Electrolytic Conductivity of Pure and Doped Molten Silver Chloride

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The electrolytic conductivity of pure molten silver chloride and of molten silver chloride doped with up to 2 mole% of $CaCl_2$, $CdCl_2$, CsCl, LiCl has been measured in the temperature range 460 °C to 620 °C.

The changes in the conductivity of silver chloride when doped with ionic salts are found to be analogous to the conductivity changes found in binary alkali halide mixtures.

1. Introduction

Recently, Schwind et al. [1] have presented results on the electrolytic conductivity of molten silver halide mixtures, $AgCl_xBr_{1-x}$. In particular new values for the absolute electrolytic conductivity and the corresponding activation energy of fused silver chloride were given. These were significantly larger than the values reported previously in the literature (see Fig. 3 of [1]). They pointed out that platinum electrodes as used in earlier investigations are attacked and partially dissolved when immersed in fused silver chloride [2]. Furthermore, they concluded that the use of high-temperature glass for the construction of the conductivity cell should lead to ion-exchange between the glass and the melt which in turn would lead to the presence of divalent cations in the melt. It was further concluded that the presence of divalent cations coming from the glass and/or the platinum electrodes had to be the cause of the lower absolute values for the electrolytic conductivity found in the literature. To confirm their hypothesis the electrolytic conductivity of silver chloride doped with 1 mole% of cadmium chloride was measured. The conductivity of the mixture was found to be of the same value as those which previous researchers had obtained for pure silver chloride.

The present work has two objectives: the first is to check the surprising results published in [1]. The second objective is to investigate the effect of dopants on the conductivity of molten silver chloride. Our interest in this question was spurred by results on the dissolution thermodynamics of silver in silver chloride doped with chloride salts [3]. From these results it was postulated that covalent structures are present in the silver-silver chloride melt. The concentration and/or lifetime of these clusters should depend on the admixture of salts whose cations have a higher charge density $(z_+ e_0)/r_+^3$ than silver ions. This change in the ionicity of the melt may affect the electrolytic conductivity of the melt.

2. Experimental

Conductivities were measured using the fused quartz conductivity cell shown in Figure 1.

A cell constant of 978 cm^{-1} was obtained by separating the glassy carbon electrodes by a 400 mm long coiled quartz capillary of 2 mm diameter. The resistance of the melt was obtained by two independent methods. In the first method the potential drop V_{cell} at the conductivity cell and the potential drop V_R at a known precision resistance R_p in series with the cell, were measured using a Philips voltmeter, model PM 2524. The resistance of the conductivity cell R was calculated according to Ohm's law

$$R = R_p\,(V_{cell}/V_R)\,.$$

The a.c. potential difference was supplied by a Rohde and Schwarz 504 B RC generator and held constant by a 1:1 booster. The resistance thus measured was found to be independent of the frequency of the applied potential difference in the range 500 Hz to 20 kHz. The variation of the applied potential difference between 2 V and 8 V had no effect on the measurements. All measurements of conductivity were made at 1 kHz and 5 V. A

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Wayne Kerr Universal Bridge 224, operated at 1592 Hz, was repeatedly used to check that the impedance of the cell was purely ohmic. Both methods gave identical results within experimental error.

The resistance varied between 200 Ω and 400 Ω. The cell was calibrated between 450 °C and 600 °C using a KCl-LiCl melt [4], the conductivity of which is of the same order of magnitude as that of the silver chloride melt. The temperature of pure and doped silver chloride melts was varied between 460 °C and 620 °C, and was measured by two movable Ni-NiCr thermocouples. These were inserted in quartz tubes which rendered it possible to measure the temperature of the melt along the whole length of the quartz cell. An additional heating element reduced the difference between the maximum and minimum temperature of the melt to 4 °C. Glassy carbon electrodes were used since they remained unchanged even after being immersed in the melt for weeks. Silver chloride was purified by dissolving it in analytical grade ammonia, filtering

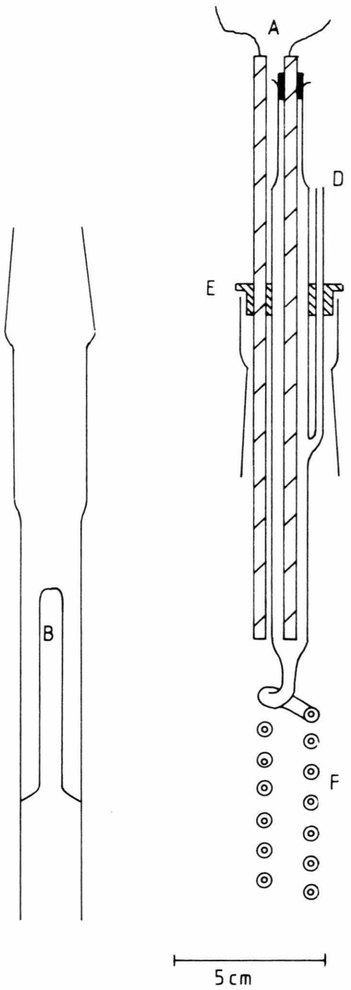

Fig. 1. Quartz conductivity cell. A: Glassy carbon electrodes, B: Quartz thermoelement tube, C: Quartz thermoelement tube (inserted in cell lid), D: Argon inlet, E: Heat-resisting cell lid, F: Coiled quartz capillary.

