J. Chem. Eng. Data **1997,** *42,* 216−220

Diffusion Coefficients of Molecular Iodine in Aqueous Solutions

Laurent Cantrel

Institut de Protection et de Sûreté Nucléaire, IPSN/DRS/SREAS, CEA Cadarache, BP No. 1,
13108 Saint Paul lez Durance, France

Rachida Chaouche and Josette Chopin-Dumas*

Ecole Nationale Supérieure de Synthèses, de Procédés et d'Ingénierie Chimiques d'Aix-Marseille,
Laboratoire d'Electrochimie Inorganique, 13397 Marseille Cedex, France

The diffusion coefficients of iodine in 0.075 mol dm^{-3} sulfuric acid have been determined between 298 K and 358 K, by measuring the limiting reduction currents at a platinum rotating disk electrode. A Stokes−Einstein relation is verified over the range of temperature studied. The experimental value obtained at 298 K is compared with some available relations for the estimation of diffusion coefficients at infinite dilution. The agreement is good.

1. Introduction

In the event of a severe accident on a light water nuclear reactor (LWR), resulting in overheating of the core, the fission products would be released into the containment building. Among the fission products, iodine represents a biological hazard for the environment by reason of the ^{131}I radioactive isotope. As iodine is a highly reactive and volatile compound, it is involved in mass transfer from the liquid phase to the gas phase of the containment vessel. In order to determine the quantity of iodine present in the gas phase, it is necessary to know the diffusion coefficient of iodine in water at several temperatures. This paper reports the measurement of diffusion coefficients of iodine in aqueous solutions.

Literature values at 298 K have been determined by electrochemical means. Kolthoff and Jordan (1953) calculated a value of 1.11×10^{-5} cm^2 s^{-1} for the diffusion coefficient of I_3^- at infinite dilution in 0.1 mol dm^{-3} $HClO_4$ from conductance data. As their experimental limiting reduction current of iodine was not measurably affected by the presence of 0.1 mol dm^{-3} potassium iodide, they conclude that $D_{I_2} = D_{I_3^-}$ Geissler et al. (1966) determined a value of 0.96×10^{-5} cm^2 s^{-1} in a mixed solution of 0.1 mol dm^{-3} $HClO_4$ + 0.4 mol dm^{-3} KNO_3, with a gallium disk electrode. Finally, Beran and Bruckenstein (1968a) found, with a platinum rotating disk electrode, 1.04×10^{-5} cm^2 s^{-1} in 0.1 mol dm^{-3} $HClO_4$ + 0.4 mol dm^{-3} $NaClO_4$ and 1.07×10^{-5} cm^2 s^{-1} in 0.1 mol dm^{-3} HCl + 0.4 mol dm^{-3} $NaClO_4$.

An analytical method for the determination of iodine in aqueous solution is linear sweep voltammetry. In an acid medium (0.075 mol dm^{-3} H_2SO_4), iodine yields a wave corresponding to the reduction of I_2 to I^-, between −0.5 and 0.0 V against a saturated mercurous sulfate electrode. The coefficient of proportionality *L*, known as the "Levich coefficient", which exists between the diffusion limiting current and the concentration, permits us to obtain the diffusion coefficient.

In this work we determine the Levich coefficient *L* between 298 K and 358 K, in increments of 15 K and derive the diffusion coefficient from the *L* values in 0.075 mol dm^{-3} H_2SO_4.

For the reduction or oxidation of an electroactive species in a supporting electrolyte with a convective-diffusion limited process, the limiting current is given by

$$I_{\mathrm{lim}} = \frac{nFSDC}{\delta} \qquad (1)$$

where δ is the Nernst diffusion layer (cm) across which mass transport occurs and *n* is the number of electrons exchanged during the reaction. Other terms have their customary meaning: *F*, the Faraday constant (96 487 C), *S*, the electrode area (cm^2), *D*, the diffusion coefficient (cm^2 s^{-1}), and *C*, the concentration (mol dm^{-3}).

