Determination of the diffusion coefficient of oxygen in sodium chloride solutions with a transient pulse technique

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Abstract

An accurate and rapid method for determining the diffusion coefficients of electrochemically active gases in electrolytes is described. The technique is based on chronoamperometry where transient currents are measured and interpreted with a Cottrell-related equation. The diffusion coefficients of oxygen were determined for NaCl solutions varying from 0.085 to 0.846 M within the temperature range 20–40°C. A relationship for the diffusion coefficient of oxygen as a function of temperature is given for the several NaCl concentrations.

Keywords: Amperometry; Sensors; Chronoamperometry; Diffusion coefficient; Oxygen; Transient pulse technique

The diffusivity of oxygen as a function of the NaCl concentration and temperature is of great importance for chemical engineers in the design of oxygen measurement devices, especially in physiological and medical studies. This holds in particular for oxygen sensors built in accordance with the Clark principle [1]. NaCl solution in a Clark cell is used as a reference electrolyte, which is separated from the test solution by a membrane. The oxygen concentration in the NaCl solution is in equilibrium with the concentration in the test solution. If in such a device a reducing potential step is applied and the corresponding transient current is followed, it is possible to measure the oxygen concentration by knowing the diffusion coefficient of oxygen in the NaCl solution at that specific temperature. It is for this reason that the diffusion coefficient has to be determined in NaCl solutions with a known oxygen concentration, using a convenient and accurate method.

Electrochemical methods that make use of data obtained from the measurement of the diffusion-controlled current are the most reliable. A valuable equation in this instance is the Cottrell equation [2], which requires a knowledge of the solubility of gases in electrolytes. The solubility of oxygen in NaCl solutions is well known as a function of temperature [3–5].

The purpose of this work was to develop a rapid method for measuring oxygen diffusion coefficients in electrolyte solutions with a simple, commercially available disc electrode. The methodology is general and can be extended to gases other than oxygen.

THEORY.

When an electrochemical system is taken from its equilibrium position into the transport-controlled region by means of an applied potential
step (potentiostatic condition) and the current variation with time is observed, it is known that the electrochemical system shows time-dependent characteristics. The applied potential in this instance has to be sufficiently high to achieve a surface concentration of the electro-active species of virtually zero. We consider the general reaction $\text{Ox} + n \text{e}^- \rightarrow \text{Red}$.

For a flat surface electrode (e.g., a platinum disc) in an unstirred solution, the diffusion is initially linear and essentially one-dimensional. This holds true as long as the extension of the concentration gradient is small compared with the diameter of the electrode surface. This linear diffusion can be described mathematically; a rigorous development was given by Kolthoff and Lingane [6]. The diffusion-controlled Faradaic current $i_F(t)$ due to the reduction of the electroactive species can be written as

$$i_F(t) = nF A_e C_o (D/\pi t)^{1/2}$$

where $n =$ number of electrons involved in the electrode reaction, $F =$ the Faraday (charge on 1 mol of electrons) (C), $A_e =$ electrode area (m$^2$), $D =$ diffusion coefficient (m$^2$ s$^{-1}$), $C_o =$ concentration of the electroactive species in the bulk solution (mol m$^{-3}$) and $t =$ time (s). This current–time equation of chronoamperometry is known as the Cottrell equation [2]. Its validity was verified in detail by the classical experiments of Laitinen and Kolthoff [7,8].

However, when a potential step is applied, the measured current, $i_{\text{tot}}$, consists of both the Faradaic current ($i_F$), which is described by the Cottrell equation, and the capacitive current ($i_C$) [9]:

$$i_{\text{tot}} = i_F + i_C = nF A_e C_o (D/\pi t)^{1/2} + (\Delta E/R_s) \exp(-t/R_s C_{\text{dl}})$$

where $\Delta E =$ magnitude of the applied potential step (V), $R_s =$ solution resistance (Ω) and $C_{\text{dl}} =$ double-layer capacitance (F). For very small times, just after applying the potential step, the capacitive current predominates over the Faradaic current. As the capacitive current decays exponentially with a time constant ($R_s C_{\text{dl}}$), its contribution will diminish and eventually $i_F$ will prevail.

