# Viscosity, Conductivity and Density of Fused Silver Chloride Doped with $MeCl_n$ (Me = Li, K, Cs, Ba) in the Mole Fraction Region $0 \leqq x_{dopant} \leqq 0.1$ *

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Z. Naturforsch. **40a,** 1151 – 1156 (1985); received September 19, 1985

The density, the electrolytic conductivity, and the viscosity of molten silver chloride doped with LiCl, KCl, CsCl, and $BaCl_2$ have been measured in the concentration range $0 \leqq x_{dopant} \leqq 0.1$ and temperature range $740\ K \geqq T \leqq 900\ K$. The molar conductivity, $\Lambda$, decreases linearly with $x_{dopant}$, the curve being independent of the charge of the added cation. Only in the case of LiCl is a very small increase of $\Lambda$ observed. The viscosity of the melt remains virtually unchanged when doped with alkali halides. Addition of $BaCl_2$ leads to a strong increase of the viscosity.

The findings show that for these systems no correlation exists between the conductivity and the viscosity. It is further suggested that there is a strong influence of the long range Coulomb interaction on the viscosity of molten salts.

## 1. Introduction

Molten silver chloride reveals an interesting feature: its electrolytic conductivity and its viscosity are typical of purely ionic liquids such as the alkali halides. Other properties are distinctly different from those of the alkali halides. These are, for instance, the volume change on melting, the enthalpy of melting, the silver solubility and the short range order of the melts as deduced from neutron diffraction [1]. The most striking phenomenon shown by fused silver chloride is the strong influence of small amounts (< 10 mol%) of certain mono- and divalent cations on the thermodynamic functions of solvation of silver in the melt [2]. Molecular dynamics calculations (see for instance [3, 4]), show that ion transport (e.g. diffusion or migration) does not occur by jumps of individual ions over discrete distances; instead a concerted mechanism prevails.

One of the aims of the present paper is to investigate whether a correlation exists between molar conductivity changes and viscosity changes, when a small percentage of silver ions is replaced by other cations.

We further desired to clarify whether the "structure breaking" properties of added cations found in [2] also influence the transport properties of the thus doped silver chloride melts.

Finally we felt that there is a lack of precise data for the densities and transport properties in the "dilute solution regime" of fused salts. Such data may be useful as a critical test for theoretical treatments of fused salt systems.

## 2. Experimental

### 2.1 Materials

Silver chloride was purified as described in [5]. The dopants were LiCl, KCl, CsCl, and $BaCl_2$, all of analytical grade purity. These dopants were chosen to enable the study of the influence of the charge and of the radius of added cations on the transport properties of silver chloride (see Table 1). Further advantages of these dopants are that they

Table 1. Properties of dopant cations.

| Salt | Cation radius | Cation molar mass | Charge |
|---|---|---|---|
| AgCl | $1.26 \cdot 10^{-10}$ m | 107.9 g/mol | 1 |
| LiCl | $0.68 \cdot 10^{-10}$ m | 6.9 g/mol | 1 |
| KCl | $1.33 \cdot 10^{-10}$ m | 39.1 g/mol | 1 |
| $BaCl_2$ | $1.34 \cdot 10^{-10}$ m | 137.3 g/mol | 2 |
| CsCl | $1.67 \cdot 10^{-10}$ m | 132.9 g/mol | 1 |

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* Part of a Dr.-Ing. thesis to be submitted by G. G. W. Greening to the Technische Hochschule Darmstadt (D 17).

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are only slightly hygroscopic (except LiCl), that they have low vapour pressures in the temperature range of the measurements, that they are chemically stable and that they can be obtained very pure. The dopants were obtained from E. Merck. They were of analytical grade or "Suprapur®" quality and were dried before use.

### *2.2 Electrolytic Conductivity*

The conductivity cell used in [5] was modified so as to increase its frequency range of constant impedance to 100 kHz. This was achieved by increasing the distance between the electrodes to 2 cm, by reducing the length of the capillary to 12 cm, and by reducing its width to 0.2 cm. Measurements were performed as in [5] but at a frequency of 10 kHz.

