Viscosity, Conductivity and Density of Fused Silver and Copper(I) Chlorides Doped with Group I and II Chlorides in the Mole Fraction Region $0 \leqq x_{\text{dopant}} \leqq 0.1$*

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The density, the electrolytic conductivity and the viscosity of molten silver chloride doped with NaCl, RbCl, $MgCl_2$, $CaCl_2$, $SrCl_2$ and $CdCl_2$, and of molten copper chloride doped with NaCl, KCl, CsCl, $MgCl_2$, $CaCl_2$ and $BaCl_2$ have been measured in the concentration range $0 \leqq x_{\text{dopant}} \leqq 0.1$: the temperature range was 740 K $\leqq T \leqq$ 900 K for silver chloride and 710 K $\leqq T \leqq$ 850 K for copper chloride. The findings show that the molar conductance in such systems is strongly dependent on the ionic radii of the cations: the viscosity, on the other hand, is mainly governed by their charge. A strong correlation exists between the formal activation energies of conductance and viscosity, E_a^{η}/E_a^{Λ} being constant for all types and concentrations of dopant used in this work.

1. Introduction

In a previous paper [1] the dependance of the viscosity and conductivity of fused silver chloride on the addition of $MeCl_n$ (Me = Li, K, Cs, Ba) in the mole fraction region $0 \leqq x_{\text{dopant}} \leqq 0.1$ has been published. It was found that the conductivity depends on the size of the added dopant cation, while the viscosity depends on its charge. It was further noticed that the ratio of the formal activation energies E_a^{η}/E_a^{Λ} is independent of the type and concentration of the dopants employed. Only four different dopants were used and the solvent was not varied. It is therefore the aim of this further paper to test if the above-mentioned properties are exhibited when other dopants are used or when copper-I-chloride is used instead of silver chloride.

2. Experimental

2.1 Materials

Silver chloride was purified as described in [2]. The surface of the commercially available copper chloride (p. a. Merck) was partially oxidized. The surface was cleaned as in [3], the purification being performed in a quartz glass apparatus [4] in which the purified copper chloride could be subsequently melted and cast into rods. The dopants were NaCl, KCl, RbCl, CsCl, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$ and $CdCl_2$. They were obtained from E. Merck and were all of analytical grade or of "Suprapur®" quality. Crystallisation water or traces of moisture were removed by heating the salts in a stream of dry hydrogen chloride. The temperature was gradually increased so as to prevent the formation of oxides, the hydrogen chloride being expelled by a stream of dry argon shortly before melting occurred.

2.2 Apparatus

The measurements of the viscosity, conductivity and density of the silver chloride systems were performed as in [1]. The same methods were used for the copper chloride systems; however, since molten copper chloride reacts with oxygen and with water vapour the melts had to be particularly well protected from air. Appropriate quartz glass cells were constructed. Figures 1 and 2 show respectively the capillary viscometer and the combined quartz glass density and conductivity cell. Only the upper part of the viscometer is shown in Fig. 1, since the bottom part is identical with that of the viscometer used

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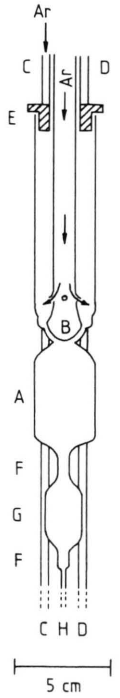


Fig. 1

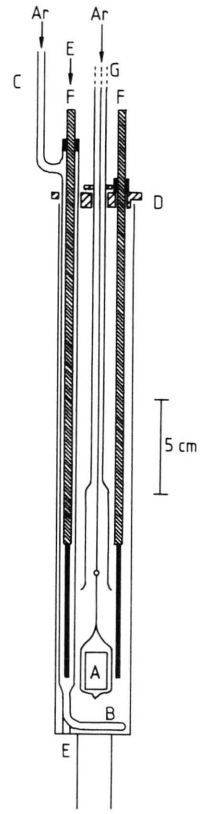


Fig. 2

Fig. 1. Capillary Viscometer: A Melt reservoir; B Spherical ground glass stopper; C Argon inlet; D Thermoelement tube; E Lid; F Windows; G Measuring bulb; H Capillary.

