Diffusion Coefficient of Iodide ions in Aqueous Medium and in Vacuum: an Appraisal.

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Summary: Diffusion Coefficient of iodide ion was determined through cyclic voltammetric technique and compared with the values in literature. The contribution of (a) the fractal surface of the electrode, and (b) possible involvement of subsequent chemical reaction (EC) to the peak current affecting the diffusion coefficient were analyzed. It was concluded that the diffusion coefficient obtained via peak current of the cyclic voltammogram corrected for sweep dependence could be relied upon. The diffusion coefficient, D, of I^- ion in aqueous media is deduced to be 1.95 ($\pm$0.05) $\times 10^{-5}$ cm^{2}s^{-1}. Fractal analysis showed there is very negligible effect of fractal surface of the electrode.
Diffusion coefficient of iodide ion in vacuum was calculated from equation $D = h / 4\pi m_{I^-}$, where h is Planck's constant and m_{I^-} is the mass of iodide ion. D of I^- in vacuum came out to be much smaller, 2.5 $\times 10^{-6}$ cm^{2}s^{-1}, as compared to the one in aqueous solution. This D may be considered as the lower limit of the diffusion coefficient of a species, here I^-.

Key words: Diffusion coefficient, Iodide Ion, Cyclic voltammetry, Fractal surface, Water medium, Vacuum.

Introduction

Electrochemistry of I^-, I_2 and I_3^- has been of interest since long [1-5]. However, the recent interest in the aforementioned three species arises from the anti-cancer cells activity of the three of them [6]. Since one of the modes of transport of a drug to the reaction site is diffusion, this can motivate one to evaluate the diffusion coefficient of a drug, here I^- or I_2 or I_3^- . And this motivated us to study and evaluate the diffusion coefficient of the simplest of the above mentioned three species, I^- . This species being the simplest in structure hence is easiest to study (I^- can be considered as a perfect sphere). Besides diffusion coefficient, the radius of I^- has also been of interest to chemists [6 -8].

A varied of numerical values of diffusion coefficients of I^- , $D(I^-)$, in aqueous media, have been reported in literature [7-10]. For example, in aqueous system, $D(I^-) =$ 1.80 x 10^{-5} cm^{2}s^{-1} as well as = 8.0 x 10^{-6} cm^{2}s^{-1} have been reported in old literature [9]. The above values of $D(I^-)$ have been obtained through conductometric measurements [9] and / or, use of Stokes-Einstein equation [9]. $D(I^-)$ in aqueous system as obtained by hydrodynamic voltammetry is reported as 1.88 x 10^{-5} cm^2 s^{-1} [7]. A range of $D(I^-)$, between 1.6 10^{-5} and 2.8 10^{-5} cm^2 s^{-1} were reported for acetonitrile-water mixture [8], with the minimum value for about 10 mole% CH$_3$CN. A rather high

value 5.4 $\pm$ 0.2 x 10^{-5} cm^2 s^{-1} has been reported in methylene chloride [10]. These later values were obtained through voltammetric method(s) [8, 10].

To investigate the reason behind such variation in the experimental values of $D(I^-)$, it deemed fit to take up the task of determining $D(I^-)$ experimentally and finding what are those parameters or factors which could influence the variation in $D(I^-)$ values. For such purpose linear scan / cyclic voltammetric method seemed quite a suitable technique for the determination of $D(I^-)$. Linear scan / cyclic voltammetry are a well established technique which is based on sound stationary electrode voltammetry theory [11].

An intriguing question arises as to what is the absolute value of $D(I^-)$, if there is such a term as absolute diffusion coefficient. In other words what is the numerical value of $D(I^-)$ which is free from the influence of any surrounding medium and other effects. Could we call such $D(I^-)$ as diffusion coefficient in vacuum. Is it possible to calculate / evaluate, such a value of $D(I^-)$?. This is an intriguing aspect of diffusion coefficient not considered before.