A forced convective diffusion regime keeps the thickness δ at a constant value. The empirical relationship (2) was suggested by Gregory and Riddiford (1956) in order to define the thickness of the diffusion layer:

$$\delta = [1.6126 + 0.5704\mathrm{Sc}^{-0,36}]\mathrm{Sc}^{-1/3}\left(\frac{\nu}{\omega}\right)^{1/2} \qquad (2)$$

ω is the angular velocity of the electrode, in rad s^{-1}, and ν, the solvent kinematic viscosity, in cm^2 s^{-1}. The Schmidt number, Sc, is defined as

$$\mathrm{Sc} = \frac{\nu}{D}$$

Later, Newman (1966) and Kassner (1967) solved the equation (1) of Levich (1942, 1944) in a more rigorous manner by taking into account the normal component for fluid velocity in terms of a series in $\mathrm{Sc}^{-1/3}$.

$$\delta = [1.61173 + 0.48031\mathrm{Sc}^{-1/3} + 0.23393\mathrm{Sc}^{-2/3} + 0.11315\mathrm{Sc}^{-1}]\mathrm{Sc}^{-1/3}(\nu/\omega)^{1/2} \qquad (3)$$

In most cases, neglecting the terms of order $^2/_3$ and 1 results in an error of less than 5% at 298 K. However, as the Schmidt number decreases strongly with temperature, its influence becomes more important at higher temperatures.

The relationship (1) can be written as

$$I_{\mathrm{lim}} = LC\omega^{1/2} \qquad (4)$$

This expression shows that the determination of the coefficient L, from which the diffusion coefficient is to be calculated, can be carried out either with a variable

S0021-9568(96)00178-1 CCC: $14.00

Table 1. Composition of the Studied Solutions for 2 L

$10^4[I_2]$/mol dm^{-3}	10^4[KI]/mol dm^{-3}	$10^4[KIO_3]$/mol dm^{-3}
11.956	19.927	4.001
6.003	10.005	2.002
3.997	6.662	1.337
2.000	3.334	0.670

concentration and a fixed rotation rate ω or with a variable rotation rate and a fixed concentration. These two possibilities are not equivalent with respect to the theory. The latter, know as the "Levich criterium" is useful to verify that the limiting current remains mass-transport controlled as the rotation rate ω increases. As iodine is volatile, it is difficult to maintain a constant concentration of the liquid solution. Hence, the Levich criterium has been checked for the anodic oxidation of iodide (Chopin-Dumas) and is assumed to be valid for the reduction of iodine, owing to the reversibility of the I_2/I^- couple. Returning to the iodine experimentation, the limiting current was determined by varying the iodine concentration, at constant rotation rate. In order to establish this concentration, another analytical method must be used.

In UV−visible spectrophotometry, I_2 exhibits a characteristic absorption peak, the maximum being located at 460 nm. The Beer−Lambert law (5)

$$\mathrm{Abs}_{460} = \epsilon_{I_2}^{\;460} l C_{I_2} \tag{5}$$

yields the iodine concentration C_{I_2}, by measuring the peak absorbance Abs_{460}, when the molar absorptivity coefficient $\epsilon_{I_2}^{\;460}$ for iodine at 460 nm and the optical path length l are introduced.

2. Experimental Procedure

Materials. All the reagents were of analytical grade, purchased from Prolabo Normapur or Fluka Puris and used without further purification. The sulfuric acid acted as supporting electrolyte and also fixed the ionic strength at approximately 0.1 mol dm^{-3}. Solutions were prepared by mass (Mettler AE240).

Aqueous solutions of iodine were prepared by the Dushman reaction (1904), which can be formally written as

$$5I^- + IO_3^- + 6H^+ \Leftrightarrow 3I_2 + 3H_2O$$

The completion of the reaction is assured owing to its high equilibrium constant, close to 10^{49} at 298 K. A consequent reaction is the formation of triiodide I_3^-. In fact, as soon as the iodine is formed, it acts very rapidly on the iodide to lead to the following equilibrium: $I_2 + I^- \Leftrightarrow I_3^-$.

We have worked with solutions in stoichiometric proportions (excess KIO_3 1%) in order to minimize the formation of triiodide and also avoid the presence of iodate. This latter can have a catalytic effect (Beran and Bruckenstein, 1968b) on the reduction wave of the iodine and therefore render the linearity which exists between the limiting current and the concentration void. Four mixtures, whose compositions are given in Table 1, suffice to cover the range of concentrations from (10^{-3} to 10^{-4}) mol dm^{-3}. The iodine concentration in solution was diminishing spontaneously over time due to its transfer to the gas phase. The first column of Table 1 shows the initial concentration in I_2 obtained without considering the iodine loss in the atmosphere. The synthesis of iodine was initiated by adding the acid.

