

# Determination of diffusivity and solubility of oxygen in phosphoric acid using a transit time on a rotating ring-disc electrode

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A transit time method on a rotating ring-disc electrode was used to simultaneously determine the diffusivity and solubility of oxygen in phosphoric acid. The method consisted of measuring the limiting current for the diffusion of dissolved oxygen on the central disc electrode, and a transit time for the diffusion of oxygen from the disc to the ring electrode. The diffusivity of oxygen was calculated from the measured transit time, electrode rotational speed and kinematic viscosity of the electrolyte without the need of its bulk concentration and the number of electrons transferred in the electrode reaction. Once the diffusivity was known, the solubility of oxygen in the bulk electrolyte was determined from the limiting current on the disc using the Levich equation. This work has demonstrated that the transit method is a swift and reproducible technique for the diffusivity measurement. The diffusivity and solubility of oxygen in phosphoric acid of a concentration range of 0.79–14.7 M were determined at 23°C and an oxygen partial pressure of 1 atm. A set of empirical equations are presented to correlate the Stokes–Einstein constant,  $D\mu/T$ , and solubility of oxygen to the phosphoric acid concentration.

## 1. Introduction

Several transient electrochemical methods have been developed [1–6], which permit the simultaneous determination of diffusivity and concentration of a diffusing species in a redox system. These methods have not been successfully used to determine the diffusivity and solubility of dissolved oxygen in phosphoric acid because of the complexity of oxygen reduction reaction. For example, the measurement period of a capillary electrode method [1] is too long (a few hours) and the total current on a microelectrode [5] is too small (about  $10^{-7}$  A) to permit an accurate measurement. The data at low frequencies are not reproducible using an alternating current method [6].

This paper describes a study using a transit time method on a rotating ring-disc electrode (RRDE) to simultaneously determine the diffusivity and concentration of oxygen in a phosphoric acid electrolyte over a concentration range of 0.79 to 14.7 M. The measurement procedure is simple and fast (a few seconds).

In this method, a potential step is applied to the central disc electrode to electrochemically generate (or deplete) a diffusing species whose diffusivity in the electrolyte is to be determined. The generated (or depleted) diffusing species is carried by the electrolyte flow to the outer ring electrode, where a potential is maintained to detect the arrival (or the depletion) of the species. A certain time, which is called the transit time, elapses before the ring current starts to rise (or to drop in the case of a depleted species) sharply in

response to the potential step at the disc electrode. Bruckenstein and Feldman [7] have shown that the transit time,  $T_s$ , is related to the electrode rotational speed in r.p.m.,  $\Omega$ , diffusivity of the diffusing species,  $D$ , solution kinematic viscosity,  $\nu$ , and electrode geometry by

$$T_s = K(\nu/D)^{1/3} \Omega^{-1} \quad (1)$$

The constant,  $K$ , in the above equation is only related to the electrode geometry. For an ideal RRDE where the surface is absolutely smooth and the ring electrode is absolutely concentric with the disc electrode,  $K$  may be calculated as follows:

$$K = 43.1 \times [\log(r_2/r_1)]^{2/3} \quad (2)$$

where  $r_1$  is the radius of the disc electrode, and  $r_2$  is the inside radius of the ring electrode. For a real RRDE,  $K$  should be experimentally calibrated using a diffusing species whose diffusivity is known. The diffusivity of a diffusing species is determined by measuring the transit time,  $T_s$ , at various rotational speed,  $\Omega$ . A plot of  $T_s$  against  $\Omega^{-1}$  would result in a straight line passing through the origin, and the diffusivity is calculated from the slope of the straight line.

Once the diffusivity is known, the bulk concentration of the diffusing species,  $C_b$ , may be calculated from the d.c. limiting current density,  $i_{lim}$ , according to the Levich equation [8]:

$$i_{lim} = 0.62nFD^{2/3}\nu^{-1/6}\Omega^{1/2}C_b \quad (3)$$

where  $n$  is the number of electrons involved in the electrode reaction and  $F$  is the Faraday constant.