Thus here we report the results of our own voltammetric studies on the determination of $D(I^-)$ in

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aqueous medium, and investigate $_-$ factor(s) influencing the variation in those $D(I^-)$-values determined voltammetrically or otherwise. Also we investigate, if there is any theoretical expression and / or experimental way to obtain the absolute value of $D(I^-)$ (or a diffusion coefficient in vacuum) – a $D(I^-)$ value completely free from the influence of any surrounding atmosphere.

Various Expressions for the Evaluation of Diffusion Coefficient

Earlier work, for obtaining diffusion coefficient of an ionic species, was based on the measurement of ionic conductance or ionic mobility [9]. The expression relating diffusion coefficient D to its mobility is given as [9], at temperature T,

$$D = (k_B T / \varepsilon) U^0 / Z \tag{1}$$

where Z is charge (valence) of the ion (in the present case of I^-, Z = 1), ε is electronic charge , U^0 is the mobility of the ionic species at infinite dilution, k_B is Boltzmann constant.

Using mobility (in the unit of cms^{-1}), D (in cm^2s^{-1}) can be obtained from, eq.(2), [9]

$$D\ (cm^2s^{-1}) = 8.57 \times 10^{-5} U^0 \tag{2}$$

For I^-, U^0 is 0.21 cms^{-1} [9] which gives $D(I^-)$ = 1.8×10^{-5} cm^2s^{-1}.

A useful expression relating D and radius of a spherical diffusing species is given as Stokes-Einstein equation

$$D = k_B T / 6\pi\eta r \tag{3}.$$

where η is the viscosity of the solvent or solution; using Walden product $r(I^-) = 0.247$ nm [9], $D(I^-)$ is obtained as 0.8×10^{-5} cm^2s^{-1} and from crystal structure radius of I^- = 0.178 nm [9], D = 1.1×10^{-5} cm^2s^{-1}.

Diffusion coefficient of an electroactive species can also be determined through linear scan- and cyclic-, voltammetry. For an uncomplicated reversible process

$$O + ne \; f \;\; R \tag{4}$$

Diffusion coefficient D is related to the peak current, i_p, as [11],

$$i_p = 0.446. \; nFAC_o * (D)^{1/2} \left(a^{1/2}\right) \tag{5}$$

where i_p is in ampere, A = the area of the electrode, generally taken as geometric area, in cm^2, C_o* = bulk concentration of species O in mole cm^{-3} and $a =,Fv / RT$, v = scan rate in Vs^{-1}; D (in cm^2s^{-1}) can easily be obtained from the measured i_p.

It is to be noted that for a chemically coupled reaction to a reversible charge transfer process, i_p can be affected by the reaction parameters (rate constant, equilibrium constant etc) of coupled chemical reaction. This then can affect the calculated value of D. Thus the D-value will be an apparent diffusion coefficient value. Also if A, the area of the electrode is the area other than the geometric area, then, D, obtained from experimental i_p will again be apparent diffusion coefficient in that solvent (for detail see later). Corrective measures have to be taken to obtain correct D-value.

An expression for a diffusion coefficient of a microscopic particle (performing the Gaussian random walk, say), free from any environmental influence or other influencing factor, can be identified as

$$D = h \; / \; 4\pi m \tag{6}$$

where h is Planck's constant and m is the mass of the microscopic particle (performing the Gaussian random walk).

Eq.(6) can be arrived at by using Heisenberg uncertainty principle relationship [12-14] and the relationship between diffusion coefficient , space (x) and time (t), and assuming the motion of the microscopic particle is following Gaussian curve [12, 13]

The application / implication of this expression, eq. (6) will be presented later.

Experimental

Instruments

A Sycopel AEW workstation and / or a CHI 600 Electrochemical Analyzer were employed for recording cyclic voltammograms.

Electrodes

Three electrode configuration of glassy carbon (3.3mm dia) or platinum (1.6mm dia) as working electrode, a Graphite (PAR) or platinum

wire (BAS) as counter electrode and a saturated calomel electrode as reference electrode, was used.

