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Hydrolysis of $MgCl_2$-Containing Melts

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The hydrolysis of pure liquid $MgCl_2$ and of the liquid NaCl–$MgCl_2$ ($x_{MgCl_2} \approx 0.62$) mixture have been investigated at 730 and 675 °C. An experimental set-up and procedure has been developed for this purpose. The amount of MgOHCl in the melt was calculated from oxide analysis results and thermodynamic data. The equilibrium constant for the reaction $MgCl_2(l) + H_2O(g) = MgOHCl(l) + HCl(g)$, $K' = x_{MgOHCl}p_{HCl}/a_{MgCl_2}p_{H_2O}$, was determined by linear regression. It was found that in pure $MgCl_2$ $K' = 0.67 \pm 0.07$, while in the NaCl–$MgCl_2$ mixture $K' = 0.35 \pm 0.04$. K' was constant in the temperature range $675 < T/°C < 730$. The results are in good agreement with comparable data in the literature.

The specific energy consumption, N, for electrolytic magnesium production may be calculated from eqn. (1)

$$N = V/0.454\eta \quad (1)$$

where N/kWh (kg Mg)$^{-1}$ is the specific energy, V/V the electrolyser voltage, and η the current efficiency. Today the energy consumption is about 13–14 kWh (kg Mg)$^{-1}$, a reduction of more than 6 kWh since the early days of the art.[1] However, the thermodynamic energy required is only about 6.8 kWh (kg Mg)$^{-1}$ at 700 °C,[2] and it may therefore still be possible to cut the energy consumption considerably.

One way to increase the energy efficiency is to obtain better control over the oxide and hydroxide species dissolved in the bath. Some of the MgO is introduced with the $MgCl_2$ feed, but in some cases the MgO is formed in the electrolyte by the reaction between moisture in the atmosphere above the electrolyte and $MgCl_2$ and Mg according to the reactions:[3]

$$Mg(l) + H_2O(g) = MgO(s) + H_2(g) \quad (2)$$

$$MgCl_2(l) + H_2O(g) = MgO(s) + 2HCl(g) \quad (3)$$

$$MgCl_2(l) + H_2O(g) = MgOHCl(l) + HCl(g) \quad (4)$$

Oxide impurities primarily affect the interfacial tensions between the electrolyte, the metal and the cathode. These impurities may deposit on the cathode surface and on the produced metal, leading to passivation and less favourable wetting between cathode, liquid magnesium and electrolyte.[4] MgO absorbed on Mg droplets in the electrolyte prolongs the time they are dispersed by hindering their coalescence.[3] Furthermore, decreased current efficiency may come as a result of water dissolved in the bath being electrolysed to form CO and H_2 at the anode and cathode, respectively.[3] Besides, a number of impurities (Fe and Ti in particular) adversely affect the electrolysis process only in the presence of magnesium oxide and hydroxychloride.[1]

Water and MgOHCl in chloride melts have been studied electrochemically by voltammetry.[5–7] It was found that water or hydroxide, as produced by reaction (4), was reduced to H_2(g) and MgO(s) at cathodic polarisation, forming a passivating film of MgO on the electrode surface. The MgO film could be reduced and the deposition of Mg restarted by a strong cathodic polarisation.[5] Two cathodic current waves have been found to originate from water and MgOHCl in chloride melts, but anodic currents have not been observed for these species.[6,7]

To our knowledge only one group has previously investigated the formation of MgOHCl in $MgCl_2$-containing melts quantitatively. Vilnyansky and Savinkova[8,9] studied the formation of MgOHCl in the solid phase and found that MgOHCl was formed in solid solution with $MgCl_2$. According to their results, pure MgOHCl(s) cannot coexist with pure HCl(g) above 300 °C. A series of papers on magnesium hydroxychloride were subsequently published by the same group. Studies of MgOHCl in molten carnallite and other $MgCl_2$-containing melts, including a visual study of carnallite containing 2–3% water[10] and quantitative studies of the hydrolysis reaction (4) in molten carnallite,[11] in other KCl–$MgCl_2$ melts,[12] and in melts of the system $MgCl_2$–NaCl–KCl[13] gave interesting information on the hydrol-