## 2. Experimental details

A platinum rotating ring-disc electrode (Pine Instrument, Model AFDT21PtPt) was used as the work electrode. The dimensions of the electrode were:  $r_1 = 0.250$  cm;  $r_2 = 0.276$  cm;  $r_3$  (outside radius of ring) = 0.358 cm; disc area = 0.196 cm<sup>2</sup>; and ring area = 0.164 cm<sup>2</sup>. A platinum wire mesh was used as the counter electrode. A Ag/AgCl electrode in a Luggin capillary tube was used as the reference electrode.

Aqueous phosphoric acid solution was used as the electrolyte. The phosphoric acid (85%, ACS certified) was purified by treating with a 10% hydrogen peroxide and heating to 50–70°C for one hour in a Teflon beaker [9]. Then it was further heated to 100°C for a few hours to decompose unreacted hydrogen peroxide and to evaporate excess water. The experimental solutions were prepared by diluting the purified acid with deionized water. The concentration and viscosity of phosphoric acid solution were determined using a specific gravity bottle and a Canon–Fenske viscometer, respectively.

A two channel potentiostat (Pine Instrument RDE3) was used to independently control the ring and disc electrodes at the same limiting current potential for oxygen reduction. A switch was used to apply a potential step to the disc electrode while keeping the ring at a constant limiting current potential. The ring current was recorded by feeding the voltage drop from the ring current output terminals of the potentiostat to a digital data acquisition system.

Before each measurement, oxygen was bubbled into the H<sub>3</sub>PO<sub>4</sub> solution for 30 min while the potentials of the ring and disc electrodes were cycled between 0.8 and –0.2 V against Ag/AgCl with a scan rate of 50 mV s<sup>–1</sup>. Then a potentiodynamic polarization experiment was carried out to determine the limiting current for oxygen reduction on the disc electrode. The transit time of the RRDE was determined by: (i) keeping the ring potential at a limiting current potential value; (ii) stepping the disc potential to the same value from the two channel potentiostat; and (iii) recording the ring current against time curve. All the measurements were carried out at a solution temperature of 23°C.

## 3. Results and discussion

### 3.1. Ring-current against time curve ( $I_R$ - $t$ curve)

Figure 1 shows a typical  $I_R$ - $t$  curve in response to a disc-potential step in a 3.76 M H<sub>3</sub>PO<sub>4</sub> solution saturated with oxygen at an oxygen partial pressure of 1 atm and an electrode rotational speed of 200 r.p.m. In this run, the potential of the disc electrode was stepped from an open-circuit potential of about 0.75 V against Ag/AgCl to 0.1 V against Ag/AgCl while the ring potential was kept at 0.1 V against Ag/AgCl. A sharp pulse on the ring-current which was synchronous with the onset of the disc-potential step, was used as the origin

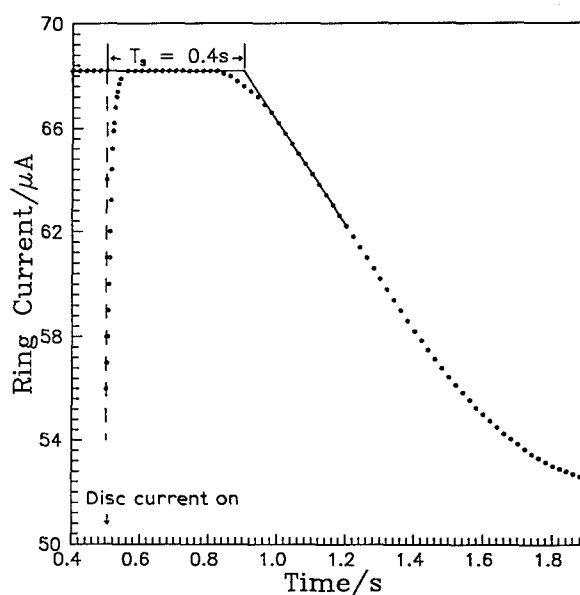


Fig. 1. Ring current against time for oxygen reduction on a rotating-disc electrode at 200 r.p.m. The ring current was recorded by stepping the disc potential from open circuit to 0.1 V against Ag/AgCl. Conditions: 3.76 M H<sub>3</sub>PO<sub>4</sub> saturated with oxygen at 23°C and oxygen partial pressure of 1 atm.

of transit time. The transit time was determined by the intersection of the base steady ring current line and the fast attenuate ring current line as shown in Fig. 1.