Fig. 2. Combined density and conductivity cell: A Sinker; B Capillary; C Argon inlet; D Lid; E Thermoelement tube; F Electrodes (upper part graphite rod, lower part glassy carbon).

in [1]. The reservoir above the measuring bulb is sealed by a spherical ground glass stopper, which was slightly opened during the measurements. The viscometer was calibrated with triply distilled water, using the values in [5].

The density and the conductivity of the copper chloride systems were both measured using the cell shown in Figure 2. It consisted of a container in which both the sinker (see [4]) and an electrode assembly could fit. The electrode assembly was made up of a tube containing a 300 mm long electrode and ending in a capillary 100 mm in length and of 1.8 mm inner diameter. The second electrode was inserted through a hole in the cell lid at a distance of 25 mm from the first electrode. The conductivity cell was calibrated with 1.0 N potassium chloride solution using the values of Jones et al. [6]. Measurements of the conductivity and density were performed as in [1].

Since the copper chloride melts were slowly attacked by traces of air the melts were renewed for every concentration, both for the viscosity measurements, and for the conductivity and density measurements.

3. Results

For each dopant concentration the transport properties were measured at 5 different temperatures between 740 K and 900 K for the silver chloride systems, and between 710 K and 850 K for the copper chloride systems. The following equations were used for the presentation of the temperature dependence of these experimental data:

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

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

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

$$\ln(\Lambda/\mathrm{m^2\,mol^{-1}\,\Omega^{-1}}) = A^{\Lambda} - E_{\mathrm{a}}^{\Lambda}/RT, \tag{4}$$

$$\ln(\eta/\mathrm{kg\,m^{-1}\,s^{-1}}) = A^{\eta} + E_{\mathrm{a}}^{\eta}/RT. \tag{5}$$

Linear regression was performed on each set of values, the correlation being better than 0.99 and usually lying at about 0.999. The coefficients of (1), (2), (3), (4) and (5) for pure and doped silver and copper(I) chloride so obtained are given in Tables 1 and 2. In evaluating the molar conductivity $\Lambda = \bar{M}\varkappa/\varrho$ ($\bar{M}$ = average molar mass) and the viscosity $\eta = \nu\varrho$. The densities were obtained from the density regression functions. The relative molar conductivity, viscosity and molar volume of the doped silver and copper chlorides (including the values published in [1]) as functions of the dopant concentration at 823 K are shown in Figures 3–8. Figures 9 and 10 show the concentration dependance of the temperature coefficient m^{ϱ}, while the activation energies E_{a}^{η} and E_{a}^{Λ} are given in Figures 11–14.

Table 1. Linear regression coefficients for ϱ, $\ln \nu$, $\ln \varkappa$, $\ln \Lambda$ and $\ln \eta$ of the silver chloride systems according to (1), (2), (3), (4) and (5) for various dopant concentrations.

