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Determination of Diffusion Coefficients of Cu(I) Ions in Concentrated Perchlorate Solutions

Short Communication

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The diffusion coefficients of Cu(I) ions in concentrated aqueous $Ca(ClO_4)_2$ solutions have been determined from the limiting currents of anodic oxidation at the rotating disc electrode.

(Keywords: Cuprous ion; Diffusion coefficient; Non-complexing medium; Rotating disc electrode)

Zur Bestimmung der Diffusionskoeffizienten von Cu*(I)-Ionen in konzentrierten Perchloratlösungen (Kurze Mitteilung)*

Diffusionskoeffizienten von Cu(I)-Ionen in konzentrierten wäßrigen $Ca(ClO_4)_2$-Lösungen wurden durch Messung der anodischen Grenzströme an der rotierenden Scheibenelektrode bestimmt.

The diffusion coefficients of Cu(I) in non-complexing aqueous media, e.g. perchlorate, nitrate or sulphate solutions, are generally not known. The value of $D_{Cu(I)} = 1.38 \cdot 10^{-5}\,cm^{-2}\,s^{-1}$ in $0.2\,M\,H_2SO_4$ reported by *Tindall* and *Bruckenstein*[1] is an exception.

Recently[2], we have investigated copper deposition on gold electrodes from concentrated aqueous $Ca(ClO_4)_2$ solutions using the rotating ring-disc electrode. For further quantitative discussion about the mechanism of this electrode process, it is of great importance to know the diffusion coefficient of Cu(I) which is an unstable intermediate.

The aim of the present work was to determine the diffusion coefficients for Cu(I) ions in 0.9-3.9 $M\,Ca(ClO_4)_2$ solutions by means of

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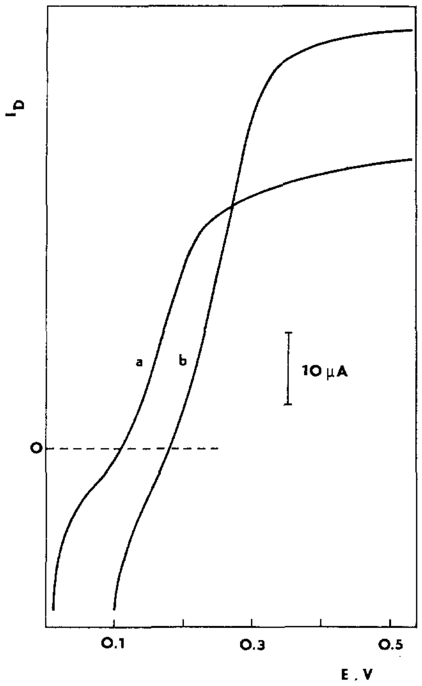

Fig. 1. Current-potential curves for Cu(I) oxidation on rotating gold disc electrode in solutions: *a* $2.2 \cdot 10^{-4}\,M\,CuClO_4 + 0.9\,M\,Ca(ClO_4)_2$, *b* $5.5 \cdot 10^{-4}\,M\,CuClO_4 + 2.9\,M\,Ca(ClO_4)_2$. Both the solutions contain $0.1\,M\,Cu(ClO_4)_2$ and $0.1\,M\,HClO_4$. Rotation speed 1800 rpm. Potential scan rate 5 mV/s

the rotating disc electrode. The Cu(I) ions were produced by chemical stripping of copper metal

$$Cu + Cu(II) \rightleftharpoons 2\,Cu(I) \qquad (1)$$

Because of the small value of the equilibrium constant for the reaction (1) in perchlorate medium[3], each solution contained $0.1\,M\,Cu(ClO_4)_2$ in order to obtain a sufficient concentration of Cu(I). Details concerning the preparation of Cu(I) solutions and determination of its concentration have been described previously[3]. The test solutions were acidified with $0.1\,M\,HClO_4$ to prevent the hydrolysis of Cu(I).

Solutions were prepared from analytical grade reagents and triply distilled water. The test solutions were deaerated with pure argon and a stream of inert gas was kept over the solution during the experiment.

The rotating disc electrode was made of gold. It had a radius of 0.25 cm and a surface area of $A = 0.196\,cm^2$. The electrode surface was polished and cleaned as described in a previous work[2]. Using a synchronous motor, the electrode could be rotated at speeds between 400-3 600 rpm. A platinum spiral and a saturated calomel electrode (NaCl) served as a counter and reference electrodes respectively were isolated from the main cell compartment by fritted glass discs.

