JOURNAL OF APPLIED ELECTROCHEMISTRY 12 (1982) 1–5

The conductivity of aqueous zinc chloride solutions

B. K. THOMAS[†], D. J. FRAY

Department of Metallurgy and Materials Science, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, UK

Received 6 November 1980

The conductivity of aqueous zinc chloride reaches a maximum of 10.7 Ω^{-1} m^{-1} at 3.7 M $ZnCl_2$. Measurements on chlorinated $ZnCl_2$ showed that at low chlorine concentrations, the conductivity increased linearly with the square root of the chlorine concentration. The increase was due to the three species: dissolved chlorine, Cl_3^- and HClO. Ammonium chloride additions increased the conductivity of aqueous zinc chloride substantially.

---

1. Introduction

In recent years the interest in chloride hydrometallurgy has increased and there have been several publications concerned with the electrowinning of zinc from aqueous zinc chloride solutions [1–3]. It can be envisaged that in an industrial process, the zinc chloride could arise from the aqueous chlorination of residues, scrap or oxidic materials and in order to optimize the electrolytic process, detailed knowledge of the conductivity is required. This is especially important in the case of zinc chloride where the solubility is very high and the range of possible electrolyte compositions is wide.

One of the major losses of electrical energy in an electrolysis is due to the resistance of the electrolyte, so that any increase in conductivity can offer substantial savings in the energy requirement. Previous work [4, 5] has shown that the conductivity rises to a peak at 3.7 M zinc chloride and then decreases as the proportion of complex ions, such as $Zn(H_2O)_6^{2+}$ and $ZnCl_4(H_2O)_2^{2-}$ increases. These species have been identified by Irish *et al.* using Raman spectroscopy [6]. In addition, additions of $CaCl_2$ and LiCl increase the conductivity of zinc chloride solutions [5].

Generally, for concentrated aqueous solutions, it has been found that the Arhennius plots are nonlinear and the results have been interpreted in terms of the free-volume model [7].

The electrolyte used in zinc chloride electrolysis is likely to contain dissolved chlorine and, secondly, with regard to deposit morphology, it has been found that ammonium chloride is a better additive than either lithium or calcium chloride [2, 3]. It is therefore of interest to measure the conductivity of chlorine-saturated aqueous zinc chloride and aqueous zinc chloride–ammonium chloride mixtures.

2. Experimental

2.1. *Conductivity cell*

The conductivity cell had a simple design (Fig. 1), consisting of two platinum electrodes, each 2.5×10^{-4} m^2, in a Pyrex test cell 0.55 m long and 0.1 m in diameter. The electrode spacing was 0.05 m and the volume of electrolyte used in each experiment was 0.25 dm^3. The cell was calibrated using twice-recrystallized 0.1 M KCl at 298 K using the data of Jones and Prendergast [8]. The cell constant was 35.70 m^{-1}, a value which varied by 0.2%.

The cell was mounted in a constant-temperature water bath, heated by a Quickfit immersion heater and paddle stirrer, and controlled by a mercury/toluene temperature control. In addition, a copper coil inside the bath carried a constant-head flow of cooling water. By using an *X–Y* recorder, temperature control was monitored and found to be consistently better than ± 0.05 K at temperatures close to the ambient.

[†] Now with IMI Rod and Wire, Witton, Birmingham.