### 3.2. $T_s$ - $1/\Omega$ curve

Table 1 lists the values of transit time measured at various rotational speeds in the H<sub>3</sub>PO<sub>4</sub> concentration range of 0.79 to 14.7 M. For a given solution concentration, the product,  $T_s\Omega$ , was essentially constant. Figure 2 shows a typical  $T_s$ - $1/\Omega$  curve in a 0.79 M H<sub>3</sub>PO<sub>4</sub> solution showing a straight line passing through the origin.

### 3.3. Diffusivity and solubility of oxygen

The constant  $K$  of the present rotating ring-disc electrode was calibrated using the transit time measurement for Fe(CN)<sub>6</sub><sup>3–</sup> ion in a 0.01 M K<sub>3</sub>Fe(CN)<sub>6</sub> + 0.1 M K<sub>4</sub>Fe(CN)<sub>6</sub> + 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution. The calibrated value of  $K$  was 6.24. Using this  $K$  value, the diffusivity of oxygen in H<sub>3</sub>PO<sub>4</sub> solution was calculated from the slope of the  $T_s$ - $1/\Omega$  line using Equation 1. The results are listed in Table 1. Figure 3 shows a semilogarithmic plot of the Stokes–Einstein constant,  $D\mu/T$ , versus concentration of H<sub>3</sub>PO<sub>4</sub>. The experimental data follow an empirical equation:

$$D\mu/T = 3.753 \times 10^{-10} \exp(0.133C) \quad (4)$$

where the left hand side quantity is expressed in g cm s<sup>–2</sup> K<sup>–1</sup> and where  $\mu$  is the viscosity of solution in poise.  $C$  is the concentration of H<sub>3</sub>PO<sub>4</sub> in M and  $T$  is the absolute temperature of the electrolyte in K.

After measuring the diffusivity, the solubility of oxygen in H<sub>3</sub>PO<sub>4</sub> solution was determined from the d.c. limiting current of oxygen reduction on the disc electrode using Equation 3. The results are given in Table 1 and are plotted semilogarithmically against

Table 1. The results of diffusivity and solubility measurement for oxygen in phosphoric acid solution at 23°C

Con. of H <sub>3</sub> PO <sub>4</sub> M(%)	$v/cm^2 s^{-1}$	$\mu/cp$	$\Omega/rpm$	$T_s/s$	$T_s\Omega/sr.p.m.$	$i_{lim}/mA cm^{-2}$	$10^6 D/cm^2 s^{-1}$	$10^{10} D\mu T/g cm K^{-2} s^{-1}$	$10^3 S_{oxygen}/M$
14.8 (85.6)	0.224	41.2	200	1.56	312		1.97	27.3	0.17
			300	1.06	318	0.05			
			400	0.78	311				
			600	0.56	334				
11.3 (72.0)	0.102	15.8	200	1.02	204		3.18	17.0	0.27
			300	0.67	202	0.13			
			400	0.50	199				
			600	0.34	205				
8.81 (60.5)	0.0550	7.21	200	0.74	148		4.21	11.2	0.25
			300	0.49	147	0.16			
			400	0.37	147				
			600	0.27	161				
4.95 (39.0)	0.0230	2.86	200	0.46	91.2		7.75	7.49	0.58
			300	0.29	87.9	0.66			
			400	0.22	88.0				
			600	0.15	92.4				
3.76 (31.1)	0.0187	2.22	200	0.40	80.0		8.39	6.29	0.83
			300	0.28	82.8	1.03			
			400	0.21	82.0				
			600	0.15	87.6				
2.27 (20.0)	0.0143	1.59	200	0.36	72.0		9.40	5.05	1.06
			300	0.24	73.2	1.48			
			400	0.18	71.2				
			600	0.12	69.8				
1.77 (15.9)	0.0124	1.35	200	0.33	65.4		10.3	4.70	1.14
			300	0.22	66.0	1.73			
			400	0.17	68.0				
			600	0.12	70.8				
0.785 (7.41)	0.0100	1.04	200	0.29	57.6		11.9	4.18	1.25
			300	0.20	59.1	2.17			
			400	0.15	60.4				
			600	0.10	61.8				