### *2.3 Kinematic Viscosity*

The kinematic viscosities were obtained by measuring the flow time of a given volume of the melt through a capillary (modified Ubbelohde viscosimeter). Since the melts have high densities, their flow times in such a viscosimeter are short and the Hagenbach correction factor becomes important. Therefore, a quartz capillary viscosimeter with a large cell constant and a small Hagenbach correction factor was constructed (Figure 1). The length of the capillary (22 cm) necessitated the use of three auxiliary heating coils to reduce the temperature varition over the length of the cell to ± 2 K. The viscosimeter was calibrated with triply distilled water. The cell constant was found to be $K = 8.547 \cdot 10^{-9}\,\mathrm{m^2\,s^{-2}}$, and the Hagenbach correction factor was $B = 2.0 \cdot 10^{-6}\,\mathrm{m^2}$. On applying pressurized argon the melt was forced from the lower bulb to the measuring bulb and was subsequently allowed to flow back freely. The time it took for the upper meniscus of the melt to pass from above to below the measuring bulb was measured. The kinematic viscosity $\nu$ was obtained from the flow time $t$ according to:

$$\nu = Kt - B/t\,.$$

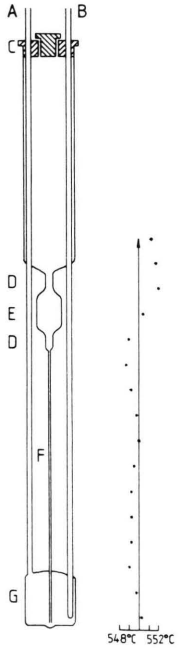

Fig. 1. Viscosimeter. A Argon inlet, B thermoelement, C heat-resisting cell lid, D windows, E measuring bulb, F capillary, G lower bulb.

### *2.4 Density*

The Archimedian technique was used to measure the densities. The experimental setup is similar to that of Bloom and Knaggs [6]. The container for the melt was made of fused silica. The construction of the sinker and its connection to the balance closely followed the techique described by Krekelberg et al. [7]. The sinker volume of about 6 cm$^3$ and its mass of about 50 g, together with an analytical balance, guaranteed a resolution of the density measurements of $\pm 1 \cdot 10^{-3}\,\mathrm{g\,cm^{-3}}$.

## 3. Results

For each dopant concentration the transport properties were measured at 5 different temperatures between 740 K and 900 K. The following equations were used for the presentation of these experimental data:

$$\varrho(T) = \varrho(750\ \mathrm{K}) - m^{\varrho}(T - 750\ \mathrm{K})\,, \tag{1}$$

$$\ln(\nu/\mathrm{m^2\,s^{-1}}) = A_\nu + E_\mathrm{a}^{\nu}/RT\,, \tag{2}$$

$$\ln(\varkappa/\Omega^{-1}\,\mathrm{m^{-1}}) = A_\varkappa - E_\mathrm{a}^{\varkappa}/RT\,. \tag{3}$$

Linear regression was performed on each set of values, the correlation being better than 0.99 and usually lying at about 0.9995. The thus obtained coefficients of (1), (2) and (3) for pure and doped silver chloride are given in Table 2. In evaluating the molar conductivity $\Lambda = \bar{M}\varkappa/\varrho$ ($\bar{M}$ = average molar mass) and the viscosity $\eta = \nu\varrho$, the densities

Table 2. Linear regression coefficients for $\varrho$, $\ln \varkappa$ and $\ln \nu$ according to (1), (2) and (3) as a function of dopant concentration.