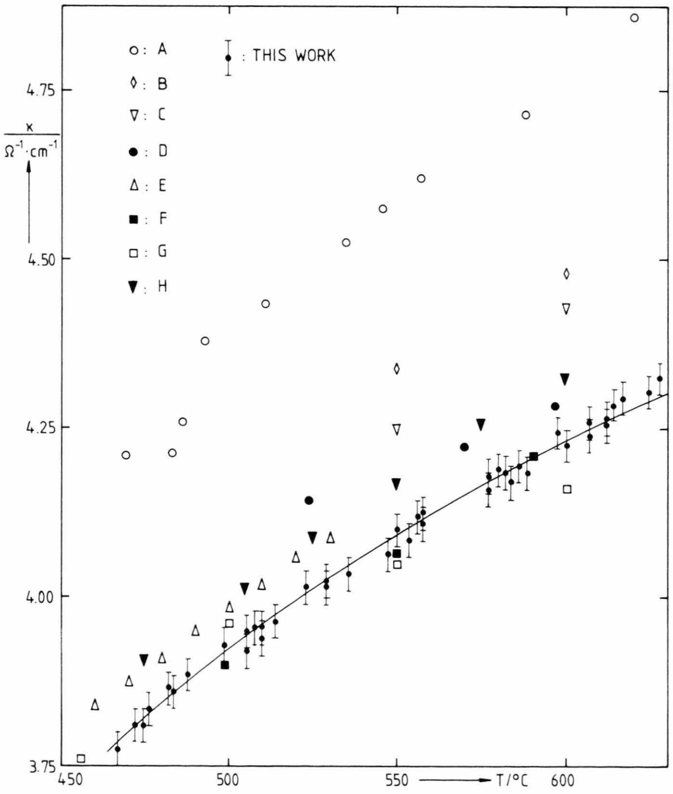

Fig. 2. Temperature dependence of the electrolytic conductivity of pure molten silver chloride.

A: A. F. Schwind, R. Vötsch, and K. G. Weil, Z. Naturforsch. **36 a,** 354 (1981).
B: K. Arndt and E. Gessler, Z. Elektrochem. **14,** 662 (1908).
C: F. Kohlrausch, Wied. Ann. **17,** 662 (1882).
D: H. Winterhager and L. Werner, Forschungsber. Wirtsch. Verkehrsminist. Nordrhein-Westfalen Nr. 341 (1956).
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F: B. S. Harrap and E. Heymann, Trans. Faraday Soc. **51,** 259 (1955).
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the solution and precipitating silver chloride with analytical grade hydrochloric acid. The achieved purity was checked by refining a portion using the zone melting process and measuring its conductivity. No difference in conductivities was found. The silver chloride melts were doped with $CdCl_2$, CsCl, LiCl, and $CaCl_2$, all of reagent grade purity. Argon was continuously bubbled through the melt, the flow being interrupted only during measurements.

3.1. Results

Figure 2 shows the results for the electrolytic conductivity of pure silver chloride. Our results are fully consistent with earlier data. The addition of dopants changed only the absolute value of the conductivity (see Figure 3). Significant changes in the temperature dependence were not observed. The experimental data can be parametrised using an Arrhenius type equation

$$\varkappa = \varkappa_0 \exp(-E_\varkappa / RT),$$

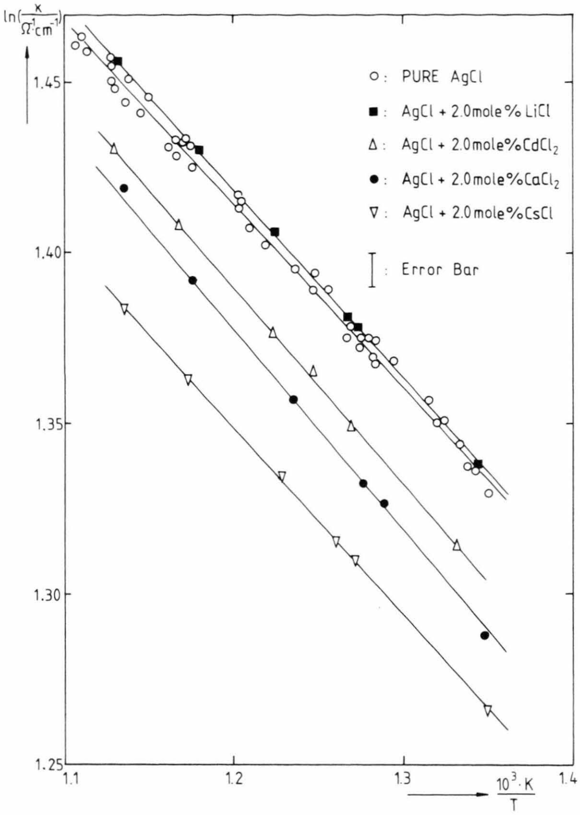

Fig. 3. $\ln \varkappa$ vs. $1/T$ for pure silver chloride and for silver chloride doped with 2 mole% of different chloride salts.