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ysis reactions. They also studied the effect of hydrolysis on the activity of $MgCl_2$ in NaCl–KCl–$CaCl_2$–$MgCl_2$ melts[14] and the kinetics of the decomposition of MgOHCl in KCl–$MgCl_2$ melts.[15] One of their conclusions is that $MgCl_2$ exhibit less negative deviations from ideality in hydrolysed melts than in water-free melts. In melts with high $MgCl_2$-contents positive deviations from ideality were observed.[13,14]

It is clear from the above discussion that oxides, water, and hydroxide species dissolved in the electrolyte play an important role during electrolytic magnesium production. In this context, however, many questions about their formation and behaviour remain unanswered. The solubility of MgO in $MgCl_2$–NaCl[16] and $MgCl_2$–NaCl–NaF[17] melts has recently been determined, and an extensive study of the oxide solubility in mixed chloride–fluoride melts containing $MgCl_2$ will be discussed in a forthcoming paper.[18] The present work is an experimental investigation of the equilibria established during hydrolysis of pure $MgCl_2$ and of a NaCl–$MgCl_2$ mixture. Reaction (4) has been studied in pure $MgCl_2$ at 730 °C and in a NaCl–$MgCl_2$ ($x_{MgCl_2} \approx 0.62$) at 730 and 675 °C, and thermodynamic equilibrium constants were obtained.

Principles

The hydrolysis of pure $MgCl_2(l)$ and a $MgCl_2$–NaCl(l) ($x_{MgCl_2} \approx 0.62$) mixture has been studied as described in the next section. In short, the experimental method implies an equilibration of a melt with a gas phase having known p_{H_2O} and p_{HCl}. The components of the system are $MgCl_2(l)$, NaCl(l), HCl(g) and $H_2O(g)$. The hydrolysis products considered are MgOHCl and MgO, both dissolved in the melt. At a given temperature the system has two and three degrees of freedom in the absence and presence of NaCl, respectively. The accessible variables are the partial pressures of the gaseous species and the magnesium chloride activity. If MgO(s) is present at equilibrium, one degree of freedom is lost. As a consequence it is impossible to perform the present investigation in pure $MgCl_2$ in the presence of MgO(s). Furthermore, the kinetics of precipitation and dissolution of MgO(s) are not known. Therefore, the gas phase composition was such that the formation of solid magnesium oxide was avoided. Accordingly, the equilibria considered are described by eqn. (4) and the equilibrium

$$MgCl_2(l) + H_2O(g) = MgO(l) + 2HCl(g) \tag{5}$$

The equilibrium constants for these two reactions are given as

$$K_4 = \frac{a_{MgOHCl}\, p_{HCl}}{a_{MgCl_2}\, p_{H_2O}}$$

and

$$K_5 = \frac{a_{MgO}\, p^2_{HCl}}{a_{MgCl_2}\, p_{H_2O}}$$

respectively. Equilibrium (5) is related to reaction (3) through reaction (6):

$$MgO(s) = MgO(l) \tag{6}$$

In order to define properly K_4 and K_5, standard states must be specified. Introducing MgO(s) as standard state for MgO(l) implies that $a_{MgO} = 1$ for a melt saturated with MgO. The solubility of MgO in $MgCl_2$–NaCl melts has been thoroughly studied by Boghosian *et al.*,[16] and can be used to calculate the activity of MgO in sub saturated melts. At 730 °C, the saturation mole fraction of MgO, x^{sat}_{MgO}, in the region $0.33 < x_{MgCl_2} < 1$ is well described by the equation:[16]

$$x^{sat}_{MgO} = -1.55 \times 10^{-4} + 4.00 \times 10^{-3} a_{MgCl_2} \tag{7}$$

If the Raoultian activity coefficient for MgO(l) is a constant up to the solubility limit for any melt composition of the NaCl–$MgCl_2$ binary, x°_{MgO} and a^{R}_{MgO} are related through the equation:

$$x^{\circ}_{MgO} = a^{R}_{MgO}(-1.55 \times 10^{-4} + 4.00 \times 10^{-3} a_{MgCl_2}) \tag{8}$$

Since we later in this paper will discuss the dissolved MgO and MgOHCl also in complexed forms, we have used x°_{i} to symbolise the total concentration of these species. We also use the superscript R and H for the Raoultian and Henryan activities of these compounds, respectively, since both definitions will be used.