Dissolved oxygen was not removed from the solutions because the iodine is volatile and the reduction current for oxygen is inhibited (Chopin-Dumas) as soon as the metallic surface of the platinum is covered with absorbed atomic iodine.

Equipment. The electrochemical cell, with a useful volume of 50 cm^3, was a pear-shaped reactor equipped with three ground mouths where the electrodes were located. It was immersed in a temperature-regulated bath, accurate to 0.2 K. The solution was stirred with a magnetic stirrer.

The rotating electrode (RDE), with a 2 mm diameter platinum disk (reference EDI from SOLEA), was connected to a speed controller (10−5000 rpm). The auxiliary electrode was made of platinum wire located in spirals around the working electrode. A saturated mercurous sulfate electrode (SME) was used as a reference electrode and was connected with the solution through a bridge maintained in thermal balance. All potentials were measured relative to the SME.

The electrode potential was controlled by a potentiostat (Princeton Applied Research, Model 273). The sweep rate was 4 mV s^{-1}. The voltammetric curves were recorded between −0.7 V and +0.7 V. The surface of the platinum was initially polished using strips of abrasive paper with a roughness of (3 and 0.3) μm. Then the reproducibility of the surface state was assured by alternative anodic (toward more positive potentials) and cathodic recordings in the same potential interval.

By diverting a fraction of the reactive mixture into a spectrophotometer cell, we can standardize and follow the iodine concentration in solution, simultaneously with the recordings of the limiting current. The advantage of this analytical method is that the molar absorptivity ϵ, which has been studied extensively (Awtrey and Connick, 1951; Allen and Keefer, 1955; Daniele, 1960; Burns et al., 1990), is almost independent of the temperature. The CARY 1 spectrophotometer was equipped with thermostated circulation microcells which have a volume of 18 μL for an optical path length of 1 cm. The rapid circulation (3.9 cm^3 min^{-1}) of the liquid in the cell was ensured by a peristaltic pump. The base line was obtained using sulfuric acid at the same concentration as in solution. The absorbance value, at each wavelength, results from the average of six measurements, the measurement interval being 0.3 nm.

3. Results and Discussion

Treatment of Data. In order to establish the concentration of iodine and triiodide, equations were used.

$$\mathrm{Abs}_{460} = \epsilon_{I_2}^{\;460}[I_2] + \epsilon_{I_3^-}^{\;460}[I_3^-] = 746[I_2] + 975[I_3^-] \tag{6}$$

$$\mathrm{Abs}_{354} = \epsilon_{I_2}^{\;354}[I_2] + \epsilon_{I_3^-}^{\;354}[I_3^-] = 18[I_2] + 26400[I_3^-] \tag{7}$$

$$\mathrm{Abs}_{287} = \epsilon_{I_2}^{\;287}[I_2] + \epsilon_{I_3^-}^{\;287}[I_3^-] = 95[I_2] + 40000[I_3^-] \tag{8}$$

The values for ϵ are those supplied by Awtrey and Connick (1951). The solutions for eqs 6 + 7 and 6 + 8 provided very close values, the difference being less than 10^{-7} mol dm^{-3}, which can be adjusted by varying $\epsilon_{I_2}^{\;354}$ in an interval ranging between 18 and 10, in reasonable agreement with the value of $\epsilon_{I_2}^{\;354}$. The concentration of I_2 and I_3^- retained was the average of (6) + (7) and (6) + (8). The concentration in iodine was always at least 10 times greater than the concentration of the triiodide.

Figure 1 shows an experimental current−potential curve obtained which exhibits a reduction limiting current between −0.5 V and 0.0 V. The raw current at −0.2 V was

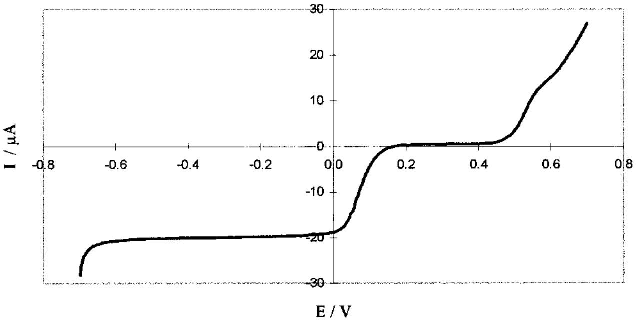

Figure 1. Anodic recording for a solution of 3 × 10^{-4} mol dm^{-3} I_2, at 298 K, in 0.075 mol dm^{-3} H_2SO_4.

