Reactivity of Various Anions Towards Electron Transfer during Cu(II)/Cu(Hg) Exchange Reaction

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Reactivity of bromide, azide, chloride, sulphate and nitrate ions at 1 mol dm^{-3} concentration during reduction of divalent copper at d.m.e. has been studied employing faradaic impedance measurements. Consistent apparent standard rate constant values (k_s) have been obtained at different frequencies by vector analysis of the faradaic impedance following the simple model. In 1 mol dm^{-3} the results show a good agreement with those reported in literature. The order of reactivities is shown to be Br$^+$ > N$_3^-$ > Cl$^-$ > SO$_4^{2-}$ > NO$_3^-$. This has been explained in the light of specific adsorption of these anions within the electrical double layer and the ionic interactions in the bulk of solution.

In a series of papers[1-7], the author and coworkers studied the reactivity of various anions and cations towards electron transfer during the reduction of Pb^{2+}, Cd^{2+}, Zn^{2+}, Sb^{3+} and In^{3+} at the d.m.e. These studies have now been extended to the reduction of Cu(II)/Cu(Hg) in molar solutions of NaBr, NaN$_3$, NaCl, Na$_2$SO$_4$ and NaNO$_3$. The apparent standard rate constant (k_s) for the exchange taken as a qualitative measure of the intrinsic speed of the electrode reaction in each medium has been determined from differential capacity measurements.

Materials and Methods

The circuit comprised a simple a.c. impedance bridge of the symmetrical Wien type[8] in conjunction with a d.c. polarising circuit. The procedure and apparatus were identical to those used in previous studies[6,7]. The solutions of NaNO$_3$, Na$_2$SO$_4$, NaCl, NaN$_3$ and NaBr (all reagent grade quality) were prepared in triply distilled water and were deoxygenated with purified hydrogen gas. The measurements were carried out at $25° \pm 1°C$. All potentials were recorded with saturated calomel electrode (SCE) as the reference electrode.

Results and Discussion

According to the theory of the faradaic admittance[9] the magnitude of the pseudo-capacity peak (C_m) at a certain frequency in one medium may be taken as a qualitative measure of the intrinsic speed of the electrode reaction in the medium. The appearance of pseudo-capacitance during reduction of Cu(II) in the various electrolyte solutions shows that the impedance is comparable in magnitude to that of the double layer capacitance and the reduction proceeds reversibly or quasi-reversibly. The plot of the pseudo-capacity at 1000 cycle/s as a function of polarisation obtained during the reduction of divalent copper at 1 mol dm^{-3}

solution of NaN$_3$ is shown in Fig. 1. Similar curves are obtained in molar solutions of NaNO$_3$, Na$_2$SO$_4$, NaCl and NaBr. In all solutions the pseudo-capacities are well-defined and the peaks have better correspondence with the half-wave potentials. The peak value, as is obvious, becomes greater with increase in the concentration of Cu(II).

For the same cationic species of supporting electrolytes and different anionic species, such as nitrate, sulphate, chloride, azide and bromide, the apparent standard rate constant (k_s) can be taken as an
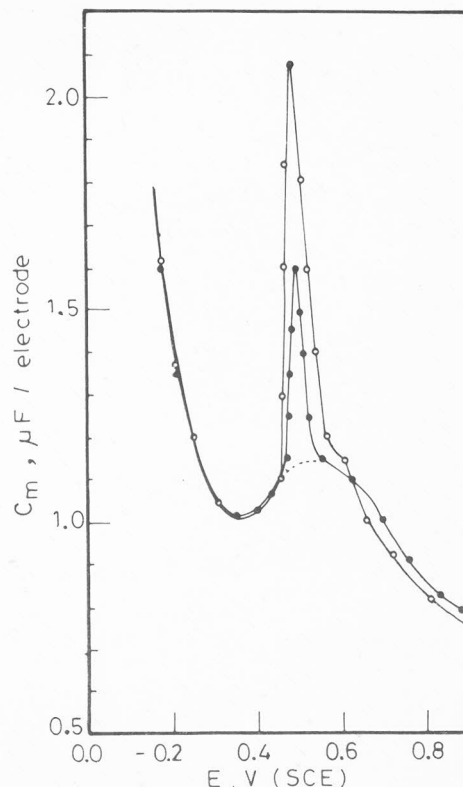

