Two-step Electron Transfer & Disproportionation of Simple Cu⁺ Ion

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The equilibrium constant for the following reaction: \( 2 \text{Cu}^+ \rightleftharpoons \text{Cu}^{2+} + \text{Cu}^0 \) in water, ethanol, methanol or acetone is shown to vary systematically with the dielectric constant of the medium in the presence of perchlorate anion. Its implications and possibility of obtaining a rare sequential two-electron transfer for simple \( \text{Cu}^{2+} \) ion by monitoring the dielectric constant of the medium are discussed.

In transition metal chemistry, the transfer of several electrons in discrete one electron steps—each step occurring at a characteristic potential—is common. The demonstrable transfer of two (or more) electrons in a single step is, however, comparatively rare. Let us consider the two one-electron steps (1) and (2) having formal

\[ \begin{align*}
A + e^- & \rightarrow B \quad \ldots (1) \\
B + e^- & \rightarrow C \quad \ldots (2)
\end{align*} \]

potential \( E^o \) (1) and \( E^o \) (2) respectively. For discrete one-electron steps,

\[ \Delta E^o = E^o(2) - E^o(1) < 0 \quad \ldots (3) \]

The other two situations, viz., \( \Delta E^o = 0 \) and \( \Delta E^o > 0 \) are relatively uncommon. Condition \( \Delta E^o = 0 \) corresponds to sequential\(^1 \) two-electron transfer. Under the condition \( \Delta E^o > 0 \), B is more readily reduced than A and it tries to reduce A, say electrochemically, the observable process shall be A → C and we have a genuine two-electron process. To go from condition (3) to \( \Delta E^o > 0 \), obviously \( E^o(1) \) and \( E^o(2) \) have to cross each other. An alternative but equivalent description of the phenomenon is in terms of the disproportionation of B (Eq. 4).

\[ \begin{align*}
K = 2 & \text{B} \rightleftharpoons \text{A} + \text{C} \\
2 \text{B} & \rightleftharpoons \text{A} + \text{C} \quad \ldots (4)
\end{align*} \]

The disproportionation constant \( K \) is related to \( \Delta E^\circ \) by Eq. (5).

\[ \Delta E^\circ_{298} = 0.059 \log K \quad \ldots (5) \]

This description is particularly meaningful when condition \( \Delta E^o > 0 \) becomes operative. In the sequel it will be shown that by suitably changing the dielectric constant \( \epsilon \) of the medium it may be possible to go from condition (3) to \( \Delta E^o > 0 \) or vice versa through a sequential two-electron transfer stage. This is exemplified by the redox behaviour of simple \( \text{Cu}^{2+} \) ion in various solvents in the presence of perchlorate anion examined from the angle of disproportionation of \( \text{Cu}^+ \) ion (Eq. 6).

\[ 2 \text{Cu}^+ \rightleftharpoons \text{Cu}^{2+} + \text{Cu}^0 \quad \ldots (6) \]

The values of the equilibrium constants (log \( K \)) for the reaction (6) in four oxygen donor solvents, viz. water (\( \epsilon \), 78.54), methanol (\( \epsilon \), 32.63), ethanol (\( \epsilon \), 24.30) and acetone (\( \epsilon \), 20.70) are: \( 6.00 \) (ref. 2), \( 3.55 \) (ref. 3), 0.55 (ref. 3) and \( -1.50 \) (ref. 4) respectively. In acetone as the solvent \( K \) was determined from voltammetric data\(^4 \) employing Eq. (5). Since the voltammetric measurements were made using mercury electrode, a correction of 0.13 V was necessary to convert the \( \text{Cu}^+ /\text{Cu}^0 \) (Hg) couple into the required \( \text{Cu}^+ /\text{Cu}^0 \) (s) couple\(^4 \).

Variation of log \( K \) with \( 1/\epsilon \) is shown graphically in Fig. 1. It is evident that as the dielectric constant of the medium is lowered \( \text{Cu}^+ \) becomes more stable towards disproportionation and constant \( K \) decreases systematically with \( \epsilon \) leading finally to a change in the sign of \( \Delta E^\circ_{298} \), i.e. the difference between the potentials of \( \text{Cu}^{2+}/\text{Cu}^+ \) and \( \text{Cu}^+ /\text{Cu}^0 \) couples.

