D , was calculated as $3.0 \times 10^{-7} \text{ cm}^2/\text{s}$.

The obtained diffusion coefficient is in good agreement with the value obtained by other workers [29-33]. In addition to using the Randles-Sevcik equation, chronoamperometry was also used. Fig. 7 shows the amperomogram obtained in the ferrocene

oxidation in nano-emulsion.

Cottrell equation, $i = nFACD^{1/2}/(\pi t)^{1/2}$ was used to obtain the value of D by plotting i versus $1/t^{1/2}$ as per the above equation which resulted in a good linear relation between the observed current and the inverse of the square root of time. This is shown in Fig. 8.

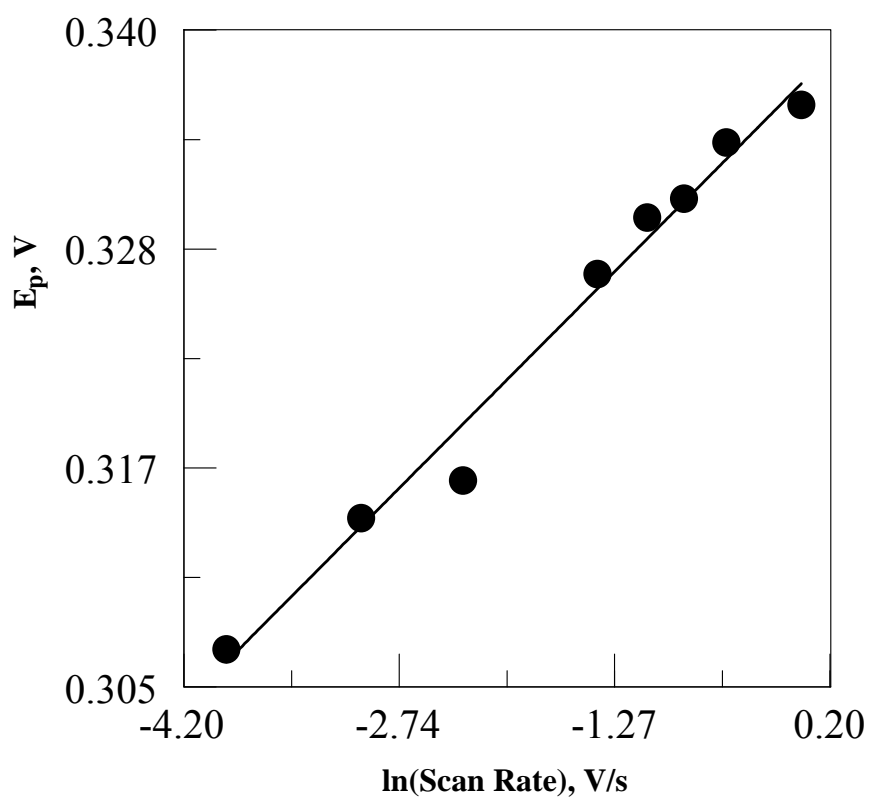


Fig. 4 Observed peak potential versus $\ln(\text{scan rate})$.