Chemicals

Potassium Iodide (Merck, 99.0 %) potassium chloride (Merck, 99.9%) were used as received (without further purification), deionized water was used.

Procedure

The experimental details of the cyclic voltammetric studies on iodide ion, has already been published [5]. Generally 1-5 mM concentration aqueous solution of KI containing 0.1 M supporting electrolyte KCl was used. Cyclic voltammograms were recorded at various scan rates from 0.05 V/s to 3.0 V/s – quite a wide range.

Results and Discussions

Diffusion Coefficient of Iodide Ion, $D(I^-)$, and Coupled Chemical Reaction

First, results of the present study are presented and commented upon. From voltammetric measurements (Fig. 1) and using i_p – D relationship, eq. (5), $D(I^-)$ - values were obtained which were found to be scan dependent - $D(I^-)$ decreasing with the increase in scan rate. $D(I^-)$ calculated from eq. (5) at various scan rates are collected in Table-1. and presented in Fig. 2, The extrapolated value of $D(I^-)$ for $V \longrightarrow \infty$, $D(I^-)\infty$, was obtained as 2.50×10^{-5} $cm^2 s^{-1}$ (however, see later).
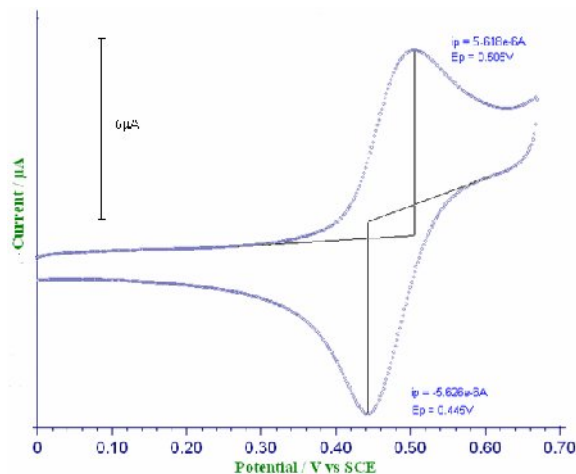

Fig. 1:   C. V of 1 mM KI in aqueous solution using 0.1M KCl as supporting electrolyte at scan rate 0.100 V/s
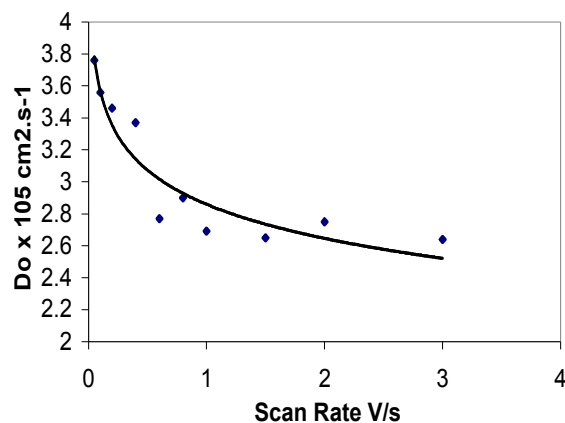

Fig. 2:   Plot of D_o vs. Scan rate (Vs^{-1}).

The reason for the difference in $D(I^-)$ – values (Table-2) can better be understood if the value of $D(I^-)\infty$ obtained in the present study is commented upon in the context (*a*) why it is different from other reported values and also (*b*) why voltammetric values are generally different from non-voltammetric $D(I^-)$'s. In other words, what could be those factors which could influence the values of diffusion coefficient.

Table-1: Diffusion Coefficients at various scan rates.

S. No.	Scan Rate Vs^{-1}	$(i_p)_a \times 10^6 A =$	$D_o \times 10^5 cm^2 s^{-1}$		
1.	0.050	3.7	3.76^a	3.75^b	3.67^c
2.	0.100	5.1	3.56	3.70	3.55
3.	0.200	7.1	3.46	3.60	3.40
4.	0.400	9.8	3.37	3.45	3.21
5.	0.600	11.0	2.77	3.30	3.08
6.	0.800	13.0	2.90	3.17	2.98
7.	1.000	14.0	2.69	3.05	2.90
8.	1.500	17.0	2.65	2.79	2.75
9.	2.000	20.0	2.75	2.66	2.65
10.	3.000	24.0	2.64	2.34	2.54

(*a*)   From eq. (5), (*b*) from eq.(13), (*c*) from eq. (14)

For reference, all the values of $D(I^-)$, mentioned above, are collected in Table-2.