| Dopant | Conc. | $10^{-3}\,\varrho$ (750 K) | $10\,m^{\varrho}$ | Conc. | $A_{\varkappa}$ | $E_a^{\varkappa}$ | $-A_{\nu}$ | $E_a^{\nu}$ |
|---|---|---|---|---|---|---|---|---|
| | mol% | kg $m^{-3}$ | kg $m^{-3}$ $K^{-1}$ | mol% | | kJ $mol^{-1}$ | | kJ $mol^{-1}$ |
| – | – | 4.871 | 9.305 | – | 6.680 | 4.503 | 16.354 | 10.761 |
| LiCl | 0.92 | 4.839 | 9.347 | 1.00 | 6.679 | 4.426 | 16.356 | 10.827 |
| | 1.92 | 4.807 | 9.286 | 2.00 | 6.684 | 4.445 | 16.331 | 10.682 |
| | 2.89 | 4.776 | 9.340 | 3.00 | 6.687 | 4.455 | 16.304 | 10.547 |
| | 4.03 | 4.744 | 9.226 | 4.00 | 6.692 | 4.485 | 16.304 | 10.586 |
| | 5.00 | 4.712 | 9.316 | 5.00 | 6.691 | 4.457 | 16.326 | 10.801 |
| | 6.00 | 4.678 | 9.093 | 6.00 | 6.690 | 4.439 | 16.334 | 10.921 |
| | 6.95 | 4.647 | 9.036 | 7.00 | 6.694 | 4.462 | 16.335 | 10.984 |
| | 8.05 | 4.618 | 9.083 | 8.00 | 6.719 | 4.609 | 16.334 | 11.018 |
| | 9.03 | 4.584 | 8.940 | 9.00 | 6.725 | 4.641 | 16.336 | 11.087 |
| | 10.02 | 4.554 | 9.028 | 10.00 | 6.734 | 4.690 | 16.347 | 11.224 |
| KCl | 1.01 | 4.822 | 9.414 | 1.00 | 6.673 | 4.525 | 16.353 | 10.869 |
| | 2.03 | 4.774 | 9.431 | 2.00 | 6.643 | 4.439 | 16.360 | 10.981 |
| | 3.04 | 4.726 | 9.438 | 3.00 | 6.639 | 4.526 | 16.380 | 11.191 |
| | 4.06 | 4.679 | 9.485 | 4.00 | 6.634 | 4.625 | 16.385 | 11.297 |
| | 5.04 | 4.632 | 9.529 | 5.00 | 6.619 | 4.645 | 16.383 | 11.355 |
| | 6.03 | 4.584 | 9.497 | 6.00 | 6.611 | 4.711 | 16.406 | 11.583 |
| | 7.03 | 4.539 | 9.571 | 7.00 | 6.599 | 4.748 | 16.410 | 11.679 |
| | 8.04 | 4.494 | 9.579 | 8.00 | 6.591 | 4.812 | 16.425 | 11.830 |
| | 9.04 | 4.449 | 9.606 | 9.00 | 6.585 | 4.895 | 16.442 | 12.025 |
| | 10.03 | 4.403 | 9.491 | 10.00 | 6.577 | 4.953 | 16.428 | 11.994 |
| CsCl | 0.95 | 4.831 | 9.424 | 1.00 | 6.653 | 4.476 | 16.356 | 10.827 |
| | 1.98 | 4.791 | 9.551 | 2.00 | 6.623 | 4.490 | 16.380 | 11,062 |
| | 3.00 | 4.756 | 9.692 | 3.00 | 6.608 | 4.603 | 16.364 | 11.009 |
| | 4.02 | 4.717 | 9.593 | 4.00 | 6.572 | 4.576 | 16.383 | 11.224 |
| | 5.03 | 4.682 | 9.727 | 5.00 | 6.555 | 4.679 | 16.390 | 11.347 |
| | 6.02 | 4.647 | 9.773 | 6.00 | 6.534 | 4.749 | 16.438 | 11.738 |
| | 7.03 | 4.611 | 9.853 | 7.00 | 6.510 | 4.797 | 16.450 | 11.903 |
| | 8.00 | 4.572 | 9.247 | 8.00 | 6.495 | 4.909 | 16.481 | 12.251 |
| | 9.00 | 4.542 | 9.808 | 9.00 | 6.474 | 4.975 | 16.511 | 12.519 |
| | 10.01 | 4.509 | 9.702 | 10.00 | 6.447 | 5.001 | 16.511 | 12.519 |
| $BaCl_2$ | 1.00 | 4.843 | 9.437 | 1.00 | 6.681 | 4.609 | 16.369 | 11.142 |
| | 1,99 | 4.816 | 9.339 | 2.00 | 6.681 | 4.765 | 16.363 | 11.334 |
| | 2.99 | 4.789 | 9.186 | 3.00 | 6.644 | 4.669 | 16.416 | 11.917 |
| | 3.98 | 4.763 | 9.313 | 4.00 | 6.692 | 5.157 | 16.450 | 12.407 |
| | 4.97 | 4.738 | 9.350 | 5.00 | 6.700 | 5.377 | 16.473 | 12.795 |
| | 5.96 | 4.714 | 9.393 | 6.00 | 6.710 | 5.608 | 16.481 | 13.120 |
| | 6.94 | 4.690 | 9.371 | 7.00 | 6.715 | 5.795 | 16.547 | 13.835 |
| | 8.05 | 4.667 | 9.279 | 8.00 | 6.731 | 6.072 | 16.553 | 14.125 |
| | 9.04 | 4.644 | 9.308 | 9.00 | 6.738 | 6.072 | 16.542 | 14.310 |
| | 10.00 | 4.623 | 9.303 | 10.00 | 6.656 | 5.854 | 16.596 | 14.949 |