Table 2. Diffusion Coefficients of Triiodide Depending on the Viscosities of Solutions

T/K	$10^2\nu$/cm^2 s^{-1} (Newson−Riddiford)	$10^5D_{I_3^-}$/cm^2 s^{-1} (Newson−Riddiford)
298	0.874	1.13
303	0.787	1.28
308	0.713	1.42
313	0.649	1.60
318	0.592	1.75
T/K	$10^2\nu$/cm^2 s^{-1} (this study)	$10^5D_{I_3^-}$/cm^2 s^{-1} (this study)
298	0.893	1.10
313	0.658	1.56
328	0.511	2.07
343	0.413	2.63
358	0.345	3.22

Table 3. Summary Table of the Linear Regression between the Current in Microamperes at − 0.2 V vs SME and the Concentration of Iodine at Various Temperatures

T/K	no. of data	L_{I_2} with $[I_3^-]^a$	L_{I_2} without $[I_3^-]^b$	10^4 ($[I_2]_{min}$ − $[I_2]_{max}$)/ mol dm^{-3}
298	49	4673 ± 4	4685 ± 4	0.68−10.31
313	41	5997 ± 6	6041 ± 8	1.14−9.08
328	54	7609 ± 7	7618 ± 6	0.76−8.60
343	52	9107 ± 11	9194 ± 11	0.19−8.24
358	45	11409 ± 27	11402 ± 16	0.23−8.24

[a] $I_{lim} = (L_{I_2}[I_2] + L_{I_3^-}[I_3^-])\omega^{1/2}$. [b] $I_{lim} = L_{I_2}[I_2]\omega^{1/2}$. L is expressed in μA mol^{-1} L rad$^{-1/2}$ s$^{1/2}$.

used without taking into account the residual current, as it has no effect on the results.

Wagner and Traud's theory (1938) suggests that the limiting current at −0.2 V can be considered as the sum of the limiting currents due to iodine and triiodide. The diffusion coefficients of I_3^-, required to calculate the triiodide participation in limiting current, have been evaluated from the $D_{I_3^-}$ values supplied by Newson and Riddiford (1961) and are stated on the top of Table 2, together with the kinematic viscosity ν of their medium. The empirical correlation (9) between these D and ν values was first established,

$$\log(D_{I_3^-}) = -1.130 \log(\nu) - 7.272 \tag{9}$$

which fitted all the data with a standard deviation of ±0.9%. Then, our viscosity data, which are those of water, were substituted into (9) to derive the diffusion coefficients presented at the bottom of Table 2.

The currents are exploited with and without taking into account the triiodide present. The L results in Table 3 (column 3) show minor modification, when the triiodide participation is neglected (column 4), because of the low values of the ratio $[I_3^-]/[I_2]$. The angular velocity, ω, set at 2000 rpm, was checked (2008 rpm). Furthermore, the area of the metallic surface was estimated at (0.0324 ± 0.0006) cm^2.

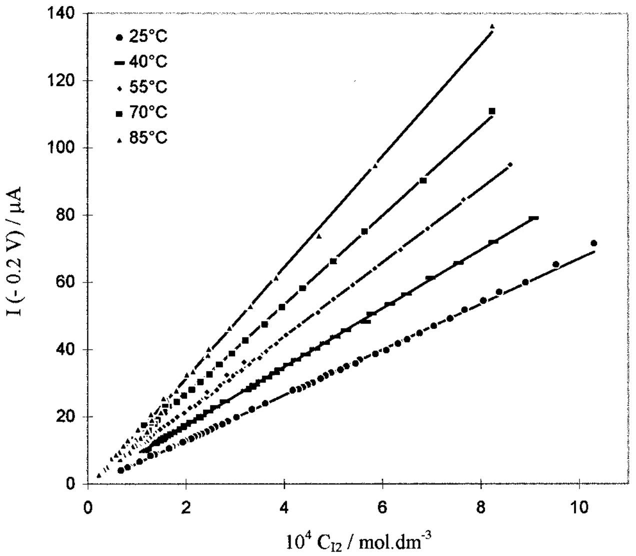

Figure 2. Plot of diffusion limiting currents of I_2 against concentration, in 0.075 mol dm^{-3} H_2SO_4.