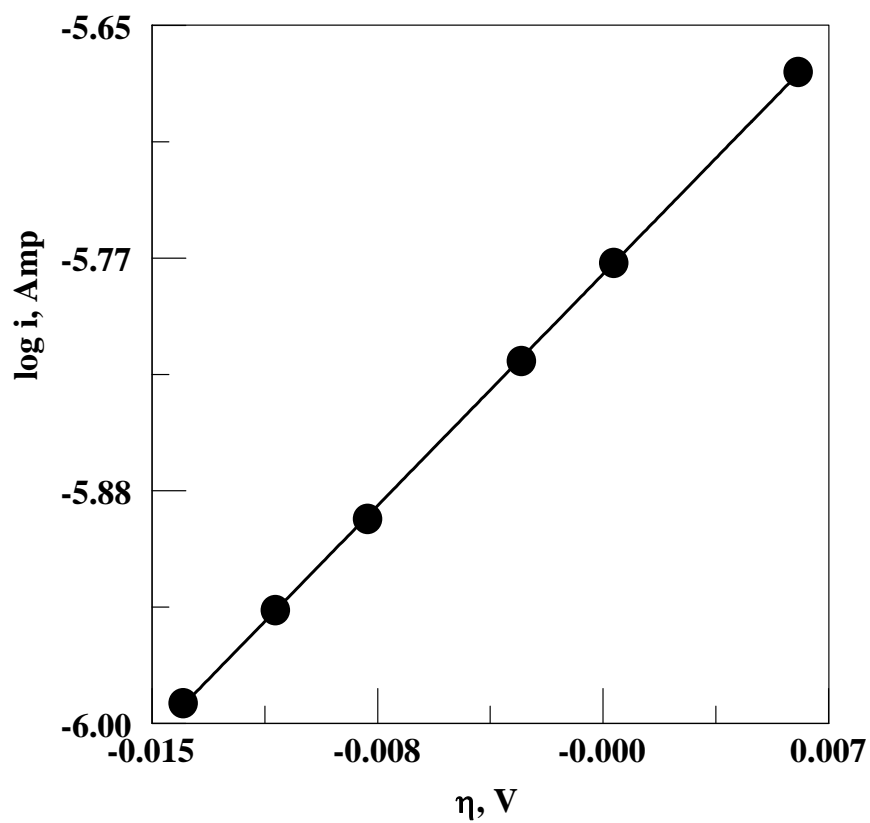


Fig. 5 Current, i (A) versus η ($E-E^0$) (V) (see text).

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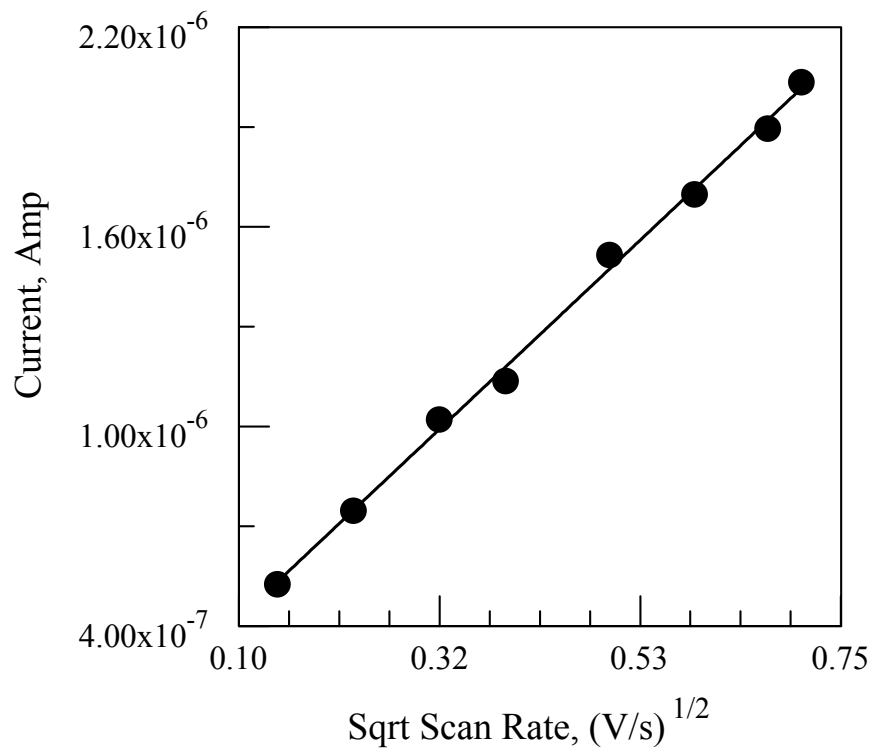


Fig. 6 Observed current (A) versus the square root of scan rate (V/s).

