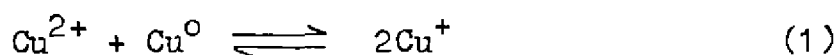


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Cu^+ has strong preferential solvation by some organic solvents in binary solvent mixtures²⁻⁹. It is because of such preferential solvation behaviour that copper(I) salts which are unstable in aqueous solutions are stabilized in water + acetonitrile ($\text{H}_2\text{O} + \text{AN}$) mixtures^{2,3}. The stabilization of copper(I) salts in $\text{H}_2\text{O} + \text{AN}$ mixtures forms the basis for the kinetics of the reversible reaction:



In $\text{H}_2\text{O} + \text{AN}$ mixtures, the forward reaction of this reversible reaction is extremely fast as compared to the backward reaction and when AN is removed from the solution by heating the backward reaction becomes extremely fast.

The investigation reported in this dissertation presents two aspects. The first aspect is concerned with the conductance studies of some 1:1 electrolytes in $\text{H}_2\text{O} + \text{AN}$ mixtures. The purpose of these conductance studies has been to investigate systematically the solvation behaviour of Cu^+ in $\text{H}_2\text{O} + \text{AN}$ mixtures and to compare the conclusions with those available in the literature using emf and NMR measurements²⁻⁴. The second and the important aspect of this investigation has been to study

the kinetics of the forward and the backward reactions of the reversible reaction (1) under different conditions.

In order to investigate the solvation behaviour of Cu^+ in $\text{H}_2\text{O} + \text{AN}$ mixtures, molar conductances of Bu_4NBPh_4 , Bu_4NClO_4 and $\text{CuClO}_4 \cdot 4\text{AN}$ in AN and in $\text{H}_2\text{O} + \text{AN}$ mixtures containing 93.6, 80.2, 71.6, 58.0 and 46.5 mol % AN have been measured in the concentration range $1-50 \times 10^{-4} \text{ mol dm}^{-3}$ at 25°C . The conductance data in all the cases have been analysed by the Shedlovsky method¹⁰⁴⁻¹⁰⁶ to get Λ_0 values of the electrolytes. The Λ_0 values have been split into the contribution of individual ions i.e. into the limiting ionic conductances (λ_i^0 values) on the basis of Bu_4NBPh_4 assumption¹³¹⁻¹³³. Evaluation of actual solvated^{140,141} radii of ions from these λ_i^0 values and the examination of these actual solvated radii as a function of solvent composition show that Cu^+ possesses a strong preferential solvation by AN in $\text{H}_2\text{O} + \text{AN}$ mixtures over the entire composition range. These results are in agreement with the results obtained by Parker and coworkers from the free energy of transfer^{2,144} as well as from NMR⁴ measurements.

The rate of the forward reaction of the reversible reaction (1) has been measured under nitrogen gas atmosphere at 25°C in 150 cm^3 of $\text{H}_2\text{O} + \text{AN}$ mixtures containing 5, 10 and 20% (V/V) AN (also 40% (V/V) AN in cases of 0.032 and $0.064 \text{ mol dm}^{-3}$ copper sulphate solutions) together with 0.032 , 0.064 , 0.16 and 0.32

mol dm⁻³ copper sulphate, 0.07 mol dm⁻³ H₂SO₄ and 1, 4 and 8 g of 2-30 μm in size copper crystals at a stirring speed of 800 r.p.m. The rate of the forward reaction has also been studied using 0.32 mol dm⁻³ copper sulphate, 1, 4 and 8 g of copper crystals (2-30 μm), 5, 10 and 20% (V/V) AN, 0.07 mol dm⁻³ H₂SO₄ at 35, 45, 55 and 65°C at the same stirring speed and with 0.32 mol dm⁻³ copper sulphate, 8 g copper crystals, 20% (V/V) AN, 0.07 mol dm⁻³ H₂SO₄ at 25, 35 and 45°C with stirring speeds equal to 0, 300, 700, 1000 and 1200 r.p.m. The effects of H₂SO₄ and the particle size and surface area of the copper crystals on the rate of the reaction have also been studied using different concentrations of H₂SO₄ and the copper crystals of 40-180 μm, 2-30 μm and 200 mesh in size and with different surface areas.