Because of the non-Faradaic current that flows just after the onset of the potential step and which at the beginning contributes to the total measured current, the current $i_F(t)$ cannot be related to an absolute value of time ($t$). What is certain are absolute values of $i_F(t)$, measured during a certain time interval ($\Delta t$). Therefore, it is necessary to rewrite Eqn. 1 as a function of time:

$$\frac{1}{[i_F(t)]^2} = \frac{\pi}{(nF A_e C_o)^2} \times \frac{1}{D \times t}$$

Hence, if the inverse square of $i_F(t)$ is plotted against $t$, a linear plot is obtained, of which the slope $h = \Delta(1/[i_F(t)]^2)/\Delta t$ gives information about the diffusion coefficient of the electroactive species:

$$D = \frac{\Delta t}{\Delta \left(\frac{1}{[i_F(t)]^2}\right)} \times \frac{\pi}{(nF A_e C_o)^2}$$

In this way, the diffusion coefficient of oxygen can be determined electrochemically. The same effect is achieved if the slope ($h$) is plotted against $t$, a linear plot is obtained, of which the slope $h = \Delta(1/[i_F(t)]^2)/\Delta t$ gives information about the diffusion coefficient of the electroactive species. If this line is not horizontal, this is an indication that another effect is playing an important role (e.g., charging of the electrical double layer, non-uniform distribution of the concentration of electroactive species at the moment of applying the potential pulse, non-linear diffusion and/or convective disruption of the diffusion layer).

**EXPERIMENTAL**

**Instrumentation**

A platinum rotating disc electrode (RDE) equipped with a Motomatic E-550-M stirring motor was used as the working electrode for the reduction of oxygen. For these experiments a Wenking POS 73 potentiostat was used, provided with a digital multimeter (Fluke 8600A). Temper-
Temperature control of the one-compartment cell was effected with a circulation water-bath (Colora NB-32981). For the potential step a Model 3300A function generator (Hewlett-Packard) was used. The current was measured instantly with the pulse application, therefore the measurement had to be made with a storage oscilloscope or another fast recording device. A Tektronix Type 2430A storage digital oscilloscope was used to record the transient currents. The resulting signal was available for display/printing and computation via a connector (IEEE) on the back of the chassis.

**Procedures**

For these experiments a three-electrode system was used in an electrolysis cell (glass vessel) with a capacity of 160 cm³. A polished platinum disc electrode (RDE) was used as the working electrode \( A_e = 0.5013 \times 10^{-4} \text{m}^2 \), together with a platinum counter electrode with a surface area of \( 5 \times 10^{-4} \text{m}^2 \) and a saturated calomel reference electrode (SCE) with Luggin capillary. A circulating water-bath was used to keep the temperature constant (±0.1°C). The solutions were prepared in distilled, demineralized water with the purest commercially available sodium chloride (Pro Analysi grade) purchased from Merck. Seven solutions were prepared, varying in NaCl concentration from 0.085 to 0.846 M and with a pH between 6.6 and 6.8. The NaCl solutions were saturated with oxygen (purchased from Hoek Loos, Netherlands) for at least 30 min at the prevailing atmospheric pressure. This was accomplished by bubbling the oxygen through the vessel before measurement and by guiding the gas above the electrolyte solution during the measurement. The solution was allowed to become quiescent for a period of at least 1 min before pulsation. The potential was stepped from +300 to -690 mV (vs. SCE). In this way the potential was changed from a value where no Faradaic processes occur to a value where diffusion is the sole mechanism of mass transport of oxygen to the electrode surface.

This procedure consisted in applying a very brief single-potential pulse (1 s at -690 mV), measurement of the response current and evaluation of the data. Before a duplicate measurement was made, the working electrode was rotated with a rotation speed of at least 40 s⁻¹ to obtain reproducible results. Owing to the force convection of this rotation, the oxygen concentration near the electrode was equilibrated and at the same time the reaction products were dissipated.

**RESULTS AND DISCUSSION**

By working out the measured transient currents as described in the theory, it is possible to determine the diffusion coefficients, but first all the parameters needed in order to apply Eqn. 3 must be known. An important factor needed for using this equation is the number of electrons \( n \) involved in the reduction of oxygen. A bipotentiostat (Type Bi-pad) from Tacussel was used together with a rotating ring disc electrode (RRDE) in separate experiments to determine the number of electrons needed for the reduction of oxygen. It was found that \( n = 3.94 \).