Dopant	Conc. / mole%	$10^{-3}\varrho$(750 K) / kg m^{-3}	$10\, m^{\varrho}$ / kg m^{-3} K^{-1}	$A^{\varkappa}$	$E_a^{\varkappa}$ / kJ mol^{-1}	$-A^{\nu}$	E_a^{ν} / kJ mol^{-1}	$-A^{\Lambda}$	E_a^{Λ} / kJ mol^{-1}	$-A^{\eta}$	E_a^{η} / kJ mol^{-1}
AgCl	**100.0**	**4.871**	**9.305**	**6.680**	**4.450**	**16.354**	**10.761**	**3.582**	**5.525**	**8.033**	**11.822**
NaCl	2.0	4.796	9.401	6.659	4.441	16.361	10.939	3.591	5.539	8.061	12.036
	4.0	4.721	9.382	6.662	4.549	16.359	11.043	3.574	5.672	8.078	12.158
	6.0	4.648	9.325	6.658	4.602	16.380	11.300	3.569	5.728	8.120	12.454
	8.0	4.575	9.377	6.641	4.561	16.400	11.575	3.569	5.742	8.168	12.819
	10.0	4.503	9.295	6.640	4.637	16.426	11.879	3.555	5.862	8.211	13.127
RbCl	5.0	4.665	9.573	6.583	4.676	16.406	11.467	3.633	5.816	8.144	12.628
	10.0	4.473	9.785	6.514	5.031	16.473	12.285	3.655	6.250	8.263	13.510
$MgCl_2$	2.0	4.792	9.911	6.648	4.534	16.395	11.410	3.590	5.701	8.106	12.568
	4.0	4.688	9.436	6.666	4.927	16.419	11.905	3.562	6.059	8.117	12.814
	6.0	4.597	9.512	6.672	5.215	16.509	12.852	3.541	6.356	8.261	14.012
	8.0	4.508	9.452	6.670	5.472	16.508	13.153	3.528	6.628	8.283	14.338
	10.0	4.420	9.545	6.666	5.708	16.586	14.045	3.513	6.907	8.386	15.256
$CaCl_2$	2.0	4.773	9.199	6.691	4.782	16.355	11.349	3.553	5.874	8.056	12.494
	4.0	4.684	8.950	6.672	4.937	16.326	11.678	3.563	5.989	8.044	12.738
	6.0	4.593	8.744	6.687	5.301	16.306	11.991	3.533	6.350	8.044	13.058
	8.0	4.508	8.517	6.683	5.537	16.321	12.588	3.523	6.589	8.074	13.628
	10.0	4.433	8.416	6.706	5.978	16.372	13.330	3.489	7.024	8.146	14.395
$SrCl_2$	5.0	4.696	9.212	6.665	5.086	16.326	11.825	3.551	6.189	8.047	12.924
	10.0	4.542	9.312	6.721	6.172	16.464	13.950	3.448	7.330	8.229	15.116
$CdCl_2$	2.0	4.828	9.684	6.656	4.531	16.366	11.073	3.580	5.675	8.063	12.191
	4.0	4.782	9.365	6.681	4.896	16.419	11.640	3.547	6.005	8.122	12.736
	6.0	4.740	9.393	6.690	5.140	16.452	12.090	3.521	6.261	8.164	13.188
	8.0	4.699	9.407	6.710	5.466	16.525	12.833	3.485	6.593	8.249	13.952
	10.0	4.661	9.517	6.724	5.732	16.563	13.297	3.457	6.866	8.299	14.441

Table 2. Linear regression coefficients for ϱ, $\ln \nu$, $\ln \varkappa$, $\ln \Lambda$ and $\ln \eta$ of the copper chloride systems according to (1), (2), (3), (4) and (5) for various dopant concentrations.

Dopant	Conc. / mole%	$10^{-3}\varrho$(750 K) / kg m^{-3}	$10\, m^{\varrho}$ / kg m^{-3} K^{-1}	$A^{\varkappa}$	$E_a^{\varkappa}$ / kJ mol^{-1}	$-A^{\nu}$	E_a^{ν} / kJ mol^{-1}	$-A^{\Lambda}$	E_a^{Λ} / kJ mol^{-1}	$-A^{\eta}$	E_a^{η} / kJ mol^{-1}
CuCl	**100.00**	**3.632**	**8.219**	**6.343**	**2.809**	**16.824**	**17.281**	**3.982**	**3.967**	**8.814**	**18.453**
NaCl	5.0	3.499	7.898	6.315	2.937	16.802	16.931	3.994	4.083	8.829	18.097
	10.0	3.376	8.312	6.308	3.184	16.770	16.578	3.972	4.419	8.848	17.835
KCl	5.0	3.457	8.350	6.267	3.147	16.811	16.720	4.010	4.368	8.861	17.951
	10.0	3.298	8.618	6.156	3.139	16.780	16.175	4.070	4.463	8.894	17.513
CsCl	5.0	3.531	8.279	6.113	2.710	16.867	16.770	4.144	3.893	8.894	17.994
	10.0	3.439	8.530	5.967	3.030	16.840	16.026	4.218	4.294	8.902	17.301
$MgCl_2$	5.0	3.477	8.005	6.326	3.341	16.811	17.895	3.954	4.513	8.846	19.072
	10.0	3.330	7.650	6.267	3.704	16.613	17.139	3.953	5.008	8.709	18.438
$CaCl_2$	5.0	3.504	7.473	6.401	3.649	16.685	17.486	3.876	4.838	8.699	18.582
	10.0	3.390	7.077	6.493	4.889	16.622	18.201	3.767	5.940	8.658	19.225
$BaCl_2$	5.0	3.631	7.769	6.396	3.739	16.887	18.538	3.885	4.836	8.863	19.618
	10.0	3.633	6.581	6.480	4.891	16.954	19.653	3.777	5.814	8.904	20.575