the H<sub>3</sub>PO<sub>4</sub> concentration in Fig. 4. The solubility of oxygen decreases exponentially with increasing concentration of H<sub>3</sub>PO<sub>4</sub>. The data follow an empirical equation:

$$S_{oxygen} = 1.38 \times 10^{-3} \exp(-0.152C) \quad (5)$$

where  $S_{oxygen}$  is the solubility of oxygen in M. Extrapolating the  $\log(S_{oxygen})-C$  line to  $C = 0$ , the solubility of oxygen in pure water at 23°C and oxygen partial pressure of 1 atm is found to be  $1.38 \times 10^{-3}$  M; this value agrees with a value of  $1.31 \times 10^{-3}$  M [10].

### 3.4. Error analysis

This work has shown that the transit time method on a RRDE has the advantages of: (i) fast measurement (a few seconds); (ii) reproducible data; and (iii) simple calculation involving only the slope of a  $T_s$  against  $1/\Omega$  plot (or the average  $T_s$  at several rotational speeds). The method is perhaps more accurate than the micro-electrode where (i) the transient current measurement may be affected by the natural convection or other flow disturbances (such as stirring or gas bubbling),

and (ii) the use of an extrapolated intercept and a slope of a current against reciprocal of the square root of time plot [5,11] may lead to a large error in the diffusivity measurement.

The maximum experimental error of the present technique may be estimated by taking the finite differences of the logarithm of Equation 1 and by taking into account the possible error involved in the calibration of constant  $K$ :

$$\frac{\Delta D}{D} = \frac{\Delta D_{cal}}{D_{cal}} + \frac{2\Delta v}{v} + \frac{6\Delta\Omega}{\Omega} + \frac{6\Delta T_s}{T_s} \quad (6)$$

where  $\Delta D_{cal}/D_{cal}$  is the measurement error of the standard diffusing species ( $Fe(CN)_6^{3-}$ ), used in the calibration of  $K$ . If  $\Delta D_{cal}/D_{cal} = \pm 5\%$ ,  $\Delta v/v = \pm 1\%$ ,  $\Delta\Omega/\Omega = \pm 1\%$  and  $\Delta T_s/T_s = \pm 3\%$ , the maximum of  $\Delta D/D$  may be estimated to be  $\pm 31\%$ . It is obvious that the main item contributing to the experimental error,  $\Delta D/D$ , is the transit time measurement. To decrease the experimental error, a possible approach is to widen the gap between ring and disc because the transit time increases with increasing  $\log(r_2/r_1)$ . For

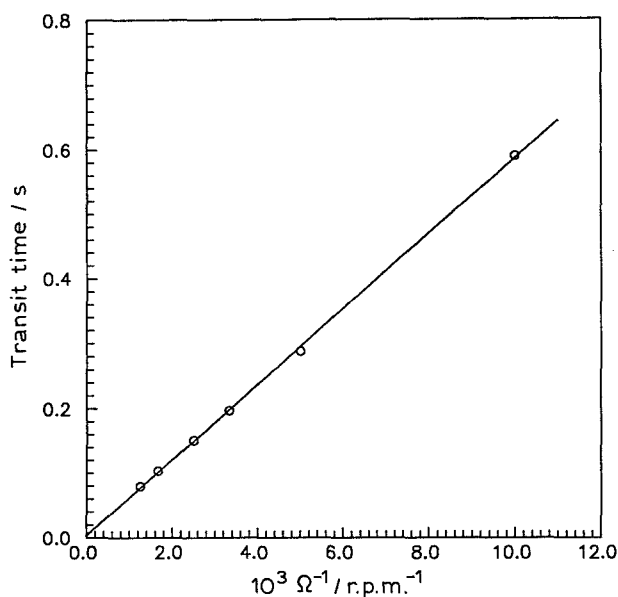


Fig. 2. Transit time against reciprocal rotational speed for oxygen on a rotating ring-disc electrode in a 0.79 M  $\text{H}_3\text{PO}_4$  solution saturated with oxygen at 23°C and oxygen partial pressure of 1 atm.