Figure 2 shows that the linear relationship between the current at −0.2 V and the iodine concentration is confirmed at each temperature. The coefficient L in Table 3 was calculated from the slope of a linear least-squares plot of I_{lim} vs $[I_2]$. The L_{I_2} values retained in order to calculate D are those taking into account the triiodide (column 3). The error limits for L correspond to a confidence level of 95% with the dispersion increasing with temperature. In the last column is given the concentration range of iodine used in the determination of the coefficient L.

Equations 2 and 3 have been used to establish the diffusion coefficient for I_2, as supplied in columns 3 and 4 of Table 4. These two equations provide similar results owing to the order of magnitude of the Schmidt number (657 > Sc > 80). The accuracy of the diffusion coefficient in column 4 is estimated from the error on L and on the metallic area of the electrode.

Constancy of (Dη/T). Two theories discuss diffusion in liquids. The hydrodynamic theory (Bird et al., 1960), which considers the solvent as a stationary environment and the solute molecule as a rigid sphere, gives, according to (10), the radius of the molecule depending on a number of parameters:

$$r = \frac{k_B T}{6\pi\eta D}\left(\frac{1 + 3\eta/\beta}{1 + 2\eta/\beta}\right) \tag{10}$$

with β as a friction coefficient, η the solvent dynamic viscosity, and k_B the Boltzmann constant, 1.381 × 10^{-23} J K^{-1}.

When β is considered as infinite—this is the "stick" model—the classic expression of the Stokes−Einstein equation is obtained.

$$r = \frac{k_B T}{6\pi\eta D} \tag{11}$$

The other limiting case where $\beta = 0$, named the "slip" model, leads to the relationship

$$r = \frac{k_B T}{4\pi\eta D} \tag{12}$$

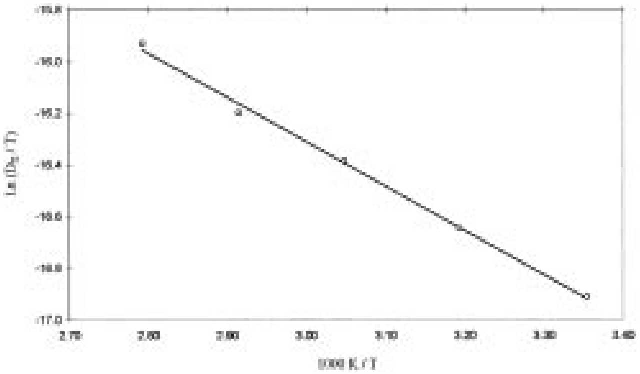

Figure 3. Logarithm of (D_{I_2}/T) versus inverse temperature, in 0.075 mol dm^{-3} H_2SO_4.

Table 4. Diffusion Coefficients of I_2 Obtained at Different Temperatures Based on the L Values

T/K	$10^3\eta$/ Pa s	10^9D/m^2 s^{-1} (Gregory−Riddiford)	10^9D/m^2 s^{-1} (Newman)	$10^{15}D\eta/T$/ (kg m s^{-2} K^{-1})
298	0.890	1.37	1.36 ± 0.04	4.03
313	0.653	1.84	1.85 ± 0.06	3.86
328	0.504	2.51	2.52 ± 0.08	3.87
343	0.404	3.15	3.17 ± 0.10	3.73
358	0.334	4.30	4.32 ± 0.15	4.03

For uncharged molecules, the experimental results are in closer agreement with values given by the slip boundary condition for Stokes law (Alder et al., 1981).

The Eyring theory (Glasstone et al., 1941), based on the concept of vacant sites in the liquid, is less satisfactory than the hydrodynamic theory for the calculation of the diffusion coefficients.

According to (12), the term $D\eta/T$, as calculated in column 5 of Table 4, should be constant. Our measurements provide an average value of $D\eta/T$ equal to (3.91 ± 0.11) × 10^{-15} kg m s^{-2} K^{-1}. The diffusion coefficients recalculated from this mean value show little difference in comparison with experimental values. Furthermore, the hydrodynamic radius based on this average is estimated at 2.81 Å, which agrees with the bond length in the I−I molecule of 2.66 Å, as tabulated by Wells, 1984.

Effect of Temperature. The variation of viscosity as a function of the temperature can be described by the Andrade (1930) equation:

$$\ln(\eta) = C + \frac{E}{RT} \tag{13}$$

where C and E are parameters. Taking into account (12), the relationship (14) is expected between the diffusion coefficient and the temperature:

$$\ln\left(\frac{D}{T}\right) = A - \frac{E}{RT} \tag{14}$$

As seen in Figure 3, the variation of D values with temperature is in good agreement with the model leading to (14). The experimental constants are $A = -11.17$ and $E = (14.24 \pm 0.41)$ kJ mol^{-1}, which can be used to calculate D at a fixed temperature.