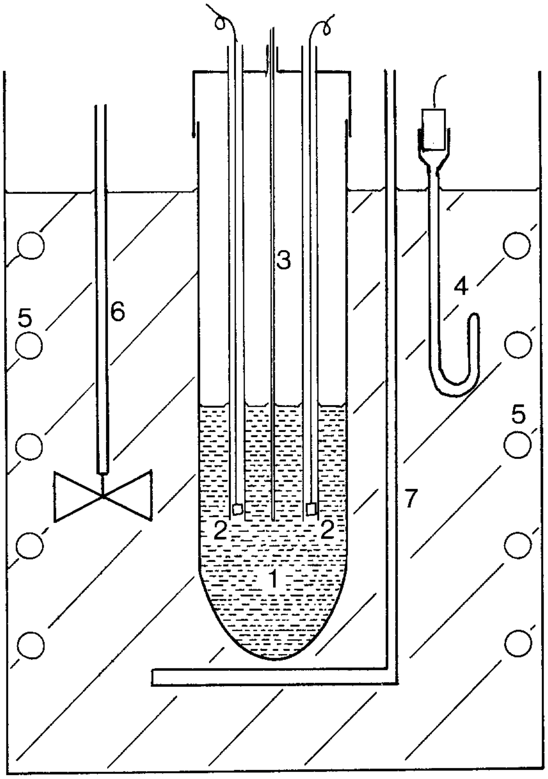

Fig. 1. Schematic diagram of conductivity cell immersed in water bath. 1, Electrolyte; 2, platinum electrodes; 3, thermocouple; 4, toluene/mercury temperature controller; 5, tap water coil; 6, stirrer; 7, heater/cooler.

2.2. *Preparation of solutions*

Because of the difficulty of purifying zinc chloride in solutions, solutions were prepared from Analar zinc and Analar hydrochloric acid. A 20 wt% $ZnCl_2$ solution was analysed as $Sb < 1.6$ mg dm^{-3}, $Cu < 0.2$ mg dm^{-3}, $Co < 0.3$ mg dm^{-3}, $Pb <$ 0.6 mg dm^{-3}, $Fe < 0.16$ mg dm^{-3}, $Ni < 0.05$ mg dm^{-3}, $Ti < 0.3$ mg dm^{-3}. The solutions were analysed for zinc using an EDTA compleximetric titration.

Ammonium chloride was twice recrystallized from Analar BDH material, dried at 373 K and analysed as: $Sb < 0.5$ mg dm^{-3}, $Fe < 0.1$ mg dm^{-3} $Ni < 0.5$ mg dm^{-3}. Distilled water used in the solution preparation had a conductivity of $1.2 \times 10^{-3}\ \Omega\ m^{-1}$ at 275.5 K.

2.3. *Conductivity measurements*

Before taking measurements, the cell was allowed to come to equilibrium for at least four hours. Each experiment was conducted over 24 hours. For the Arrhenius plots, readings were taken over a heating and cooling cycle, and found to correspond well. Chlorinated solutions were prepared *in situ* by bubbling a nitrogen–chlorine mixture. Measurements were taken with no gas flowing, and at the same time a 5 cm^3 sample was removed for chlorine analysis using a standard iodine/thiosulphate titration, adding starch at the end point. The nitrogen and chlorine gas flows were measured in independent flow-meters.

3. Results and discussion

Conductivities for the system $ZnCl_2$–H_2O are shown in Fig. 2. Measurements were made at 298 K and it can be seen that the conductance rises to a maximum at ~ 3.7 M $ZnCl_2$. At higher concentrations, decreasing conductance is associated with increased viscosity. Results by previous workers [5, 9] on this system are included in the figure, and indicate the precision of these present measurements.

In most electrolyte cells, high protein additives are added as levelling agents. Their effect on electrolyte conductivity has not been measured before. Measurements on a 0.66 M $ZnCl_2$ solution at 298 K indicated that additions of levelling agents in the concentration range 0.1 to 1000 mg dm^{-3} gave consistently 5% reductions in conductivity. The levelling agents examined were the high molecular weight (750 000) extract glues, and the results were attributed to the formation of an adsorbed monomolecular layer on the electrodes of the conductivity cell.

3.1. *The NH_4Cl–$ZnCl_2$–H_2O system*

Conductivity measurements were made at 274.4 K, and the results are plotted in Fig. 3 for the NH_4Cl–H_2O, $ZnCl_2$–H_2O and $ZnCl_2$–NH_4Cl–H_2O systems up to 2.0 M. Considerable benefits are obvious from using a mixed electrolyte rather than the binary electrolyte ($ZnCl_2$–H_2O). The figures suggest a substantial increase in conductivity. Experiments with other cations, notably Na^+, Ca^{2+} and K^+ gave similar conductance results, but zinc electrowinning trials [2, 3] indicated a preference for the $ZnCl_2$–NH_4Cl–H_2O electrolyte.