Equation 3 requires also the solubility of the electroactive species in the electrolyte. For the solubility of oxygen in NaCl solutions, the following equation is used [3]:

\[
10^3 \alpha = \exp \left( \left\{ -7.424 + \frac{4417}{T} - 2.927 \ln T + 4.238 \times 10^{-2} T \right\} - \left[ m_{Cl} \right]\left\{ -0.1288 + \frac{53.44}{T} - 4.442 \times 10^{-2} \ln T + 7.145 \times 10^{-4} \right\} \right) \tag{5}
\]

where \( \alpha = \) Bunsen absorption coefficient, i.e., the volume of gas \( (T = 0°C \text{ and } 760 \text{ Torr}) \) dissolved in a volume of the solvent when the partial pressure of the gas is 760 Torr [10], \( [m_{Cl}] = \) amount of chloride in grams per 1000 g of solution and \( T = \) temperature (K). It gives the dependence of oxygen solubility on temperature and salt concentration. The coefficients for this equation are based on measurements for \( 273.16 \leq T \leq 308.16 \) and \( 0 \leq [m_{Cl}] \leq 3\% \) and agree to better than ±1% with values from the literature [4,5].
Figure 1 shows some measured transient curves in a 0.154 M NaCl solution (physiological salt concentration) for various temperatures. In Figure 2 the inverse square of $i_p(t)$ is plotted against time. This plot is linear, so its derivative plotted as a function of time (Fig. 3) is horizontal. In Fig. 3 time zero corresponds to the beginning of the potential step ($t = 0.125$ in Figs. 1 and 2). The advantage of plotting the differential quotient of Eqn 2 as a function of time lies in the fact that sometimes the slope of $1/[i_p(t)]^2$ vs. $t$ looks almost straight, but will not give a horizontal line if the derivative of the plot is plotted. In this instance the measured current is being perturbed by other factors, e.g., changing properties of the electrode and/or convective interference. The experimental diffusion coefficients for oxygen ($D_{O_2}$) in NaCl solutions as a function of temperature over the concentration range 0.085–0.846 M are given in Table 1. These values are compared with the diffusion coefficient of oxygen in pure water. Unfortunately, literature values of the oxygen diffusion coefficient vary considerably even under the same conditions. For example, at 25°C, its values range from $1.87 \times 10^{-9}$ to $2.60 \times 10^{-9}$ m$^2$ s$^{-1}$ [11]. Despite this, the tabulated values show close agreement with the values reported by Ferrel and Himmelblau [12].

For all NaCl concentrations, $D_{O_2}$ increases as a function of temperature. Maintaining the temperature constant is very important as the solubility of oxygen is strongly influenced by it. A fluctuation of ±0.5 K will give an average deviation of...
±0.8% in oxygen concentration in this specific temperature range, which will give a deviation in $D_{O_2}$ of ±1.6%.

In general, the presence of ions results in a decrease in $D_{O_2}$. However, in the study presented here, this effect of increasing the NaCl concentration in the range 0.085–0.846 M on $D_{O_2}$ is negligible. These results are inconsistent with the results reported by Ju and Ho [13]. They determined the diffusion coefficient for oxygen with steady-state concentration measurements of dissolved oxygen with a commercially available polarographic oxygen electrode, where they found a rapid decrease in the $D_{O_2}$ values for the same NaCl concentration range. On the other hand, in better agreement with our measurements is the work of Akita [14]. He predicted with an empirical relationship, for which the diffusion in pure water and the densities of the solutions must be known, only a slight decrease in the diffusivity of oxygen as a function of NaCl concentration.

According to the Eyring theory of rate processes [15], the temperature variation of $D_{O_2}$ can be expressed in the form

$$D_{O_2} = A_2 \exp\left(-\frac{E_a}{RT}\right)$$

(6)

where $A_2$ is a constant [frequency factor (m$^2$ s$^{-1}$)], $E_a$ is the activation energy (J mol$^{-1}$) for the diffusion process and $R$ is the gas constant (J mol$^{-1}$ K$^{-1}$). By taking the natural logarithm of $D_{O_2}$ and plotting it against 1/T, for each NaCl concentration an Arrhenius plot (Fig. 4) is obtained. These Arrhenius plots give straight lines with a slope of $-E_a/R$ and an intercept of $\ln A_2$. Equation 6 proves to be a good fit to the values in Table 1, as shown in Fig. 4. The value of $E_a$ for the various NaCl concentrations could be calculated accurately using this Arrhenius plot. The activation energy seemed to be independent of the NaCl concentration in the observed range of 0.085–0.846 M NaCl (Fig. 5). For $E_a$ an average value of $1.79 \times 10^4$ J mol$^{-1}$ was found with a relative standard deviation of 3.8%. However, the intercept ($\ln A_2$) is greatly dependent on the devi-

### Table 1

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<th>Temperature (°C)</th>
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<td>3.26$^a$</td>
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$^a$ Values for $D_{O_2}$ in pure water according to Ferrel and Himmelblau [12]. $^b$ Values in parentheses are [m$_{Cl}$] = amount of chloride in grams per 1000 g of solution (Eqn. 5).
Fig. 5. Activation energy as a function of NaCl concentration. 

Fig. 6. Plot of $D_0 \eta / T$ versus NaCl concentration.

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References