Comparison with Some Estimates and Some Experimental Results. Five prediction methods are used in order to estimate the binary diffusion coefficient $D°_{AB}$ of A diffusing into B, at infinite dilution of A in B, in cm^2 s^{-1}. These estimations, based on the properties of the solvent and solute, used M as the molecular weight and V as the molar volume at normal boiling temperature (V_B = 18.7 cm^3 mol^{-1} for water and V_A = 71.5 cm^3 mol^{-1} for iodine).

The correlation (15) is that recommended by Wilke and Chang (1955):

$$D°_{AB} = 7.4 \times 10^{-8}\,(\phi M_B)^{1/2}\frac{T}{\eta_B V_A^{\ 0.6}} \tag{15}$$

ϕ is a dimensionless association factor for solvent B. For water, ϕ is taken as 2.6 by Wilke and Chang (1955), or more recently as 2.26 by Hayduk and Laudie (1974).

Hayduk and Minhas (1982) suggest (16) for aqueous solutions:

$$D°_{AB} = 1.25 \times 10^{-8}(V_A^{\ -0.19} - 0.292)T^{1.52}\eta_B^{\ \alpha} \tag{16}$$

with

$$\alpha = (9.58/V_A) - 1.2$$

Tyn and Calus (1975) recommend formula (17).

$$D°_{AB} = 8.93 \times 10^{-8}\left(\frac{V_A}{V_B^{\ 2}}\right)^{1/6}\left(\frac{P_B}{P_A}\right)^{0.6}\frac{T}{\eta_B} \tag{17}$$

The parafactor P is defined by $P = V\sigma^{1/4}$, σ being the surface tension (dyn cm^{-1}). The P values are respectively (52.6 and 180.6) cm^3 g$^{1/4}$ s$^{1/2}$ mol^{-1} for water and for iodine.

The Nakanishi (1978) method refers to the empirical parameters denoted by A, I, and S in order to take into account the interaction between the solvent and the solute.

$$D°_{AB} = \left[\frac{9.97 \times 10^{-8}}{(I_A V_A)^{1/3}} + \frac{2.40 \times 10^{-8} A_B S_B V_B}{I_A S_A V_A}\right]\frac{T}{\eta_B} \tag{18}$$

with $A_B = 2.8$ and $S_B = 1$ for water and $I_A = S_A = 1$ for I_2.

The Othmer and Thakar (1953) equation gives

$$D°_{AB} = \frac{14.0 \times 10^{-5}}{\eta_B^{\ 1.1} V_A^{\ 0.6}} \tag{19}$$

The comparison between experimental and predicted values is summarized in Table 5. In general, one notes that all these evaluations underestimate (by approximately 10%) our experimental value of the diffusion coefficient, except the Nakanishi (1978) evaluation which is also the best prediction.

The experimental values found in the literature, for example that of Beran and Bruckenstein (1968a), who

Table 5. Comparison between the Diffusion Coefficient D of I_2 and Estimations at 298 K[a]

	experimental		theory	estimations				
	this study	B−B[b]	slip model	W−CH	H−M	T−C	N	O−T
10^9D/m^2 s^{-1}	1.36	1.07	1.31	1.22	1.23	1.10	1.39	1.23
ΔD[c]/%		−21.3	−3.7	−10.0	−9.8	−19.5	+2.5	−9.7

[a] B−B, Beran−Bruckenstein; W−CH, Wilke−Chang; H−M, Hayduk−Minhas; T−C, Tyn−Calus; N, Nakanishi; O−T, Othmer−Thakar. [b] The value of Beran and Bruckenstein (1968a) is an experimental data. [c] ΔD is the average error between the measured diffusion coefficient and other values.

worked with ω variable with a constant concentration of 6.7×10^{-4} mol dm^{-3} for I_2, seem to be too low in comparison with the predictions and with our experimental value. A plausible explanation is that the true concentration of the iodine in solution has been overestimated by neglecting the losses in the gas phase, resulting in underestimation of the diffusion coefficient of I_2. Another explanation would be a decrease of the value of the diffusion coefficient in relation to the addition of salt in a pure acid medium. Experiments will be performed in the near future to verify this hypothesis of an environmental effect.