Since the redox processes concerned are reversible-quasireversible, we can treat the problem thermodynamically in the following manner. If \( \Delta G^o \) (g) is the standard free energy for reaction (6) in gas phase and \( \Delta G^o \), that in a solvent, we have Eq. (7) where \( A \) and \( B \) are the standard free energy changes involved in transferring simple \( \text{Cu}^{2+} \) and \( \text{Cu}^+ \) ions respectively to the solvent under consideration from gas phase.

\[ \Delta G^o = \Delta G^o \text{(g)} + (A - 2B) \quad \ldots (7) \]

Considering ion-solvent interaction to be purely of electrostatic origin (Born solvation) we have

\[ \begin{align*}
A & = \frac{2Ne^2}{\tau_2} (1/\epsilon - 1) \\
B & = \frac{Ne^2}{2r_1} (1/\epsilon - 1)
\end{align*} \]

In aqueous medium the potentials of \( \text{Cu}^{2+}/\text{Cu}^+ \) and \( \text{Cu}^+ /\text{Cu}^0 \) (Hg) couples given by Kolthoff and Lingane\(^5 \) are respectively \(-0.08 \) and \( 0.15 \) V (vs SCE). The potentials of \( \text{Cu}^{2+}/\text{Cu}^+ \) and \( \text{Cu}^+ /\text{Cu}^0 \) (s) couples as determined by Fenwick\(^2 \) in aqueous medium are \(-0.075 \) and \( 0.28 \) V (vs SCE) respectively. Comparing these two sets of data it is found that due to amalgam formation \( \text{Cu}^+ /\text{Cu}^0 \) potential is lowered by 0.13 V in aqueous medium. Assuming that the corresponding free energy change (due to amalgam formation) is transferable to other solvents, the calculated \( \Delta E^\circ_{298} \) in acetone from the data of Coetzte and Siao\(^* \) comes out to be \(-0.09 \) V.
where \( r_2 \) and \( r_1 \) are ionic radii of \( \text{Cu}^{2+} \) and \( \text{Cu}^+ \) respectively. From Eqs (7), (8a) and (8b) the linear variation of \( \Delta E' \) with \( 1/\varepsilon \) is apparent. The Born solvation (Eq. 8), though notoriously approximate for cations seems for our purpose satisfactory, as from the least square fit in Fig. 1 it is found that \( \Delta G' (g) (at \varepsilon = 1) \) comes out to be 278 kcal/mol as against the experimental value\(^3\) of 214 kcal/mol.

Thus it is indicated that there might exist a very simple relationship between \( \Delta E_{298}' \) for \( \text{Cu}^{2+}/\text{Cu}^+ \) and \( \text{Cu}^+/	ext{Cu} \) (s) couples for simple \( \text{Cu}^{2+} \) ion and solvent dielectric constant in the presence of the perchlorate anion for non-coordinating or weakly coordinating solvents. Figure 1 shows that at \( \varepsilon = 23.00 \), \( \Delta E_{298}' = 0 \). Evidently it can be surmised that for simple \( \text{Cu}^{2+} \) ion the sequential two-electron transfer can be exacted by manipulating the dielectric constant of an oxygen donor medium to 23.00.

So far reversible sequential two-electron transfer is unequivocally established only in the case of binuclear copper(II) triketonate complexes\(^6\). It is interesting to speculate in view of the above discussion whether the phenomenon observed is solvent-induced, since only dimethylformamide was used for the study\(^6\). Encouragingly enough, later Kida and coworkers\(^7\) have observed that quasiirreversible sequential two-electron transfer of some alkoxo bridged binuclear copper(II) complexes with \( \text{N, N-dialkyl-N'-hydroxyalkylalkanediamine} \) in dimethylformamide medium is resolved into two distinct one-electron steps in acetonitrile. However, the separation between the two redox couples is too large (~200 mV) to be attributed simply to the change of dielectric constant of the medium.

Reaction (6) can be viewed as one-electron transfer between two \( \text{Cu}^+ \) ions so as to permit us to apply Marcus’ electron transfer theory\(^8\). For this purpose rough calculations for inner and outer sphere reorganisation energies were done estimating the average ionic radii of solvated \( \text{Cu}^+ \) and \( \text{Cu}^{2+} \) ions from Fig. 1. Valuable information is obtained about the reaction that it is actually controlled by the diffusion step.

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References