

# Electrical conductivity, density, and viscosity of molten MgCl<sub>2</sub>—CaCl<sub>2</sub>—NaCl—KCl quaternary system

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Received 21 May 1990

The electrical conductivity, density, and viscosity of the molten MgCl<sub>2</sub>—CaCl<sub>2</sub>—NaCl—KCl quaternary system have been investigated over a temperature range of 100 K in the composition range of 6—18 mass % MgCl<sub>2</sub>. Very low temperature coefficients and smooth isotherms were obtained over the whole temperature and respectively composition range investigated. Frenkel equation was also verified, which proves that the acting forces upon the moving ions are mutually compensated in the mixtures. An optimum composition of the electrolyte for magnesium electro-winning was recommended.

Although the molten MgCl<sub>2</sub>—CaCl<sub>2</sub>—NaCl—KCl quaternary system is of special interest for magnesium electrolysis, there are no data in literature on the physicochemical properties of the system. Therefore, the present investigation supplies a new set of data on electrical conductivity, density, and viscosity as a function of MgCl<sub>2</sub> content within the composition range of practical interest. It is thus intended to provide some information on the nature of ionic interaction on mixing in order to establish the optimum composition of the electrolyte, as the above-mentioned parameters are directly responsible for the current efficiency of the electrolysis.

Thus, a high conductivity of the electrolyte allows for the process to take place at higher current densities and larger interpolar distances which reduce the occurrence of the secondary reactions among the electrolysis products. Controlling the hydrodynamic processes in the melt, the density and viscosity, when kept within convenient limits, ensure a proper separation of the liquid metal-molten electrolyte phases, as well as more efficient hindrance of the mass transfer from the cathode to the anode compartment, avoiding thus the recombination of the electrolysis products.

Even if the MgCl<sub>2</sub>—CaCl<sub>2</sub>—NaCl—KCl system has not yet been studied, the literature reports some data on electrical conductivity, density, and viscosity of the ternary and binary mixtures of MgCl<sub>2</sub> or CaCl<sub>2</sub> with sodium and potassium chlorides [1—5], which offer interesting information as a starting point for the present investigation. Due to the different degree of covalency characterizing

$\text{MgCl}_2$  and  $\text{CaCl}_2$  melts [6—10], as well as to the typical ionic character of the  $\text{NaCl}$  and  $\text{KCl}$  melts, the mixing of these components should be accompanied by important structural changes. It has been noted that in the  $\text{MgCl}_2$ — $\text{CaCl}_2$  binary mixture [1, 2] the excess values are negative for the molar volume and positive for the electrical conductivity over the whole composition range, both facts indicating an increase in the ionic character on mixing. Certainly, the addition of  $\text{CaCl}_2$  with a more pronounced ionic character to  $\text{MgCl}_2$  leads to a destruction of the remanent structure of the latter, accompanied by a more compact structure in the mixture and an increase of the number of the current carriers.

Contrary to the above-mentioned behaviour, the excess volumes for the  $\text{MgCl}_2$ — $(\text{Na}, \text{K})\text{Cl}$  and/or  $\text{CaCl}_2$ — $(\text{Na}, \text{K})\text{Cl}$  binary systems [2, 3] are positive, while a pronounced minimum was reported on conductivity isotherms at around 33 mole % alkaline-earth chloride [1, 3]. These trends are usually explained in terms of formation of the much larger  $\text{Mg}(\text{Ca})\text{Cl}_4^{2-}$  complex ion which is responsible for the looser packing of the melt, as well as for the decrease in the number of the effective current carriers and their velocity under the applied electric field.

Regarding the viscosity, according to literature data [4, 5], it is less sensitive to the degree of the covalency of the melt because the viscous flow implies simultaneous displacement of all constituent ions in the melt (due to the electroneutrality reasons). Thus, the experimental viscosity data indicate a linear dependence on the content for the binary mixtures mentioned above, regardless the constituents involved. Most probably the relaxation time of the complex  $\text{MgCl}_4^{2-}$  and/or  $\text{CaCl}_4^{2-}$  is so much shorter that it is not manifested in the viscous flow.

In conclusion, it is obvious that  $\text{CaCl}_2$  has to be one of the components of the bath for  $\text{MgCl}_2$  electrolysis and that the content of these two components must be kept below 33 mole % in order to avoid the specific interactions on mixing which could affect strongly the melt properties.