From Table-2 it is noted that the numerical value of diffusion coefficient of I^-, $D(I^-)$, varies with the measurement techniques and with the solvent,. These observation needs to be commented upon.

Table-2: Various Diffusion Coefficient values.

S. No	$D(I^-) \times 10^5 cm^2 s^{-1}$	Method / Ref.
1	1.80	mobility method, eq. (2), [9]
2	2.50	Present method. Eq. (5) and fig. (1)
3	1.88	Hydrodynamic voltammetry [7]
4(a)	2.80	Voltammetry [8] in water
4(b)	1.66	Voltammetry [8] 10 mole % MeCN
5(a)	0.8^a	from Stokes-Einstein Eq. (3) [9]^a
5(b)	1.1^b	from Stokes-Einstein Eq. (3) [9]^b
6	0.26	Absolute or limit value, from eq.(6)
7	5.4 (+0.2)	Voltammetry [10] in Methylene chloride
8	1.95 (+ 0.05)	Present method, from eq. (13,14)

(*a*)   Radius of I^- = 0.247 nm [9], (*b*) Radius of I^- = 0.178 nm [9],

Taking the question (*b*) first , the cause of a higher value of D(I⁻) obtained by the voltammetric method could be due to either the electrode surface effect or involvement of subsequent chemical reaction(s), involving some (undefined) kinetic current.. The effect of these two factors on D(I⁻) are discussed below with reference to the present study (re (*a*), above).
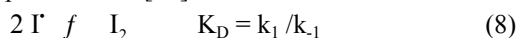
In the present case the diffusion coefficient of I⁻ was obtained, using eq, (5), assuming I⁻ to be undergoing the process, eq. (7)

$$I^- - e \rightleftharpoons I^\bullet \qquad\qquad (7)$$

D(I^-) depended upon experimental magnitude of the peak current, i_p, which according to eq. (5), depended upon the area of the electrode. To understand the effect of electrode area on i_p one has to invoke fractal dimension analysis (see later).

But experimental i_p, may also be the result of other coupled (kinetic) process(es).

For the possibility of involvement of some coupled chemical reactions, follow-up chemical reaction(s), like eq. (8) and /or. eq.(9), can be pertinent in the present case. These coupled chemical reactions can contribute some extra current to the peak current [11].

$$2 I^\bullet \rightleftharpoons I_2 \qquad K_D = k_1 /k_{-1} \qquad (8)$$
$$I_2 + I^- \rightleftharpoons I_3^- \qquad\qquad (9)$$

Depending upon k_1 and K, the ratio of $(i_p)_{kinetic}$ / $(i_p)_{reversible}$ is always greater than unity, $(i_p)_{reversible}$ is the one which follows eq. (5) [11]. Thus diffusion coefficient calculated from $(i_p)_{kin}$ will always be greater than that obtained from $(i_p)_{rev.}$, eq.(5).

The elctro-oxidation of iodide ion, as depicted through mechanism through eqs. (7-9), can explain the observed dependence of D(I⁻) on the scan rate as observed in the present case. Larger value of D(I⁻) at slower scan rate is indicative of contribution of some kinetic current to i_p [11]. At higher scan rate the contribution of the kinetic current due to the follow-up, here dimerization, kinetic current may become smaller – provided the follow-up reaction is slow. In the case of iodide ion the rate of dimerization is indeed slow [6]. From the work of Olmstead, Hamilton and Nicholson on dimerization of an electrochemically generated species [15], it is clear, the peak current, i_p, depends upon the ratio k_1 / a, (a = nFv / RT, v being scan rate). Thus at higher

scan rate i_p becomes smaller and hence the numerical value of diffusion coefficient decreases with the increase in scan rate.