were obtained from the density regression functions, the value being linearly corrected to the exact dopant concentration, where necessary.

The relative changes of the density, molar conductivity, and viscosity as functions of the dopant concentration at 823 K are shown in Figs. 2–4. Figure 5 shows the concentration dependence of the temperature coefficient $m^{\varrho}$, the activation energies $E_a^{\eta}$ and $E_a^{\Lambda}$ being depicted in Figs. 6 and 7.

## 4. Discussion

### 4.1 Reliability

Since we calibrated with substances other than silver chloride, the measured transport coefficients for silver chloride can be critically compared with literature data. This has already been done for the electrolytic conductivity [5]. The presented value for the density of pure silver chloride at 823 K

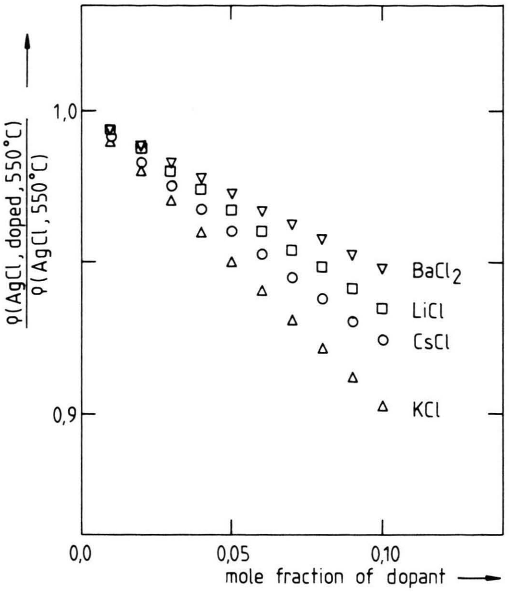

Fig. 2. Relative change of the density vs. dopant concentration.

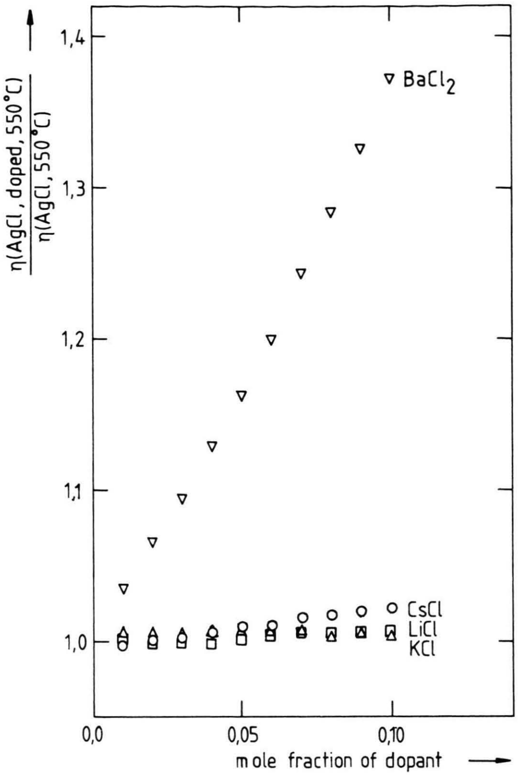

Fig. 4. Relative change of the viscosity vs. dopant concentration.