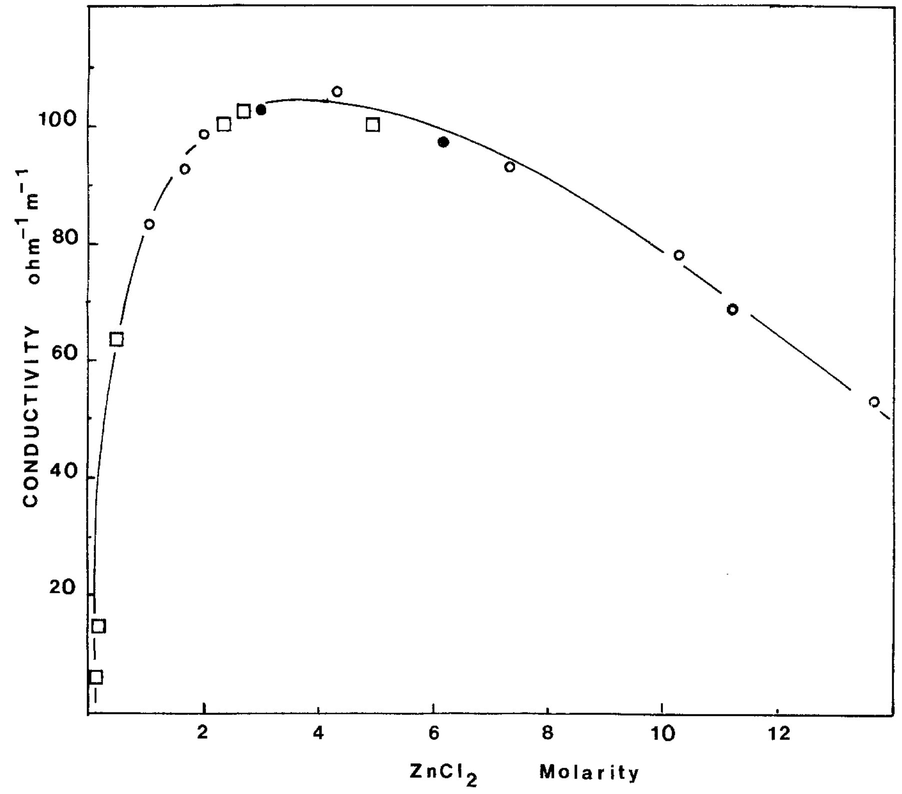

Fig. 2. Conductivity of aqueous zinc chloride at 298 K. ●, [5] ; □, [9] ; ○, this work.