The diffusion coefficients of the other iodine compounds are relatively well-known since a great deal of work has been done (Newson and Riddiford, 1961; Beilby and Crittenden, 1960; Geissler and Landsberg, 1961; Darrall and Oldham, 1968; Mills and Lobo, 1989; Spiro and Creeth, 1990). Let us take $D_{I^-} = 1.99 \times 10^{-9}$ m^2 s^{-1} (in 0.125 mol dm^{-3} H_2SO_4, Beilby and Crittenden, 1960) and $D_{I_3^-} = 1.13 \times 10^{-9}$ m^2 s^{-1} (in 0.1 mol dm^{-3} KI, Newson and Riddiford, 1961). We observed then that $D_{I_2} = 1.36 \times 10^{-9}$ m^2 s^{-1} is located between the D values of I^- and I_3^-, which is consistent with the size and molecular weight of the species considered.

4. Conclusion

The diffusion coefficients of I_2 have been determined between 298 and 358 K by potentiostatic voltammetry by means of a platinum rotating disk electrode using the Newman equation. The procedure employed (coupling between the voltammetry and the absorption spectrophotometry for the determination of iodine concentration) is imposed by the volatile nature of iodine. In sulfuric medium, the values obtained are $(1.36 \pm 0.04) \times 10^{-9}$ m^2 s^{-1} at 298 K, $(1.85 \pm 0.06) \times 10^{-9}$ m^2 s^{-1} at 313 K, $(2.52 \pm 0.08) \times 10^{-9}$ m^2 s^{-1} at 328 K, $(3.17 \pm 0.10) \times 10^{-9}$ m^2 s^{-1} at 343 K, and $(4.32 \pm 0.15) \times 10^{-9}$ m^2 s^{-1} at 358 K. These data will be useful to improve the modeling of transport processes in nuclear safety computer codes. The diffusion coefficients have also been correlated as a function of temperature. The diffusion coefficient of iodine has often been replaced for convenience sake by the coefficient of triiodide because these two compounds are often present simultaneously in solution. If this approximation only results in a relative error of 16% at 298 K, it should be noted that the difference increases with temperature (25% at 358 K).

Acknowledgment

The authors wish to express their gratitude to professor J. L. Chevalier for his judicious advice concerning the discussion along with E. Belval-Haltier for the attention that she gave to this work.

Literature Cited

Alder, B.; Alley, W. E.; Pollock, E. L. Validity of Macroscopic Concepts for Fluids on a Microscopic scale. *Ber. Bunsen-Ges. Phys. Chem.* **1981**, *85* (11), 944−952.

Allen, T. L.; Keefer, R. M. The formation of Hypoiodous Acid and Hydrated Iodine Cation by the Hydrolysis of Iodine. *J. Am. Chem. Soc.* **1955**, *77*, 2957−2960.

Andrade, E. N. da C. The Viscosity of Liquids. *Nature* **1930**, *125*, 309−310.

Awtrey, A. D.; Connick, R. E. The Absorption Spectra of I_2, I_3^-, I^-, IO_3^-, $S_4O_6^-$ and $S_2O_3^-$. Heat of the Reaction $I_3^- = I_2 + I^-$. *J. Am. Chem. Soc.* **1951**, *73*, 1842−1843.

Beilby, A. I.; Crittenden, A. L. Non-additive Polarographic Waves in the Anodic Oxidation of Iodide. *J. Phys. Chem.* **1960**, *64*, 177−178.

Beran, P.; Bruckenstein, S. Voltammetry of Iodine(I) chloride, Iodine, and Iodate at Rotated Platinum Disk an Ring-disk Electrodes. *Anal. Chem.* **1968a**, *40* (7), 1044−1051.

Beran, P.; Bruckenstein, S. A Rotating Disk Electrode Study of the Catalytic Wave of Iodine in the Presence of Iodate. *J. Phys. Chem.* **1968b**, *72* (10), 3630−3635.

Bird, R. B.; Stewart, W. E.; Lightfoot, E. N. *Transport Phenomena*; Wiley: New York, 1960; Chapter 16.

Burns, W. G.; Matsuda, M.; Sims, H. E. Temperature Dependence of the Equilibrium Constant for Iodine Hydrolysis at Temperatures between 25 and 120°C. *J. Chem. Soc., Faraday. Trans.* **1990**, *86* (9), 1443−1447.