The following important conclusions have been drawn from the results of the kinetic measurements of the forward reaction:

- i) The increased copper sulphate concentration increased the rate of the reaction. The optimum Cu²⁺ concentration has been found to be 0.32 mol dm⁻³.
- ii) The increased amount of AN in H₂O + AN mixtures increased the rate of the reaction upto 20% of AN. At higher concentration of AN in the mixture, the rate of the reaction increased slightly but the increase was not significant. With 0.32 mol dm⁻³ copper sulphate, the optimum AN concentration to give the maximum rate was found to be 20%.

- iii) Under nitrogen gas atmosphere the rate of the reaction was found to be slightly dependent on H_2SO_4 concentration i.e. on the pH of the solution. The rate of the reaction, however, was affected significantly by the pH of the reaction solution when no nitrogen gas was bubbled through the reaction solution.
- iv) Using optimum concentration of copper sulphate (0.32 mol dm^{-3}), 5, 10 and 20% AN in $\text{H}_2\text{O} + \text{AN}$ mixtures and a given amount of copper crystals the rate of the reaction in each $\text{H}_2\text{O} + \text{AN}$ mixture at 35°C was more than double the rate at 25°C and the rate at 45°C was almost double the rate at 35°C . The rate of the reaction at 55 and 65°C within the experimental uncertainty was, however, practically equal to the rate at 45°C in each case. This established an optimum temperature for this reaction to be 45°C .
- v) The amount and the particle size of the copper crystals strongly affected the rate of the reaction. The smaller the particle size of copper crystals the more was the rate of the reaction. The reaction rate with 200 mesh copper crystals was found to be almost 6 times the rate with $2\text{-}30 \mu\text{m}$ copper crystals and almost 30 times the rate with $40\text{-}180 \mu\text{m}$ copper crystals.
- vi) The increased amount of copper crystals i.e. the increased surface area of copper crystals increased the rate of the reaction.

- vii) The rate of the reaction was found to be strongly affected by the rate of stirring of the solution. The maximum rate was found with maximum stirring speed. The relation between the rate of the reaction and the stirring speed was a power law obeying the relation: $\text{rate} \propto (\text{r.p.m.})^{0.63}$.
- viii) The plots using dimensionless parameters showed that the reaction was first order in Cu^{2+} concentration.
- ix) The reaction was extremely fast to reach almost to the completion within 0.5 to 5 hours.
- x) As the rate of the forward reaction was drastically increased by increasing the stirring speed, this indicated that reaction under investigation was transport controlled¹⁵⁶.

It has been established that under certain other conditions the backward reaction of the reversible reaction (1) becomes significant as compared to the forward reaction and pure copper powder starts separating out from the solution. In order to establish optimum conditions for the backward reaction of reaction (1) kinetic studies under different conditions in $\text{H}_2\text{O} + \text{AN}$ mixtures have also been carried out. The kinetics of the backward reaction of reaction (1) have been studied in $\text{H}_2\text{O} + \text{AN}$ mixtures using $0.40, 0.30, 0.20$ and $0.10 \text{ mol dm}^{-3} \text{ Cu}_2\text{SO}_4$ in 10, 20, 30 and 40% (V/V) AN, $0.60 \text{ mol dm}^{-3} \text{ Cu}_2\text{SO}_4$ in 20, 30 and 40% (V/V) AN, $1.12 \text{ mol dm}^{-3} \text{ Cu}_2\text{SO}_4$ in 40% (V/V) AN, 1.45, 1.57 and $1.93 \text{ mol dm}^{-3} \text{ Cu}_2\text{SO}_4$ in 50% (V/V) AN and $1.82 \text{ mol dm}^{-3} \text{ Cu}_2\text{SO}_4$ in

60% (V/V) AN in the presence of $0.07 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ in all the cases at $80 \pm 2^\circ\text{C}$.

The following important conclusions have been drawn from the results of the kinetic measurements of the backward reaction:

- i) The rate of the reaction increased almost linearly with the increase in Cu^+ concentration in the concentration range 0.10 to 2.40 mol dm^{-3} , showing that the reaction is first order in Cu^+ concentration.
- ii) The optimum Cu_2SO_4 concentration which can be of industrial use has been found to be close to 1.80 mol dm^{-3} in 50% AN.

The importance of the present kinetic investigation for developing a novel, cheap and quick hydrometallurgical method for the purification of copper from crude samples in large scale has also been emphasised.