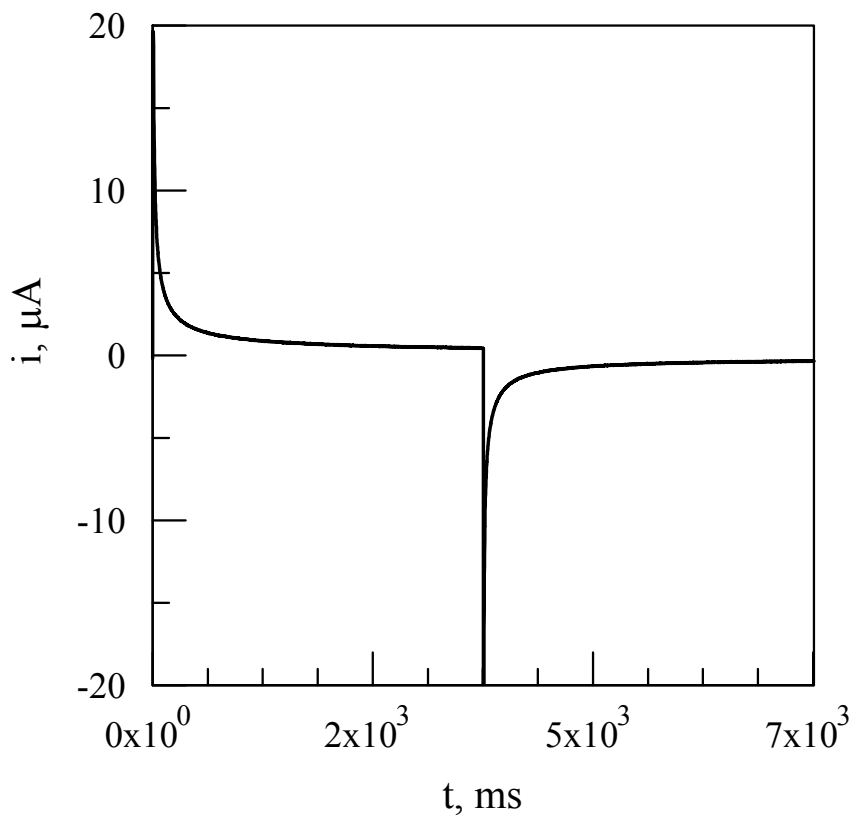


Fig. 7 Chronoamperogram of ferrocene in nano-emulsion.

The slope of this plot was used to get the value of D of $3.2 \times 10^{-7} \text{ cm}^2/\text{s}$. Furthermore, the Stoke-Einstein relation, Eq. (4), was also used:

$$D = kT/6\pi r\eta \quad (4)$$

In this equation, k is the Boltzmann constant, T is the absolute temperature and r and η are the crystallographic radius of ferrocene and viscosity, taken from Refs. [34, 35], respectively. The obtained D value is $3.9 \times 10^{-7} \text{ cm}^2/\text{s}$. As can be seen from Table 3 there is a close agreement of D obtained by these three different techniques.

It is noteworthy that the D obtained by Stokes-Einstein equation is purely theoretical and gives a higher value

due to approximations in its derivation.

3.4 Determination of Heterogeneous Rate Constant, k_s

In other to determine k_s we first determined the dimensionless electrochemical kinetic parameter, ψ , using the equation proposed by Magno and his co-workers shown in Eq. (5) [36].

$$\psi = (-0.6288 + 0.0021X) / (1 - 0.017X) \quad (5)$$

where X is peak separation, ΔE_p at each scan rate. This equation is a simulation using Digism [37] with some experimental data. Inserting the appropriate values in this equation, Eq. (6) results in [38]:

$$\psi = (D_o/D_R)^{0.2} k_s / (\pi D_o F \nu)^{1/2} \quad (6)$$

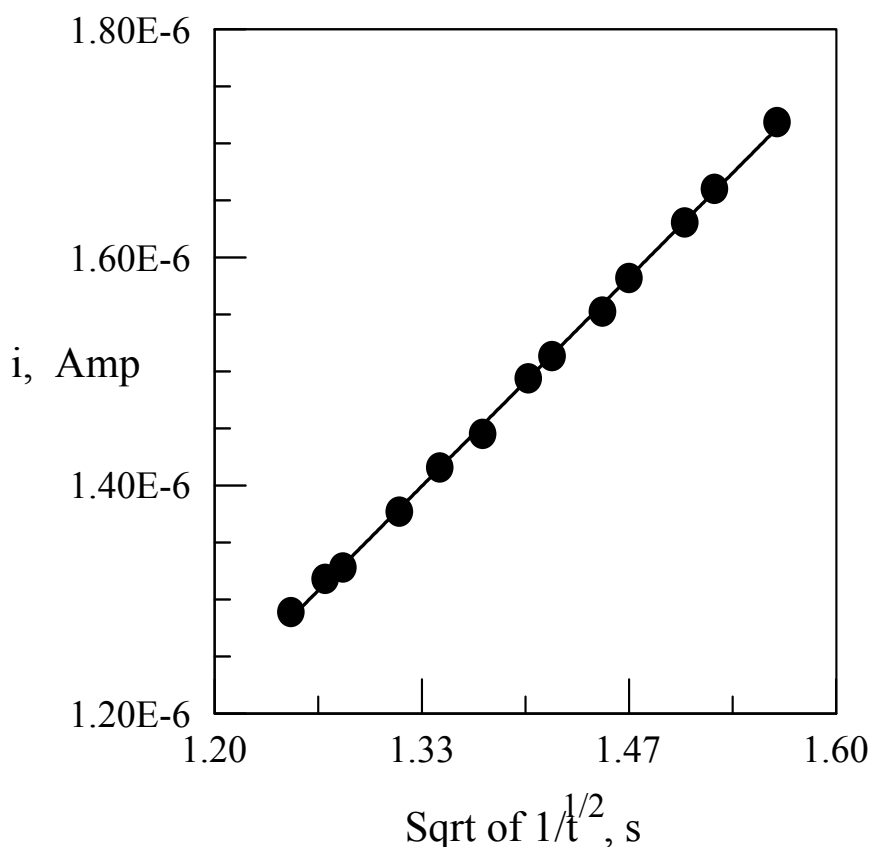


Fig. 8 Observed current (A) versus 1/square root of time in seconds using Cottrell equation.

Table 3 Diffusion coefficient of ferrocene obtained with the different techniques.

Obtained diffusion coefficient	Technique
$3.0 \times 10^{-6} \text{ cm}^2/\text{s}$	CV (Randles-Sevcik equation).
$3.2 \times 10^{-6} \text{ cm}^2/\text{s}$	Chronoamperometry (Cottrell equation)
$3.9 \times 10^{-6} \text{ cm}^2/\text{s}$	Stokes-Einstein equation