Therefore, in the present study we have maintained a constant  $\text{CaCl}_2$  content, established as optimum at about 7 mole %, while  $\text{MgCl}_2$  content has been varied below the 20 mole % limit.

## Experimental

The mixtures were prepared by using commercially available  $\text{NaCl}$ ,  $\text{KCl}$ , and  $\text{CaCl}_2$  reagents of 99 % or better purity, which after recrystallization from distilled water were dried at least for 48 h at 423—473 K. Special care was taken in melting them by a technique previously established in our laboratory [10], which ensured the removal of any trace of water and hydrolysis products.

Anhydrous  $\text{MgCl}_2$  was used, either of commercially available grade or prepared in our laboratory by dehydrating the double salt  $\text{NH}_4\text{Cl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , according to the recommended method [11]. All mixtures were obtained by remelting the individual components in the required amounts, under the same precautions as mentioned above [10]. Important  $\text{MgO}$  residues were obtained whenever using commercially available  $\text{MgCl}_2$ . They were always removed by filtering of the melt.

The content of  $\text{MgCl}_2$  was determined in all mixtures before and after each run, by titration in the presence of complexon and eritron T [12]. No variation in the initial  $\text{MgCl}_2$  content has been noticed. In order to ensure the samples anhydrous, all single salts as well as all obtained mixtures after freezing were kept under liquid  $\text{CCl}_4$ .

The electrical conductivity was measured with a precision of  $\pm 0.1\%$  by means of an autobalance precision Wayne Kerr B 331 bridge at a fixed frequency of 1592 Hz (internal operating frequency of the bridge oscillator). U-shaped silica cells [3, 13] with cell constants of  $500$ — $700\text{ cm}^{-1}$  were employed.

The viscosity was determined with a precision of  $\pm 3\%$  by oscillating sphere method and density with a precision of  $\pm 0.5\%$  by hydrostatic method, both previously set up in our laboratory [5, 14].

All experiments were performed in closed systems under carefully dried and purified argon, in order to prevent any contact with the atmosphere.

The temperature was measured with a Pt—Pt10Rh thermocouple and kept constant within  $\pm 0.5\text{ K}$  during measurements.

## Results and discussion

The experiments were made within the composition range of 6—16 mass %  $\text{MgCl}_2$  for the eight compositions of the quaternary mixtures,  $\text{MgCl}_2$ — $\text{CaCl}_2$ — $\text{NaCl}$ — $\text{KCl}$ , as summarized in Table 1. Of the eight mixtures in Table 1, the last two were prepared by using anhydrous  $\text{MgCl}_2$  obtained in our laboratory. Their intermediary  $\text{MgCl}_2$  content was chosen so that it allowed the comparison with the experimental data obtained with the other mixtures.

The electrical conductivity, the viscosity, and the density were measured over a temperature range of about 100 K and for each studied mixture a number of 8—12 experimental points was recorded. They were fitted to the polynomial or linear equations as given in Tables 2—4, where the numerical values of the constants  $a$ ,  $b$ , and  $c$  as determined by the least-squares method are listed together with the validity temperature range. According to these data, the temperature coefficient for each of the three measured properties is less than 1 % over the temperature range of 10 K. This finding is of a practical interest because it proves a convenient steadiness of the electrolysis parameters even without any strict temperature control. On the other hand, a satisfactory agreement was observed (the differences did not exceed  $\pm 1\%$ ) between the values obtained for

Table 1

The composition of the studied quaternary mixture  $\text{MgCl}_2\text{—CaCl}_2\text{—NaCl—KCl}$ 

Mixture	$w_i/\%$			
	$\text{MgCl}_2$	$\text{CaCl}_2$	$\text{NaCl}$	$\text{KCl}$
1	6.9	5.3	43.9	43.9
2	7.7	5.3	43.5	43.5
3	8.3	5.3	43.2	43.2
4	12.4	5.0	41.3	41.3
5	13.8	5.0	40.6	40.6
6	16.4	5.0	39.3	39.3
7	6.0	5.0	44.5	44.5
8	12.0	5.0	41.5	41.5