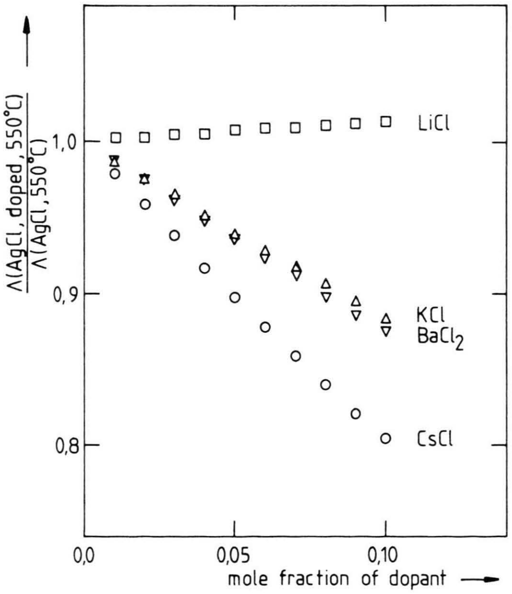

Fig. 3. Relative change of the molar conductivity vs. dopant concentration.

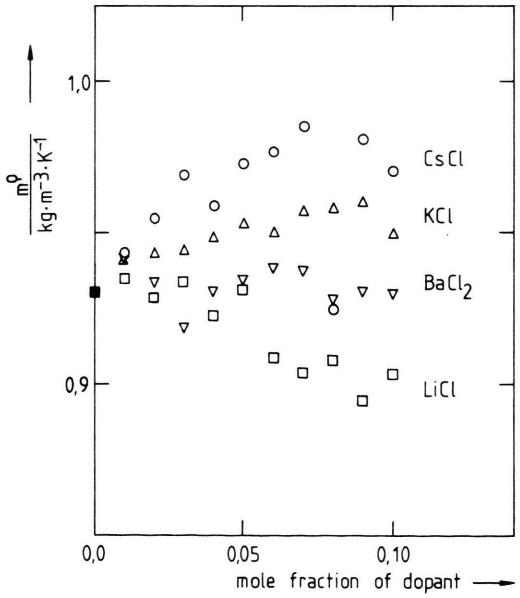

Fig. 5. Temperature coefficient $m^{\varrho}$ vs. dopant concentration.

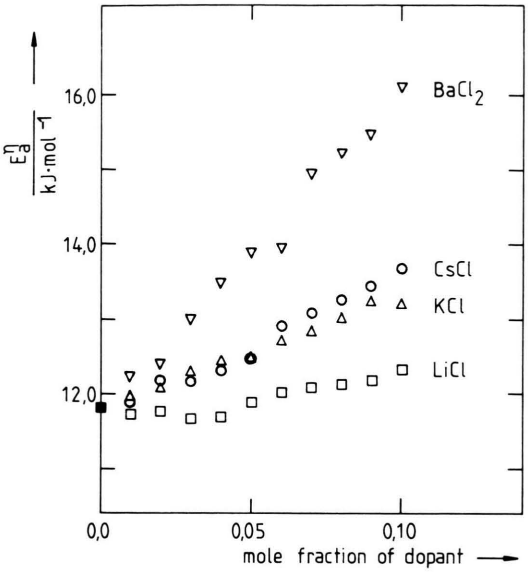

Fig. 6. Formal activation energy $E_a^\eta$ vs. dopant concentration.

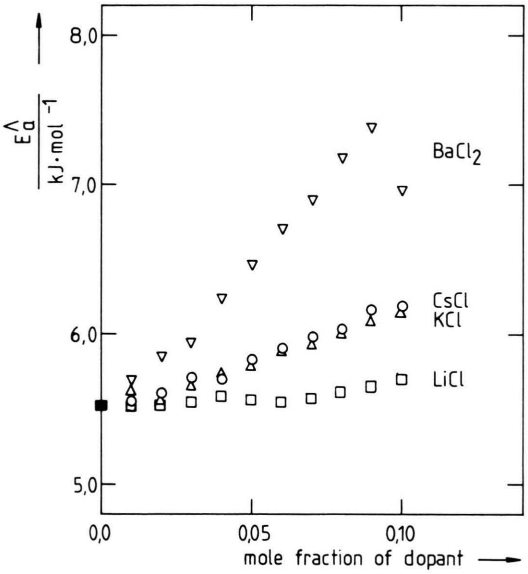

Fig. 7. Formal activation energy $E_a^\Lambda$ vs. dopant concentration.