Chopin-Dumas, J. Results to be published.

Daniele, G. Measurement of Equilibrium Constants of Potassium Triiodide with a Spectrophotometric Method. *Gazz. Chim. Ital.* **1960**, *90*, 1068−1081 (in Italian).

Darrall, K. G.; Oldham, G. The Diffusion Coefficients of the Tri-iodide Ion in Aqueous Solutions. *J. Chem. Soc. A* **1968**, 2584−2586.

Dushman, S. The Rate of the Reaction between Iodic and Hydriodic Acids. *J. Phys. Chem.* **1904**, *8*, 453−482.

Geissler, W.; Landsberg, R. Oxidation of Iodide at Graphite Disk Electrodes. *Z. Chem.* **1961**, *1*, 308−309.

Geissler, W.; Nitzche, R.; Landsberg, R. Electrochemical Oxidation of Iodide and Iodine into Hypoiodite on Graphite Electrodes. *Electrochim. Acta* **1966**, *11* (4), 389−400.

Glasstone, S.; Laidler, K. J.; Eyring, H. *Theory of Rate Processes*; McGraw-Hill: New York, 1941; Chapter IX.

Gregory, D. P.; Riddiford, A. C. Transport to the Surface of a Rotating Disk. *J. Chem. Soc.* **1956**, 3756−3764.

Hayduk, W.; Laudie, H. Prediction of Diffusion Coefficients for Nonelectrolytes in Dilute Aqueous Solutions. *AIChE J.* **1974**, *20* (3), 611−615.

Hayduk, W.; Minhas, B. S. Correlations for Prediction of Molecular Diffusivities in Liquids. *Can. J. Chem. Eng.* **1982**, *60*, 295−299.

Kassner, T. F. Rate of Solution of Rotating Tantalum Disks in Liquid Tin. *J. Electrochem. Soc.* **1967**, *114*, 689−694.

Kolthoff, I. M.; Jordan, J. Voltammetry of Iodine and Iodide at Rotated Platinum Wire Electrodes. *J. Am. Chem. Soc.* **1953**, *75*, 1571−1575.

Levich, B. The Theory of Concentration Polarization. *Acta Physicochim. U.R.S.S.* **1942**, *17*, 257−307.

Levich, V. G. Theory of Concentration Polarization. *J. Phys. Chem. (U.R.S.S)* **1944**, *18*, 335−355.

Mills, R.; Lobo, V. M. M. *Self-diffusion in Electrolytes Solution*; Elsevier: Amsterdam, 1989.

Nakanishi, K. Prediction of Diffusion Coefficient of Nonelectrolytes in Dilute Solution Based on Generalized Hammond-Stokes Plot. *Ind. Eng. Chem. Fundam.* **1978**, *17* (4), 253−256.

Newman, J. Schmidt Number Correction for the Rotating Disk. *J. Phys. Chem.* **1966**, *70* (4), 1327−1341.

Newson, J. D.; Riddiford, A. C. Limiting Currents for the Reduction of the Tri-iodide Ion at a Rotating Platinum Disk Cathode. *J. Electrochem. Soc.* **1961**, *108* (7), 695−698.

Othmer, D. F.; Thakar, M. S. Correlating Diffusion Coefficients in Liquids. *Ind. Eng. Chem.* **1953**, *45*, 589−593.

Spiro, M.; Creeth, A. M. Tracer Diffusion of I^-, I_3^-, Fe^{2+} and Fe^{3+} at Low Temperatures. *J. Chem. Soc., Faraday Trans.* **1990**, *86* (21), 3573−3576.

Tyn, M. T.; Calus, W. F. Diffusion Coefficients in Dilute Binary Liquid Mixtures. *J. Chem. Eng. Data* **1975**, *20* (1), 106−109.

Wagner, C.; Traud, W. The Interpretation of Corrosion Phenomena by Super-Imposition of Electrochemical Partial Reactions and the Formation of Potentials of Mixed Electrodes. *Z. Elektrochem.* **1938**, *44*, 391−402.

Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, U.K., 1984; p 385.

Wilke, C. R.; Chang, P. Correlation of Diffusion Coefficients in Dilute Solutions. *AIChE J.* **1955**, *1* (2), 264−270.

Received for review May 24, 1996. Accepted October 30, 1996.⊗

JE960178U

⊗ Abstract published in *Advance ACS Abstracts,* December 15, 1996.