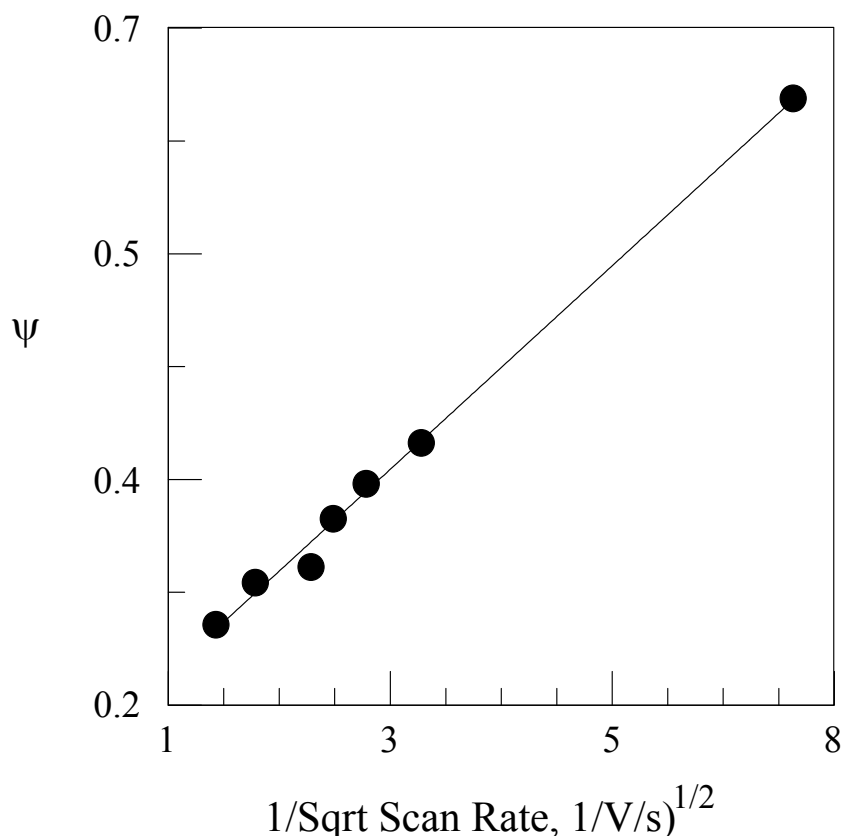


Fig. 9 Electrochemical kinetic parameter, ψ , versus the inverse of square root of scan rate (V/s).

Then plotting ψ as a function of the inverse of the square root of the scan rate in accordance with the relation in Eq. (6) gives a linear curve as can be seen in Fig. 9. Taking $D_o/D_R = \text{unity}$, $n = 1$ and the rest of the symbols having their usual meaning, the slope of the plot will be $k_s/(\Delta\pi nF/RT)$ from which a value of 6.547×10^{-3} cm/s for k_s was extracted. This value is reasonably comparable to value obtained for ferrocene in heterogeneous system by other workers [39, 40].

3.5 Determination of $E^{1/2}$

Typical voltammogram of ferrocene in nano-emulsion is shown in Fig. 10.

Having established that the oxidation of ferrocene in this medium is quasi-reversible, we proceeded to plot the applied potential, E , as a function of the logarithm of the current ratio, $i/i_d - i$, according to the relation in Eq. (7) [41] as is normal in electrochemical practices.

$$E = E^{1/2} - 0.059/n \log(i/i_d - i) \quad (7)$$

where, i_d in this relation is the diffusion current; $E^{1/2}$ is the half-wave potential. The resulting plot is shown in Fig. 11 and it can be seen that the plot of E versus $\log(i/i_d - i)$ is linear whose intercept gives $E^{1/2}$ as per Eq. (7).

This gives a value of 0.25 V which is comparable to the value obtained by other workers [18, 40-43].

3.6 Determination of Current Function

One of the criteria of obtaining a mechanism for kinetics of electron transfer reaction in electrochemistry is the current function [24]. This is determined in this work. In Table 4, we tabulate the scan rate, ν , the observed current, i ; and the current function, $i/\nu^{1/2}$ values. A plot of these data is shown in Fig. 12.

This plot shows a typical EC reaction mechanism, that is, at low scan rate, the very steep portion of the curve illustrates the case of charge transfer taking place while the apparent constant portion, high scan