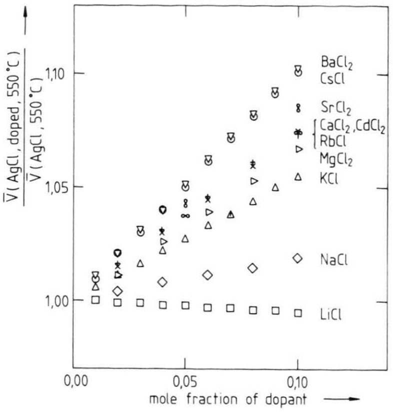
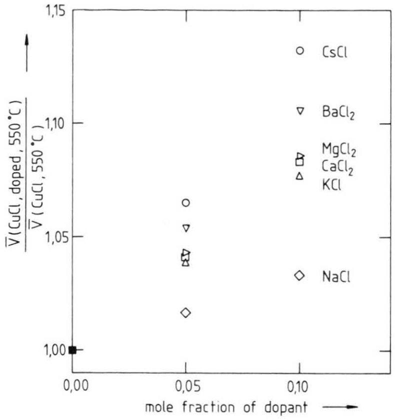


Fig. 3



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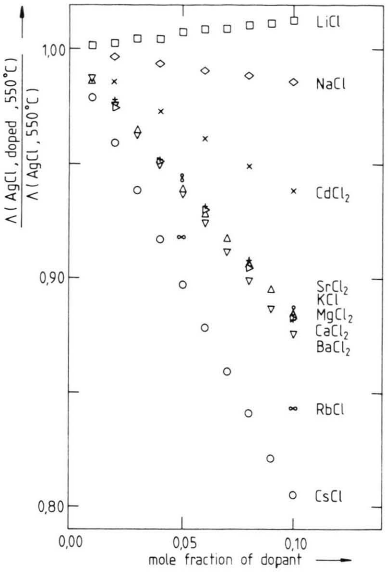


Fig. 5

Fig. 3. Relative molar volume of doped silver chloride vs. dopant concentration.

Fig. 4. Relative molar volume of doped copper chloride vs. dopant concentration.

Fig. 5. Relative molar conductance of doped silver chloride vs. dopant concentration.

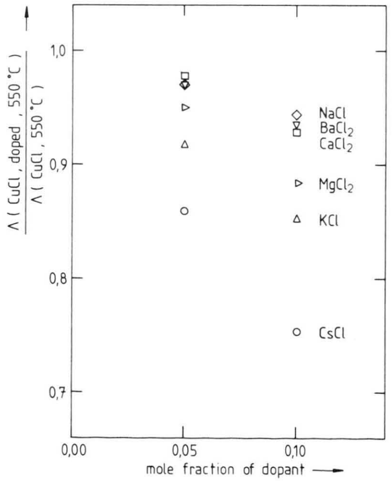
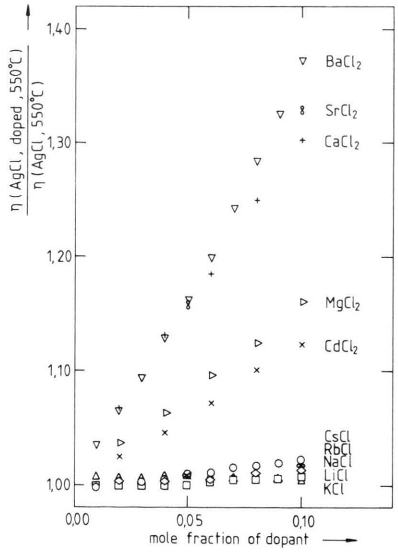