Table 2

Constants of the equation for temperature dependence of the electrical conductivity ( $\kappa/(\text{S m}^{-1})$ )

$$\kappa = -a + bT - cT^2$$

Mixture	$\frac{a \cdot 10^2}{\text{S m}^{-1}}$	$\frac{b \cdot 10^6}{\text{S m}^{-1} \text{K}^{-1}}$	$\frac{c \cdot 10^8}{\text{S m}^{-1} \text{K}^{-2}}$	$T/\text{K}$
1	2.2814	0.62759	1.7917	
2	4.3012	1.01574	3.6537	
3	3.7796	0.89943	3.0847	
4	6.9966	1.56304	6.5186	
5	3.6799	0.91085	3.3446	930—1030
6	5.6209	1.27600	5.0805	
7	5.7949	1.31036	5.1044	
8	3.1183	0.78358	2.6251	

Table 3

Constants of the equation for temperature dependence of viscosity ( $\eta/(\text{mPa s})$ )

$$\eta = a - bT + cT^2$$

Mixture	$\frac{a \cdot 10^{-1}}{\text{mPa s}}$	$\frac{b \cdot 10^2}{\text{mPa s K}^{-1}}$	$\frac{c \cdot 10^5}{\text{mPa s K}^{-2}}$	$T/\text{K}$
1	1.6506	2.6293	1.115	930—1000
2	3.3561	6.1726	2.963	920—1020
4	4.3927	8.4230	4.194	920—990
5	4.5700	8.8083	4.397	930—1000

Table 4

Constants of the equation for temperature dependence of density ( $\rho/\text{g cm}^{-3}$ )

$$\rho = a - bT$$

Mixture	$\frac{a}{\text{g cm}^{-3}}$	$\frac{b \cdot 10^4}{\text{g cm}^{-3} \text{ K}^{-1}}$	$T/\text{K}$
1	2.1122	5.72	920—1020
2	2.1119	5.67	930—1000
4	2.1191	5.65	920—1010
5	2.1380	5.78	920—1020

all eight mixtures, no matter what was the origin of the employed  $\text{MgCl}_2$ . Since these mixtures have not been investigated so far, a comparison with literature data was possible only for pure components and some of the binary systems. Details on this are given in our previous papers [3, 5, 10, 13, 14].

Regarding the influence of  $\text{MgCl}_2$  content in the mixture, as illustrated by the isotherms in Fig. 1, there is a smooth dependence on the content.

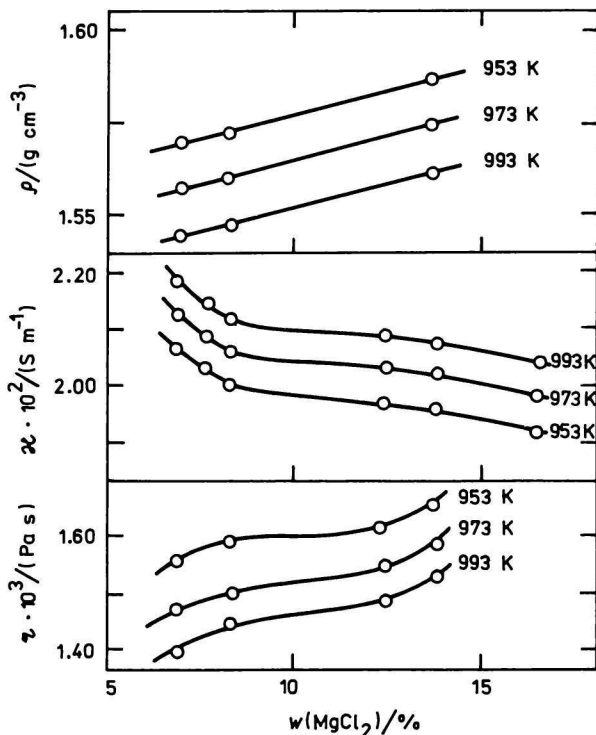


Fig. 1.  $\nu$ ,  $\eta$ , and  $\rho$  vs.  $\text{MgCl}_2$  content in the molten  $\text{MgCl}_2\text{--CaCl}_2\text{--NaCl--KCl}$  system.