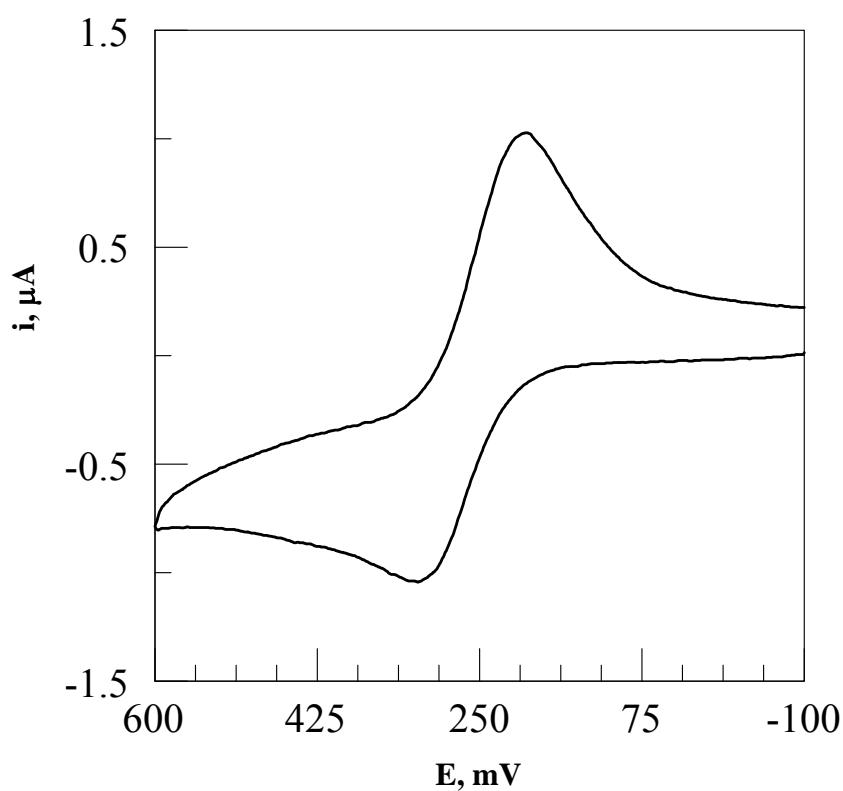


Fig. 10 Typical curve of current versus applied potential for 5.4 nM ferrocene in nanoemulsion at scan rate of 100 mV/s.

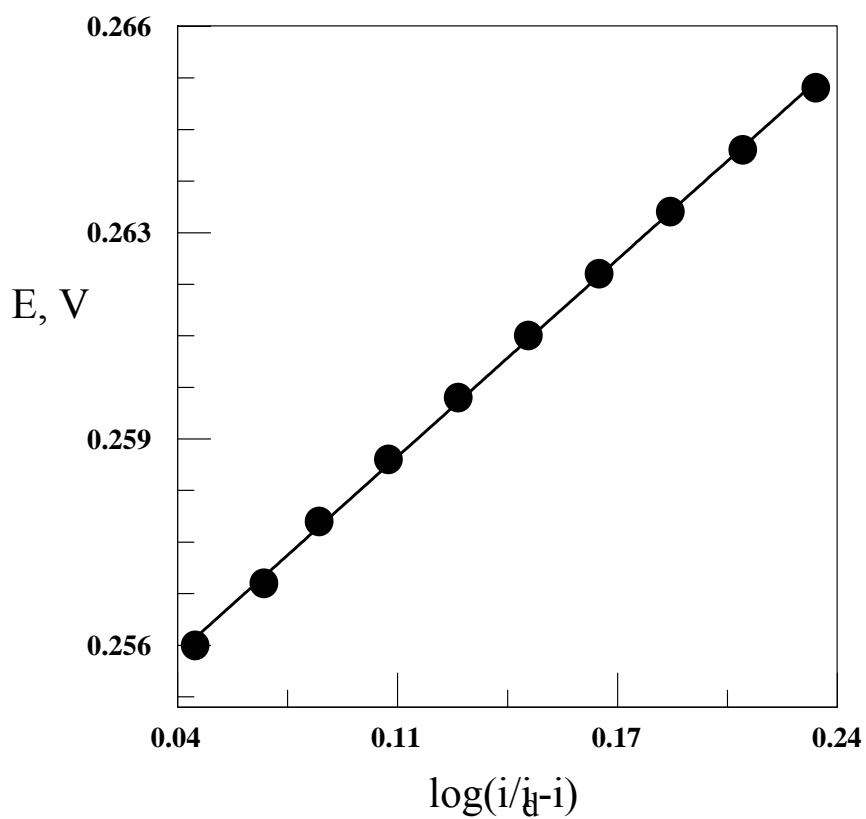
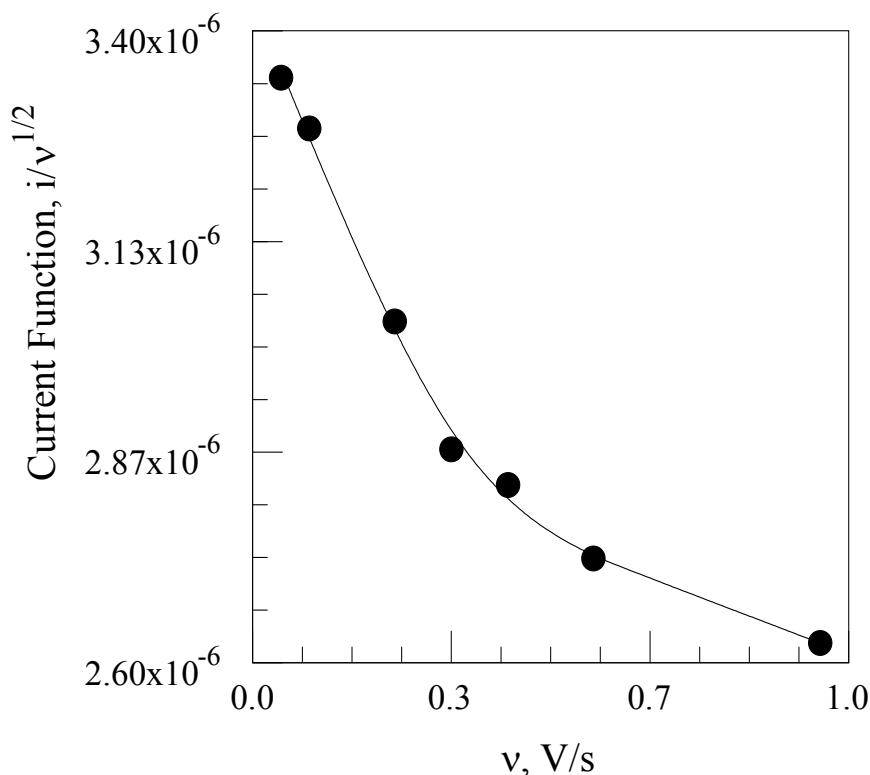