Fig. 6



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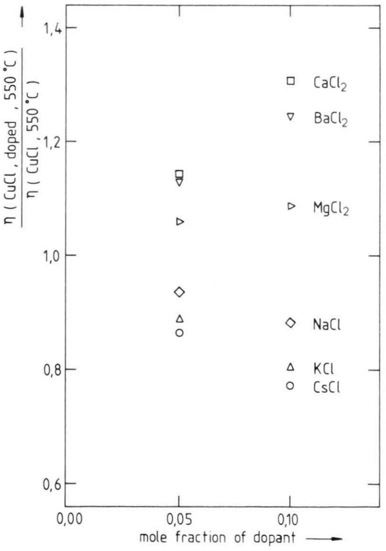

Fig. 8

Fig. 6. Relative molar conductance of doped copper chloride vs. dopant concentration.

Fig. 7. Relative viscosity of doped silver chloride vs. dopant concentration.

Fig. 8. Relative viscosity of doped copper chloride vs. dopant concentration.

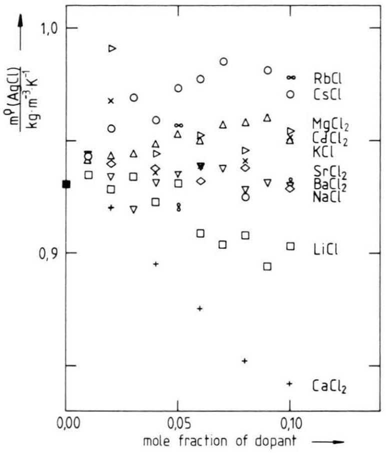

Fig. 9

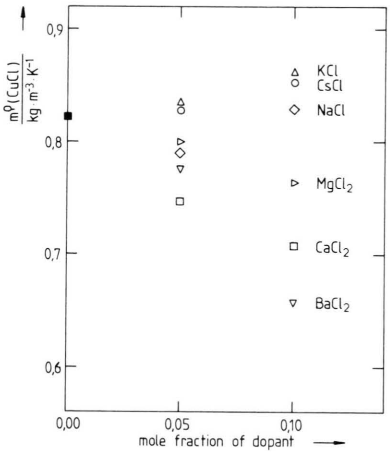

Fig. 10

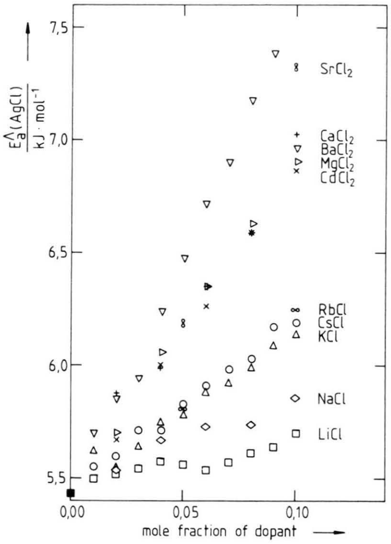

Fig. 11

Fig. 9. Temperature coefficient m^{ϱ} of doped silver chloride vs. dopant concentration.

Fig. 10. Temperature coefficient m^{ϱ} of doped copper chloride vs. dopant concentration.

Fig. 11. Formal activation energy E_{a}^{Λ} of doped silver chloride vs. dopant concentration.