Fig. 1—Pseudo-capacities in the reduction of Cu(II) in 1 mol dm^{-3} NaN$_3$ {[Cu^{2+}] = 1 m mol dm^{-3}, O — O; 0.3 m mol dm^{-3}, ● — ●}

appropriate kinetic parameter to compare the catalytic activity towards electron transfer of various anions. Calculation of the specific rate constant from the results of the above measurements was mainly based on Randles' relations[10],

$$R_r = \frac{RT}{n^2F^2AC}\left(\frac{2}{\omega D}\right)^{1/2} + \frac{RT}{n^2F^2AC} \cdot \frac{1}{k_s} \qquad \ldots (1)$$

$$\frac{1}{\omega C_r} = \frac{RT}{n^2F^2AC}\left(\frac{2}{\omega D}\right)^{1/2} \qquad \ldots (2)$$

$$R_r - \frac{1}{\omega C_r} = \frac{RT}{n^2F^2AC} \cdot \frac{1}{k_s} \qquad \ldots (3)$$

where k_s (cm s^{-1}) is the specific rate constant, C is the concentration (g ion cm^{-3}), A the area (cm^2), n the number of electrons involved in the reaction, R_r and C_r are respectively the resistive and capacitative components of the faradaic admittance; $\omega = 2\pi f$ where f is the frequency, and R, T and F have their usual significance. The results so obtained together with the various quantities involved in the calculations are given in Table 1.

The results presented in Table 1 show that the agreement between the k_s values obtained in each supporting electrolyte at $f = 1000$ and 3000 cycle/s are highly satisfactory. The values of k_s obtained in NaNO$_3$ (1 mol dm^{-3}) agree with those reported by Randles and Somerton[10] in KNO$_3$ (1 mol dm^{-3}). The k_s values reveal that the catalytic activity of anions towards electron transfer of Cu(II)/Cu(Hg) follows the order: $Br^- > N_3^- > Cl^- > SO_4^{2-} > NO_3^-$. A similar order is observed for some redox reactions in ionizing solutions[11]. The results also show that the catalytic activity of azide ion lies almost between those of the bromide and chloride ions. Our findings seem to be in accord with Frumkin's theory[12] on the effect of double layer on reaction rate, which also deals with the effect of anionic adsorption on φ_2 potential. k_s should increase with increasing negative φ_2 potential according to Eq. (4)

$$k_s = k_{s(t)} \exp[(\alpha n - Z)\varphi_2 F/RT] \qquad \ldots (4)$$

where α is the transfer coefficient, n the total number of electrons involved, Z the valency of the cations and φ_2 the potential at the plane of closest approach. The observed order of reactivities in different media parallels, in fact, the variation in φ_2 in 0.1 mol dm^{-3} chloride, azide and bromide solutions as has been experimentally before[6]. However, for the SO_4^{2-} and NO_3^- ions where Γ_{max} are almost negligible[13]; it is still difficult to reconcile the order of reactivities with the theory. A supplementary but not necessarily completely independent alternative is Heyrovsky's theory of ion-pair formation[14]. Association of SO_4^{2-} and NO_3^- anions with the metal cations to give complexes and ion-pairs is known[15]. The results, in general, serve to bridge Frumkin's theory which attributes anion and cation catalysed electron transfer to purely double layer effects, and Heyrovsky's view which assumes ion-pair or complex formation in the bulk of solution.

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Table 1—Apparent Standard Rate Constant k_s of Cu(II)/Cu(Hg) Exchange at 298.15 K

{$[Cu^{2+}] = 1.0 \times 10^{-3}$ g ion dm^{-3}; [electrolyte] = 1 mol dm^{-3}}

f (cycle/s)	C_m (μF)	R_m (ohm)	R_r (ohm)	$1/\omega C_r$ (ohm)	$k_s \times 10$ (cm s^{-1})
		NaNO$_3$			
1000	1.74	153	200	72.5	0.42
3000	0.90	83	190	66.3	0.43
		Na$_2$SO$_4$			
1000	1.94	115	160	84.2	0.63
3000	1.70	61	150	52.0	0.60
		NaCl			
1000	2.06	80	119	96.2	2.7
3000	1.69	51	70	45.0	2.7
		NaN$_3$			
1000	2.06	86	117	101.1	4.2
3000	1.60	66	72	56.2	4.2
		NaBr			
1000	3.02	74	80	88.2	8.02
3000	2.60	36	120	120.5	8.05