Fig. 11 The observed potential (in V) versus the log of the current ratio (see text).

Table 4 Scan rate in (V/s), observed current, i (in A) and the current function $i/v^{1/2}$.

Scan rate, v (V/s)	Current, i (A)	Current function, $i/v^{1/2}$, A/Sqrt v
0.050	0.747×10^{-6}	334×10^{-6}
0.1	1.021×10^{-6}	3.28×10^{-6}
0.25	1.516×10^{-6}	3.032×10^{-6}
0.35	1.698×10^{-6}	2.87×10^{-6}
0.45	1.895×10^{-6}	2.82×10^{-6}
0.60	2.116×10^{-6}	2.73×10^{-6}
1.00	2.625×10^{-6}	2.62×10^{-6}

**Fig. 12** Current function $i/v^{1/2}$ versus scan rate (in V/s).**Table 5** Determined electrochemical parameter.

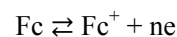
Parameter	Value	Unit
Diffusion coefficient, D	3.0×10^{-7}	cm^2/s
Redox potential, E^0	0.33	V
Half-wave potential, $E^{1/2}$	0.25	V
Heterogeneous rate constant, k_s	6.547×10^{-3}	cm/s
Electron transfer coefficient, α	0.60	-

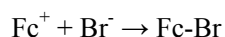
rate, the plot indicates an irreversible chemical reaction.

We give in Table 5 the observed kinetic data obtained in this work.

With the overall observed and determined data as shown in Table 5 for the oxidation of ferrocene in

nano-emulsion, together with one of the criteria given in Table 4 and Fig. 1, here we give a plausible reaction mechanism of the electro oxidation of ferrocene in nano-emulsion that is consistent with the observed data.





4. Conclusion

We have shown in this work that ferrocene undergoes an EC and quasi-reversible reaction in nano-emulsion without a supporting electrolyte. The remarkable observation is that some of the parameters used in this heterogeneous system obey the same equation used in conventional homogeneous solution with supporting electrolyte. The voltammograms obtained without a supporting electrolyte are well defined within the confines of the scan rate range used in this work. We conclude that nano-emulsion may therefore be a good medium for electrochemical studies without an added electrolyte.

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