Diffusion Coefficient of Iodide Ion, D(I^-), and Electrode Surface Area.

It has been mentioned above, another factor which can affect the value of diffusion coefficient, is the surface area of the electrode. A 'blocked' electrode has lesser surface area. This is more explicitly explained by fractal theory. Since fractal theory and its application in electrochemistry is rather unfamiliar to many electrochemists, its use here is being given in little detail

From eq. (5) it is deduced that

$$i_p \; \alpha \; v^{1/2} \qquad\qquad (10)$$

However, according to fractal theory, for an electrode process as given by eq. (4), one has [16].

$$i_p \; \alpha \; v^\gamma \qquad\qquad (11)$$

When □ is given, for 2 – dimension system [16], as

$$\gamma = \frac{d_f + 1}{2} \qquad\qquad (12)$$

where d_f is the fractal dimension parameter. For □ = ½, d_f = 2 i.e. 2-D surface area, so □ and / or, d_f tells us the "departure" from the perfect 2-D or geometric area.

A plot of *ln* i_p vs. *ln* v (Fig. 3) gave the slope □ = 0.45. This gives d_f = 1.90 which indicates lower reaction site value or electrochemical area by the ratio 1.90/2.00. Since according to eq. (5), i_p is proportional to A, the area (in fact reactive or electrochemical area) hence experimental current should be smaller in the present case. Besides, this fractal surface electrode effect does not explain why diffusion coefficient be scan rate dependent, observed in the present case.

After diagnosing the cause of higher value of D(I⁻) and attributing it (mainly) to follow-up dimerization kinetics, the value obtained in the present study, 2.50 x 10⁻⁵ cm²s⁻¹ seems reasonable as compared to the other reported values of 5.4 x 10⁻⁵ cm²s⁻¹ [10], and 2.80 x 10⁻⁵ cm²s⁻¹ [8],. However, it is felt that it may still very well be on higher side (see

below) because the curve fitting in Fig. 2, as given, may not be the perfect fit to the data.
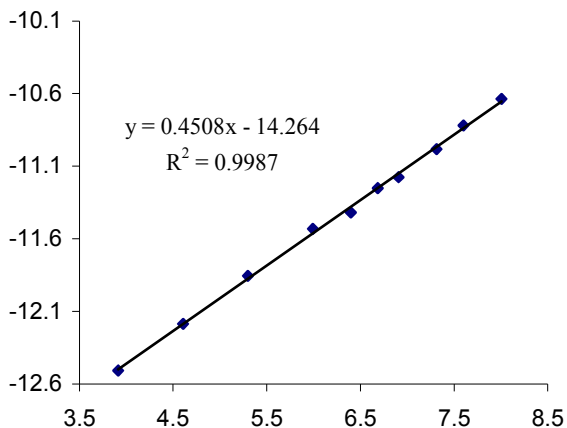

$$y = 0.4508x - 14.264$$
$$R^2 = 0.9987$$

Fig. 3:　Evaluation of fractal dimension parameters, Plot of *ln* i_p vs. *ln* v.

The data for $D(I^-)$ at various scan rate may be fitted to an empirical equation as,

$$D_v = 1.9 \text{ x} 10^{-5} \left[1 + e^{-0.5v} \right] \text{ cm}^2\text{s}^{-1} \qquad (13)$$

However another equation:

$$D = 2.0 \text{ x} 10^{-5} [1 + e^{-\sqrt{v}}] \text{ cm}^2\text{s}^{-1} \qquad (14)$$

Gives even superior fit to the "experimental data, (Table-1 , Fig. 2**)**

From these two curve fitting equations one can conclude $D(I^-) = 1.95 (\pm 0.05) \times 10^{-5}$ cm^{2}s^{-1}. This value is quite close to the one obtained by hydrodynamic voltammetry and conductometry, Table-2.