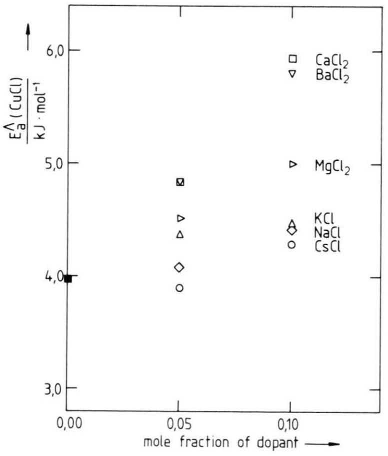

Fig. 12

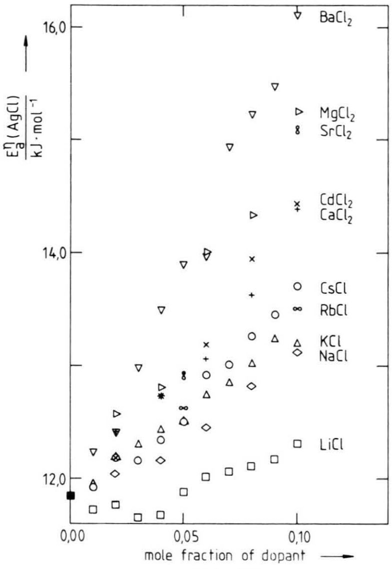

Fig. 13

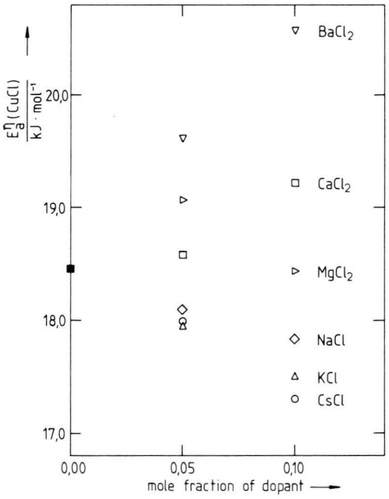

Fig. 14

Fig. 12. Formal activation energy E_a^{Λ} of doped copper chloride vs. dopant concentration.

Fig. 13. Formal activation Energy E_{a}^{η} of doped silver chloride vs. dopant concentration.

Fig. 14. Formal activation energy E_{a}^{η} of doped copper chloride vs. dopant concentration.

4. Discussion

4.1 Reliability

The measured values for pure silver chloride were compared with literature data in [1] and [2]. Comparison of the specific conductance of the 10 mol% KCl–AgCl and CsCl–AgCl mixtures reported in [2] with values recently published by Boßmann et al. [7] confirms the reliability of our experiments.

Since we calibrated with substances other than copper chloride, the measured transport coefficients for copper chloride can be compared with literature data. The value for the density of pure copper chloride at 823 K ($3.57 \cdot 10^3$ kg m^{-3}), which is presented here, is 2.2% higher than the recommended NSRDS data reference base value of Janz and McIntyre [8]. The specific conductance at 823 K (376 Ω^{-1} m^{-1}) is 6.0% higher than the recommended value [9], yet it is in excellent agreement with the value which Poignet and Barbier (377.7 Ω^{-1} m^{-1}) have recently obtained [10]. The viscosity at 823 K ($2.20 \cdot 10^{-3}$ kg m^{-1} s^{-1}) is 5.4% lower than the only other value found in the literature [11]. The reproducibility of the density, the electrolytic conductivity and the kinematic viscosity for the copper chloride systems was ± 0.2%, ± 0.5% and ± 0.9% respectively.

4.2 General Discussion

The cationic radii of the salts employed have been determined by X-ray diffraction (r_x^+) on the solid state – see for example [5]. The radii can also be estimated from the inter-nuclear distances obtained by neutron diffraction on the molten chlorides (r_n^+) – see for example [12] – assuming the chlorine ion radius to be 180 nm. As can be seen from Table 3, the values for r_x^+ and r_n^+ are in general very similar: however, in the case of the silver and copper ions, the neutron diffraction measurements lead to much smaller radii than X-ray diffraction. The radii given in Table 3 are for pure salts and should therefore be considered as being approximate values when applied to binary salt mixtures: consequently one is at liberty to choose the set of values (r_x^+ or r_n^+) to be used. In the present work it was found that the r_n^+ values gave a better fit to the experimental data and have therefore been used in the following discussion.