($4.803 \cdot 10^3$ kg m$^{-3}$) is only 0.3% higher than the recommended NSRDS data reference base value of Bell and Flengas [8]. Since the temperature coefficient $m^\varrho$ (+ 0.93 kg m$^{-3}$ K$^{-1}$) is higher than that given by [8] (+ 0.85 kg m$^{-3}$ K$^{-1}$) the difference in the density values diminishes at higher temperatures. The viscosity at 823 K ($1.827 \cdot 10^{-3}$ kg m$^{-1}$ s$^{-1}$) is 1% lower than that measured by Harrap and Heyman [9], the recommended NSRDS data base. The reproducibility of the density of pure silver chloride was ± 0.2%. In the case of the electrolytic conductivity and the kinematic viscosity the reproducibility was ± 0.3% and ± 0.7%, respectively.

### *4.2 General Discussion*

The density of molten silver chloride depends only weakly on the addition of $BaCl_2$ (see Figure 2). This illustrates the different behaviour of crystalline and molten salts: in the solid state, replacement of silver ions by barium ions leads to vacancy formation on cation sites. The decrease of the density of the AgCl−$BaCl_2$ melt should, therefore, be more pronounced than that caused on doping with cesium ions, which have almost the same mass as barium ions. Richter [7] measured the density of molten silver chloride, containing 10 mol% of alkali halides. Within the error limits, his results are confirmed by our measurements. Even in the case of the alkali halides, there is no correlation between the density change and the molar mass of the added cation.

The influence of doping on the molar conductivity of fused silver chloride (Fig. 3) clearly shows that at a given dopant concentration the conductivity ratio $\Lambda(x)/\Lambda(x=0)$ depends on the size of the added cation, not on its charge. On the other hand, in the case of the viscosity, substitution of silver ions by univalent cations has virtually no effect on the viscosity (see Fig. 4), while barium ions cause a drastic increase. A comparison of the results for $\Lambda(x)$ with those for $\eta(x)$ definitely shows that there is no correlation between these quantities. A correlation exists, however, between the formal activation energies: from Figs. 6 and 7 one can see that the relationship $E_a^\eta/E_a^\Lambda = 2.1 \pm 0.2$ holds, independently from the nature and the concentration of the dopant.

The results of the molar conductivity measurements of doped silver chloride melts are consistent with the picture of concerted motions of many ions. Those of the viscosity measurements are more difficult to understand. Qualitatively, ideal mixing rules lead to the observed results: fused alkali chlorides have viscosities close to that of fused silver chloride, while barium chloride has a much higher viscosity, even at substantially higher temperatures. Yet it must be borne in mind that the short range order in an $MX_2$-melt should differ from that in an MX-melt. This means that at low mole fractions an individual barium ion should see an environment which is typical for an MX-melt. If this assumption is correct, one is led to the conclusion that the long range Coulomb part of the potential is responsible for the pronounced effect of the divalent cation on the viscosity of fused silver chloride.

None of the investigated properties shows irregularities in their concentration dependence which could be attributed to the structure-breaking effect which is indicated by the thermodynamics of solvation of silver in these melts. Apparently, the lifetime of the relevant structures is too short to allow them to influence the transport properties. A similar effect was observed by Dumas et al. [10] in $Mg^{2+}$ containing chloride melts and by Zuca and Borcan [11] in $Ca^{2+}$ containing chloride melts. These authors reported that in some cases even the presence of $MgCl_4^{2-}$ complexes, which are well characterized spectroscopically, could not be deduced from viscosity data.

Admittedly, some conclusions drawn from the data in this paper are still tentative. Further experiments are necessary in order to obtain a final understanding of the transport properties in the dilute solution regime of molten salts.

## *Acknowledgement*

This work was sponsored by the Deutsche Forschungsgemeinschaft. Additional financial support by the Fonds der Chemischen Industrie is greatly acknowledged.

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