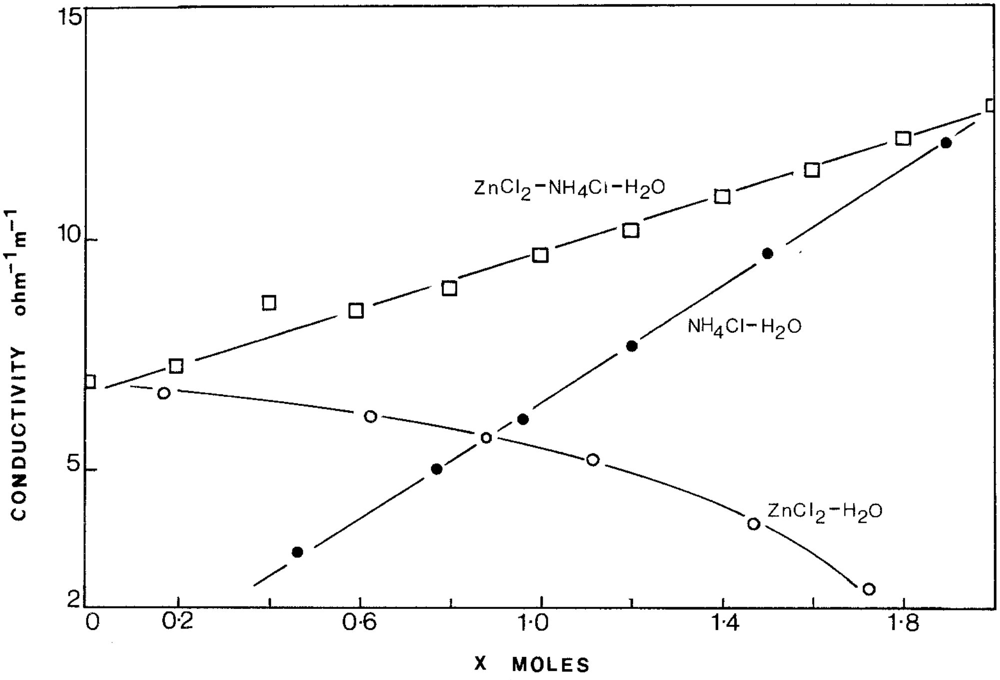

Fig. 3. Conductivity of the $ZnCl_2$–NH_4Cl–H_2O system at 274.4 K. X = moles NH_4Cl; $(2 - X)$ moles $ZnCl_2$; X moles NH_4Cl + $(2 - X)$ moles $ZnCl_2$.

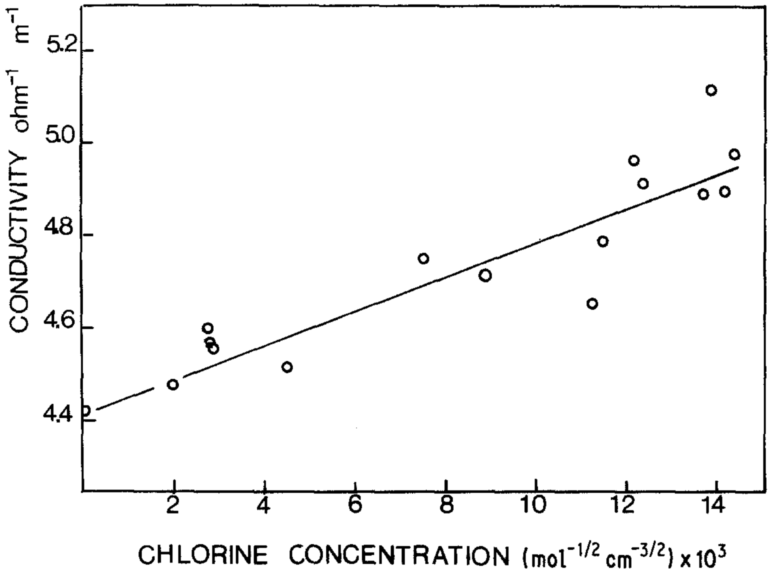

Fig. 4. Conductivity versus (chlorine concentration)$^{1/2}$ at 276.5 K in 0.7 M zinc chloride.

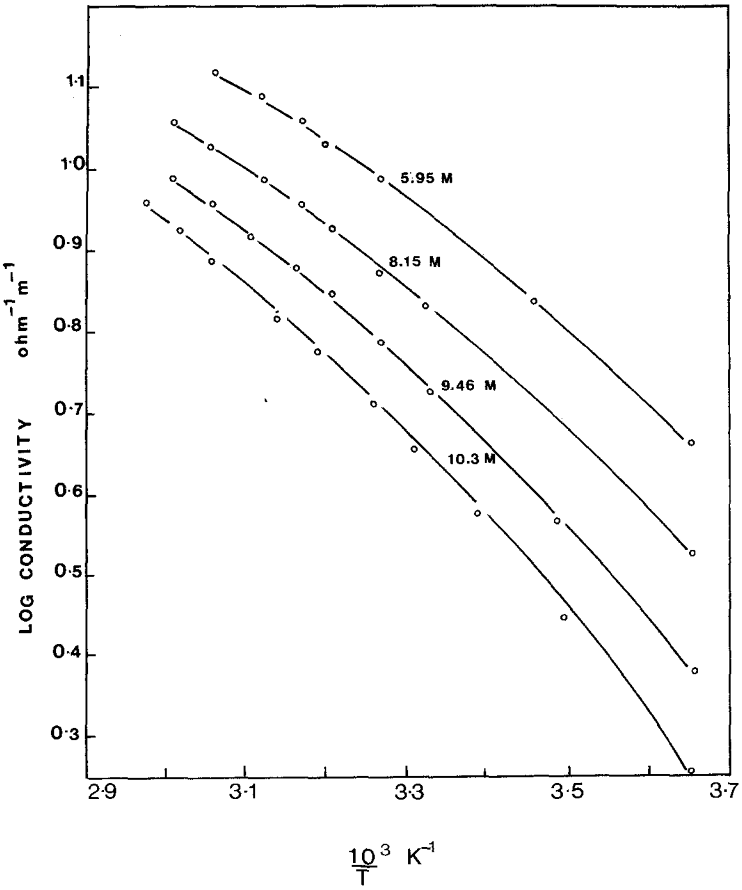

Fig. 5. Arrhenius plots of conductivity of zinc chloride solutions.