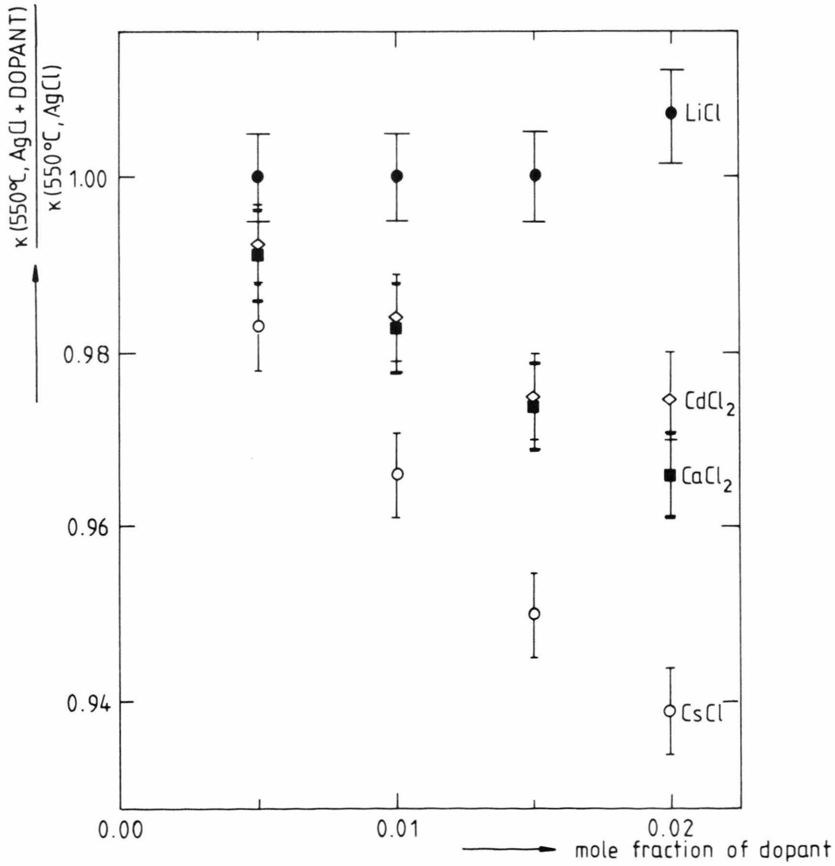

Fig. 4. Relative electrolytic conductivities of doped silver chloride at 550 °C vs. mole% of dopant added.

where $\varkappa$ is the electrolytic conductivity and $E_\varkappa$ is the "activation energy" for conduction. The $\ln \varkappa$ vs. $1/T$ plots for pure and doped silver chloride are straight lines with nearly identical slopes, as shown in Figure 3. In Fig. 4 the results are summed up as relative electrolytic conductivities at 550 °C vs. the mole percent of dopant added.

4. Discussion

Figure 2 shows that the results of [1] for pure silver chloride could not be confirmed: the conductivity of silver chloride, obtained in the present work confirms the values reported by Harrap and Heymann [5]. On the other hand results from [1] for the conductivity of silver chloride doped with 1 mole% CdCl were confirmed. We can only presume that Schwind et al. [1] obtained incoherent values for pure silver chloride, while other results from the paper remain valid.

The experiments reported here were performed with the intention of testing whether the structure-breaking effect of ionic dopants reported [3] also shows up in the electrical conductivity. As one can see from Fig. 4, this is not the case: in no instance did the addition of dopants lead to an increase in the conductivity. Since calcium, cadmium and lithium ions all have a significantly larger charge density than silver ions, it is evident that the charge density effect is not the decisive parameter in ordering the conductivities. On the other hand, comparison of the results with those obtained for binary alkali chloride mixtures [4] and for $CaCl_2$-alkali chloride mixtures [6], suggests that silver chloride-metal chloride systems show normal excess behaviour. In all these systems, when salts with a higher conductivity or smaller cation radius (e.g. AgCl, LiCl, NaCl) are doped with salts of a lower conductivity or larger cation radius (e.g. $CdCl_2$, $CaCl_2$, KCl), sharp reductions in the conductivity result. In the opposite case only very small changes in the conductivity are measured. Since doped silver chloride shows normal excess behaviour in its conductivity, it follows that if covalent structures are present in the melt they have no effect on its conductivity. This indicates that the lifetime of such covalent structures is shorter than the time between two elementary steps of the charge transport process. Further work in this field, particularly on molar conductivities in doped silver chloride, should shed more light on this problem.

Acknowledgement

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