example, if  $r_2/r_1$  increases from 1.104 (used in this work) to 1.324,  $T_s$  will increase by a factor of 2;  $\Delta T_s/T_s$  may be reduced to  $\pm 1.5\%$ ; and  $\Delta D/D$  would decrease from  $\pm 31\%$  to  $\pm 22\%$ .

#### 4. Conclusions

The transit time method on a RRDE is a swift and reproducible technique for the simultaneous determination of diffusivity and bulk concentration of a

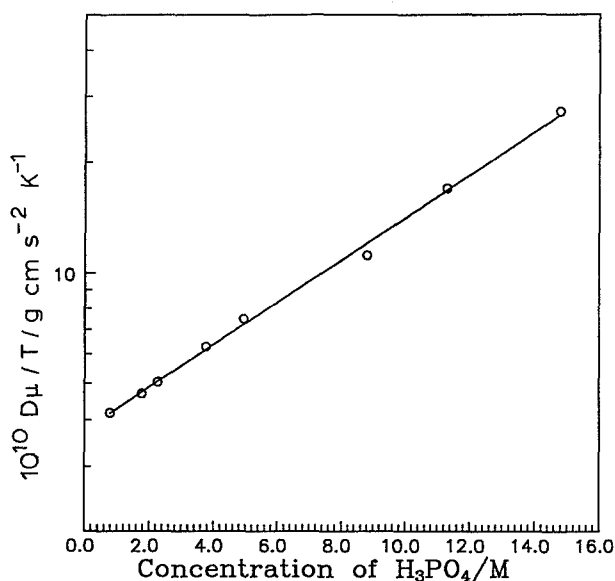


Fig. 3. Stokes-Einstein constant for oxygen in phosphoric acid as a function of  $\text{H}_3\text{PO}_4$  concentrations.

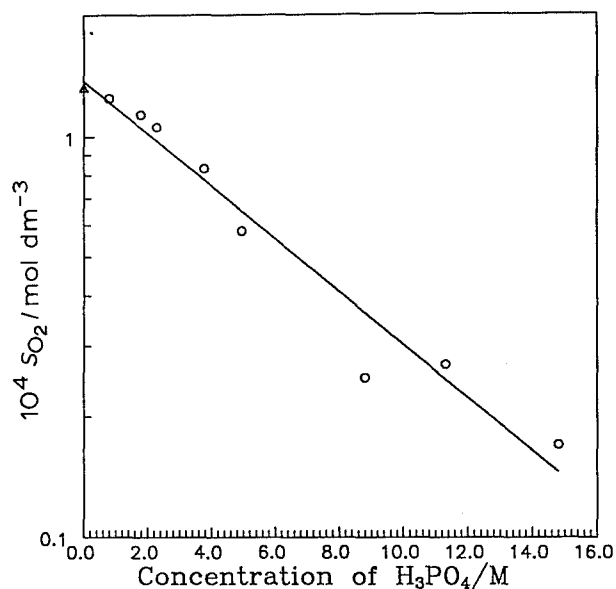


Fig. 4. Solubility of oxygen in phosphoric acid as a function of  $\text{H}_3\text{PO}_4$  concentrations at 23°C and an oxygen partial pressure of 1 atm. (O) Experimental data. (Δ) Solubility of oxygen reported in [10].

diffusing species in a redox system. Using this method, the diffusivity and solubility of oxygen in phosphoric acid solution in a concentration range of 0.79–14.7 M at 23°C were determined.

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