3.2. *Effect of dissolved chlorine*

The effect of dissolved chlorine on the conductivity of a 0.7 M $ZnCl_2$ electrolyte was measured at 276.5 K (Fig. 4). In this figure conductivity is plotted against the square root of chlorine concentration ($mol^{1/2}\ cm^{-3/2}$). Up to $2 \times 10^{-6}\ mol\ cm^{-3}$ the conductivity increases linearly. This increase is due to the dissolved species: molecular chlorine, Cl_3^- and, to a small extent, some hypochlorous acids. Kim and Jorné [10] have calculated the diffusion coefficients for these species at 298 K in 2.2 M $ZnCl_2$ to be $0.8 \times 10^{-9}\ m^2\ s^{-1}$, $\sim 0.7 \times 10^{-9}\ m^2\ s^{-1}$ and $1.45 \times 10^{-9}\ m^2\ s^{-1}$ respectively. The scatter in the data of Fig. 4 is due to chlorine loss when extracting the small (5 cm^3) liquid samples for chlorine analysis.

At higher chlorine concentrations the increase in conductivity stopped, and even decreased slightly, when chlorine hydrate was formed.

3.3. *Conductivity Arrhenius plots*

Fig. 5 shows log Ω versus $1/T$ conductivity Arrhenius plots for four concentrated zinc chloride solutions. The water/zinc chloride mole ratio (R) for these solutions lay in the range 2.9–4.2. Non-Arrhenius behaviour is apparent and can be explained in terms of the free-volume theory [7].

4. Conclusions

The conductivity of pure aqueous $ZnCl_2$ electrolyte was measured at 298 K. In common with measurements by previous workers, the conductivity rose to a peak of $10.7\ \Omega^{-1}\ m^{-1}$ at 3.7 M. Dissolved protein compounds, commonly used as levelling agents in electrowinning cells, decreased electrolyte conductivity by 5% over a wide range of concentration. This was interpreted as being due to a monolayer of protein molecules on the electrodes. The presence of molecular chlorine, Cl_3^- ions and hypochlorous acid in chlorinated zinc chloride increased its conductivity.

Conductivities in the mixed electrolyte system NH_4Cl–$ZnCl_2$–H_2O were higher than in the corresponding binary systems $ZnCl_2$–H_2O and NH_4Cl–H_2O. Thus the addition of 1 M NH_4Cl to a 2 M $ZnCl_2$ electrolyte would increase conductivity with the attendant benefit in an electrowinning cell.

The nature of concentrated $ZnCl_2$ solutions was examined. Conductivity Arrhenius plots for four concentrated solutions were nonlinear, indicating that the transport properties of these solutions are more closely associated with glass-forming fused salts.

Acknowledgements

The authors are grateful to National Research Development Corporation for financial support and for a studentship for B. K. Thomas.

References

[1] D. J. Mackinnon, J. M. Brannen and V. I. Lakshmanan, *J. Appl. Electrochem.* 9 (1979) 603.

[2] B. K. Thomas, PhD thesis, University of Cambridge (1979).

[3] B. K. Thomas and D. J. Fray, submitted to *Trans. IMM.*

[4] D. Mead and R. Fuoss, *J. Phys. Chem.* 49 (1945) 480.

[5] A. Easteal, E. J. Sare, C. T. Moynihan and C. A. Angell, *Solution Chem.* **11** (1974) 807.

[6] D. E. Irish, B. McCarroll and T. F. Young, *J. Chem. Phys.* 39 (1963) 3436.

[7] C. A. Angell, *J. Phys. Chem.* 69 (1965) 2137.

[8] G. Jones and M. Prendergast, *J. Amer. Chem. Soc.* 59 (1937) 731.

[9] 'International Critical Tables', McGraw-Hill, New York (1929).

[10] J. T. Kim and J. Jorné, *J. Electrochem. Soc.* **125** (1978) 89.