The reason for higher $D(I^-)$ values obtained through LSV or CV, in aqueous solution, has been now explained, The matter of lower value of $D(I^-)$ reported in literature, in solution, and that in vacuum (the present case) are now deliberated upon.

The lower value of $D(I^-)$, reported in the literature are (Table-2**)** 1.88 x 10^{-5} cm^{2}s^{-1} (hydrodynamic voltammetry), 1.60 x 10^{-5} cm^{2}s^{-1} (LS or cyclic- voltammetry) in the presence of 10 mole % of acetonitrile, and 1.80 x 10^{-5} cm^{2}s^{-1} (conductometry). Quite low value of $D(I^-) = 1.1$ x 10^{-5} cm^{2}s^{-1} had been obtained through the use of Stoke-Einstein equation, eq.(3), using crystallographic $r(I^-) = 0.178$ nm, say. The lower

values of $D(I^-) = 1.88$ x 10^{-5} cm^{2}s^{-1} and 1.60 x 10^{-5} cm^{2}s^{-1} can be attributed to the noninterference from follow up dimerization.

It is known that acetonitrile, in at least some cases, does reduces the dimerization process of electrochaemically generated species as is the case in methyl viologen cation radical as well as methyl viologen neutral [17]. It is possible; acetonitrile is playing the same role here too. In the case of hydrodynamics voltammetry, it seems this technique is better suited for such electrochemical processes as slow follow-up chemical reaction. The dimerization process does not affect the conductivity method - the $D(I^-)$-value obtained by this method is close to the one obtained by hydrodynamic voltammetry. Apparently the use of "conductance or mobility at infinite dilution" values eliminate the effect of dimerization effect on diffusion coefficient obtained by this method.

The value of $D(I^-)$ obtained by using Stokes-Einstein equation, eq.(3), can really be not relied upon because of factors such as, (a) assumption that the radius of iodide ion, in crystal remains the same as in solution and (b) that Stokes-Einstien equation as given in eq. (3) above is an oversimplified version of much more complicated equation [18] .

This brings us to discuss something about the "absolute" $D(I^-)$ or $D(I^-)$, in vacuum.

The Value of $D(I^-)$ in Vacuum.

The *absolute* or "limiting" value or value in vacuum, of diffusion coefficient of a particle moving under *no* external influence, is obtained from eq.(6). For iodide ion, I^-, $D(I^-)$, it is 2.50×10^{-6} cm^{2}s^{-1}, much smaller than that in aqueous medium and also smaller than in any dielectric medium. Also this value remains unaffected by increase or decrease in temperature.

Also a most amazing conclusion is arrived that the "absolute or in vacuum or the limit-value" diffusion coefficient is that it is only dependent on mass of the particle – not on size, not on charge, not on any external or internal factor.

Some aspects of this equation, eq.(6), and random walk motion have been discussed by Feynman [19].

Conclusion

From this study it is concluded that evaluation of diffusion coefficient of an electroactive species by voltammetric method may be affected by

two factors and step(s) be taken to take care of these two "factors". The two factors being, (a) the area of electrode and (b) possibility of a follow-up chemical reaction. To be sure the two factors are taken care of, it is necessary that for (a) a fractal analysis of area of electrode be done and necessary step be taken that ☐☐is close to 0.5, and for (b) diffusion coefficient, D, be evaluated at various scan rates – ranging from slowest permissible scan rate to several order of magnitude higher. Diffusion coefficients thus evaluated be plotted against the scan rate and extrapolated to the "infinite volt per sec" scan rate or else fitted in an equation similar to eq. (13 or 14). After taking care of these two factors the value of the diffusion coefficient will be closer to the true value of diffusion coefficient in that environment.

For the absolute or limit or in vacuum value of diffusion coefficient of any species, it can be claimed that D, evaluated through eq.(6) gives the minimum value of diffusion coefficient of a microscopic particle. An experimental diffusion coefficient obtained through some measurement, lower than the one absolute value (of diffusion coefficient) indicates existence of some external or internal factor under which the particle is moving.

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