The variations are more marked in the composition range of 6–8 mass %  $\text{MgCl}_2$  where the decrease in conductivity and the increase in viscosity are both of about 3 %; then, for an increase of  $\text{MgCl}_2$  content up to 18 mass %, both variations reach only 4 %. The density is less dependent on  $\text{MgCl}_2$  content as the observed increase does not exceed 1.1 % over the whole  $\text{MgCl}_2$  composition range. According to the data in Fig. 1, it is obvious that within the mentioned composition range, the mixing takes place without significant structural changes. Even more, we have established that Frenkel equation

$$\lambda^n \eta = C \quad (1)$$

which relates the electric forces to the shear viscosity  $\eta$  in the case of a sphere moving in a continuum [15], is very well verified by the experimental data. In eqn (1)  $\lambda$  stands for the molar conductivity ( $\lambda = \kappa V_m$ , where  $V_m$  is the molar volume) and  $n$  has the meaning of a proportionality factor between the activation energies of the two transport properties involved,  $n = E_\eta/E_\lambda$ , a statement which requires the validity of the linear relationship

$$n \log \lambda + \log \eta = C \quad (2)$$

The numerical values of  $n$  and constant  $C$  (mediated over the temperature range 920–1020 K), as calculated by the least-squares method from the slope and the intercept of  $\log \lambda$  vs.  $\log \eta$  lines, respectively are summarized in Table 5 for some representative mixtures.

Table 5

Coefficients of Frenkel equation for the  $\text{MgCl}_2$ – $\text{CaCl}_2$ – $\text{NaCl}$ – $\text{KCl}$  system

Mixture	$n$	$C$	$C_{\text{mean}}$
1	1.832	3.804	
2	1.918	3.850	
4	1.443	3.446	
5	1.556	3.746	$3.71 \pm 0.13$

Examination of the data in Table 5 shows that the factor  $n$  is getting closer to the unit with increasing  $\text{MgCl}_2$  content. As usually accepted [10], this trend suggests that the rate-determining entities in conductive and viscous flow become somewhat similar. Since the viscous flow involves the translation of ions of both signs, it follows that the anion is also involved in the conduction mechanism, probably due to an enhancement of interionic association promoted by increasing of  $\text{MgCl}_2$  addition.

The applicability of eqn (1) at 973 K is illustrated in Fig. 2 for the whole studied range of  $\text{MgCl}_2$  content. We consider this behaviour of some interest for Mg electrowinning. If the forces which act upon the moving ions compensate each other, then the energy efficiency of the electrolysis should not be affected by the diminishing of  $\text{MgCl}_2$  content in the electrolyte over a relatively large composition range of 6–18 mass %.

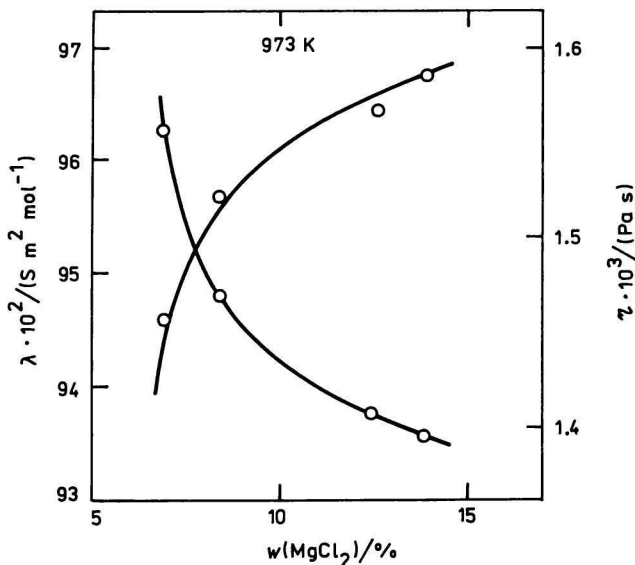


Fig. 2. Validity of Frenkel equation in the molten  $\text{MgCl}_2$ — $\text{CaCl}_2$ — $\text{NaCl}$ — $\text{KCl}$  system. — Calculated curve, O experimental data.

In conclusion, on the basis of all the above discussed data one can recommend the following optimum composition of the electrolyte

(16–18) mass %  $\text{MgCl}_2$ —5 mass %  $\text{CaCl}_2$ —(38.5–39.5) mass %  
 $\text{NaCl}$ —(38.5–39.5) mass %  $\text{KCl}$

where the content of the electrochemically active component is not to decrease below 6 mass %  $\text{MgCl}_2$  during electrolysis.

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