The voltammetric experiments were carried out with a Cobrabid PLP-226 C three-electrode polarograph and a Riken Denshi F-3 CP XY recorder.

Measurement were performed at 25 ± 0.2 °C.

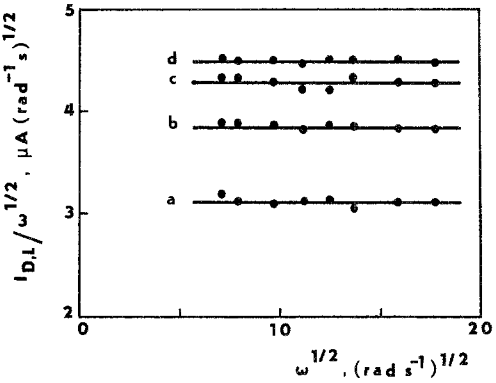

Fig. 2. Plot of $I_{D,L}/\omega^{1/2}$ vs. $\omega^{1/2}$ for the solutions: *a* $2.2\cdot10^{-4}$ *M* $CuClO_4$ + 0.9 *M* $Ca(ClO_4)_2$, *b* $3.3\cdot10^{-4}$ *M* $CuClO_4$ + 1.9 *M* $Ca(ClO_4)_2$, *c* $5.5\cdot10^{-4}$ *M* $CuClO_4$ + 2.9 *M* $Ca(ClO_4)_2$, *d* $1.0\cdot10^{-3}$ *M* $CuClO_4$ + 3.9 *M* $Ca(ClO_4)_2$. All the solutions contain 0.1 *M* $Cu(ClO_4)_2$ and 0.1 *M* $HClO_4$

When the reaction (1) was near the equilibrium, the current-potential curves for the anodic oxidation of Cu(I) to Cu(II) at the rotating disc were recorded. After this measurement, the copper electrode was removed from the test solution and concentration of Cu(I) was determined. The voltametric curves obtained show well reproducible limiting currents. Typical curves are depicted in Fig. 1.

The limiting current, $I_{D,L}$, is proportional to the square root of the angular velocity, $\omega^{1/2}$, over the whole concentration range of Ca $(ClO_4)_2$ studied as it follows from Fig. 2. From these data, the diffusion coefficients of the Cu(I) ions were calculated using *Levich*'s equation

$$D_{\mathrm{Cu(I)}}^{2/3} = \frac{1.61}{n F A \nu^{-1/6} c^{0}_{\mathrm{Cu(I)}}} \frac{I_{D,L}}{\omega^{1/2}} \qquad (2)$$

where $c^{0}_{\mathrm{Cu(I)}}$ is the bulk concentration of Cu(I) and all other symbols have their usual meaning. Kinematic viscosity values, ν, were taken

Table 1. *Diffusion coefficients of* Cu(I) and Cu(II) ions in concentrated perchlorate solutions at 25 °*C*

$c_{Ca(ClO_4)_2}$ + $c_{Cu(ClO_4)_2}$ *mol dm*−3	$D_{Cu(I)}$ cm^2 s^{-1}	$D_{Cu(II)}{}^a$ cm^2 s^{-1}	$\frac{D_{Cu(I)}}{D_{Cu(II)}}$
1.0	$1.3 \cdot 10^{-5}$	$5.5 \cdot 10^{-6}$	2.4
2.0	$1.0 \cdot 10^{-5}$	$4.2 \cdot 10^{-6}$	2.4
3.0	$6.1 \cdot 10^{-6}$	$2.6 \cdot 10^{-6}$	2.3
4.0	$2.9 \cdot 10^{-6}$	$1.3 \cdot 10^{-6}$	2.2

[a] From polarographic data[6].

from Ref.[4]. In consideration of the relatively high *Schmidt*'s numberes for Cu(I) in the studied solutions, corrections for equation (2) introduced by *Newman* could be neglected[5].

The $D_{Cu(I)}$ values obtained are listed in Table 1. Each of them represents a mean value of three independent measurements. This table also includes the diffusion coefficients of Cu(II) in solutions of a similar composition.

It follows from the data given in Table 1 that the ratio $D_{Cu(I)}/D_{Cu(II)}$ is higher than 2 for all solutions investigated. This fact can be explained as due to a significant difference in the hydration numbers of these ions[3].

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