Salt	r_x^+	r_n^+
AgCl	126	80
CuCl	96	50
LiCl	57	–
NaCl	97	90
KCl	133	140
RbCl	147	140
CsCl	167	160
$MgCl_2$	66	–
$CaCl_2$	99	100
$SrCl_2$	112	110
$BaCl_2$	134	130
$CdCl_2$	97	–

Table 3. Ionic radii of the employed cations from X-ray spectroscopy r_x^+ and estimated from neutron scattering experiments r_n^+.

The molar volumes (Figs. 3 and 4) increase with increasing radius of the dopant cation. The lithium and sodium ions, whose radii equal roughly that of the silver ions, hardly change the molar volume, whereas the bigger caesium ions lead to a large increment in its value. The doubly charged cations increase the molar volume even more than expected from the larger molar volumes of the respective pure salts.

The molar conductances (Figs. 5 and 6) decrease with increasing radius of the dopant cations and remain practically unchanged when the dopant and solvent cations are of similar size. The viscosities (Figs. 7 and 8) remain unchanged or decrease when monovalent dopant cations are used, and increase when doping with divalent cations. The influence of doping on the molar conductivity and the viscosity observed in [1] is thus confirmed by the results presented here: the conductivity depends mainly on the radii of the dopant cations, while the viscosity depends mainly on their charge. These results are in full accordance with the observation of Morrison and Lind [13] that the coulomb potential in molten organic salts plays a decisive role in the viscosity of such systems. The strong correlation between the formal activation energies found in [1] – where the relationship $E_a^\eta / E_a^\Lambda = \text{constant}$, holds independently from the nature and concentration of the dopant – is valid for all the measured silver chloride systems (Table 4). The correlation is not so strong in the case of the copper chloride systems (Table 5).

It is further interesting to observe that, although the viscosity and the molar conductance are not correlated with one another, there is nevertheless a strong correlation between the formal activation energies themselves and also between the activation

Table 4. E_a^η / E_a^Λ for the silver chloride systems.

Conc. mole %	LiCl	NaCl	KCl	RbCl	CsCl	$MgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$	$CdCl_2$
0	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
1	2.1	–	2.1	–	2.1	–	–	–	2.1	–
2	2.1	2.2	2.2	–	2.2	2.2	2.1	–	2.1	2.1
3	2.1	–	2.2	–	2.1	–	–	–	2.2	–
4	2.1	2.1	2.2	–	2.2	2.1	2.1	–	2.2	2.1
5	2.1	–	2.2	2.2	2.1	–	–	2.1	2.1	–
6	2.2	2.2	2.2	–	2.2	2.2	2.1	–	2.1	2.1
7	2.2	–	2.2	–	2.2	–	–	–	2.2	–
8	2.1	2.2	2.2	–	2.2	2.2	2.1	–	2.1	2.1
9	2.1	–	2.2	–	2.2	–	–	–	2.1	–
10	2.1	2.2	2.2	2.2	2.2	2.2	2.0	2.1	2.3	2.1

Table 5. E_a^η / E_a^Λ for the copper chloride systems.

Conc. mole %	NaCl	KCl	CsCl	$MgCl_2$	$CaCl_2$	$BaCl_2$
0	5	5	5	5	5	5
5	4	4	5	4	4	4
10	4	4	4	4	3	4

energies and the viscosity (Figs. 7, 11, 13 and 8, 12, 14).

Finally, a change in the colour of molten silver chloride was noticed when it was doped. Pure silver chloride is an orange liquid on melting, its colour changing to red and finally black when its temperature is raised. At any given temperature the addition of a dopant changed the colour of the melt to a lighter red or even to yellow. Since the same concentration of different dopants led to different degrees of colour change, this cannot be a trivial dilution effect, but could be due to changes in the interionic interactions within molten silver chloride on doping. Work on UV-VIS spectroscopy of these melts is currently in progress.

Acknowledgements

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