The Raoultian $MgCl_2$ activity coefficient in NaCl–$MgCl_2$ melts, γ_{MgCl_2}, using pure $MgCl_2(l)$ as standard state, has been reported by several authors.[19–24] The four most recent of these investigations[21–24] are all very well described by the equation below given by Karakaya and Thompson[24]

$$\begin{aligned} RT \ln \gamma_{MgCl_2} &= (-16.78x^2_{NaCl} - 5.680x^3_{NaCl} - 23.19x^4_{NaCl} \times 10^3 \\ &\quad - T(-2.405x^2_{NaCl} - 2.65x^3_{NaCl}) \end{aligned} \tag{9}$$

This equation has been used to calculate a_{MgCl_2} in the present study.

In order to define the activity of MgOHCl, a standard state must be chosen. Unfortunately, pure magnesium hydroxychloride is not stable at the temperatures of this investigation, neither in the solid nor in the liquid state. A Raoultian equilibrium constant can therefore, not be obtained without performing hydrolysis experiments at lower temperatures with MgOHCl(s) present. However, according to thermodynamic data it is not possible at 1 bar total pressure to have a melt in equilibrium with MgOHCl(s) without precipitating MgO(s) simultaneously.[2,25] As the system will have only one degree of freedom when a four-phase equilibrium is established, it cannot be investigated by the method utilised in the present study.

Since it is impossible experimentally to obtain a_{MgOHCl} using a Raoultian standard state, we will define the activity of MgOHCl using a Henryan standard state through the equation

$$a^{H}_{MgOHCl} = x^{\circ}_{MgOHCl}\gamma^{H}_{MgOHCl} \qquad (10)$$

It seems reasonable to assume that MgOHCl obeys Henry's law since the concentration of MgOHCl is very low in the present melts.

Experimental

The chemicals used for the hydrolysis experiments were $MgCl_2 \cdot 6H_2O$ (Merck 99%), NaCl (Merck 99.5%), HCl (Messer Griesheim 99.995%), and Ar (Hydrogas, 99.998%). HCl (Messer Griesheim 99.8%) and N_2 (Hydrogas, 99.998%) were used for the dehydration of $MgCl_2 \cdot 6H_2O$. This dehydration was done by heating $MgCl_2 \cdot 6H_2O$ from room temperature to 450 °C under a stream of HCl. The temperature was lowered to 100 °C, and the dehydrated chloride was flushed with N_2 for at least 24 h to remove remaining HCl. The rate of heating varied from 3 to 25 °C h^{-1}, depending on temperature range and HCl flow rate. The dehydrated $MgCl_2$ was destilled under vacuum ($\approx 10^{-8}$ bar) at about 1000 °C, and stored in sealed quartz ampoules. NaCl was dried under vacuum at 400 °C for 3–4 h, and recrystallised twice from the molten state in a platinum crucible under N_2 atmosphere.

The experimental cell used for the hydrolysis experiments is shown in Fig. 1. The cell was made of quartz, and was mounted in a water cooled tube furnace by means of a brass flange glued to the top. A special Teflon arrangement placed above the flange simultaneously constituted the cell lid and prevented contact between the corrosive gas mixture and the brass flange. A Viton O-ring gasket was used between the lid and Teflon plates to obtain a gas-tight arrangement. A sketch of the cell lid is shown in Fig. 2. A brass plate was placed on top of the Teflon cell lid in order to obtain physical strength. The radiation shields inside the cell were made of sintered alumina and had holes to accommodate the thermocouple, the gas

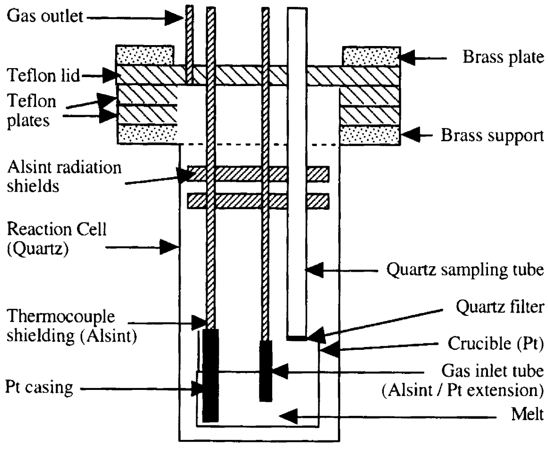

Fig. 1. The experimental cell used for the hydrolysis experiments.

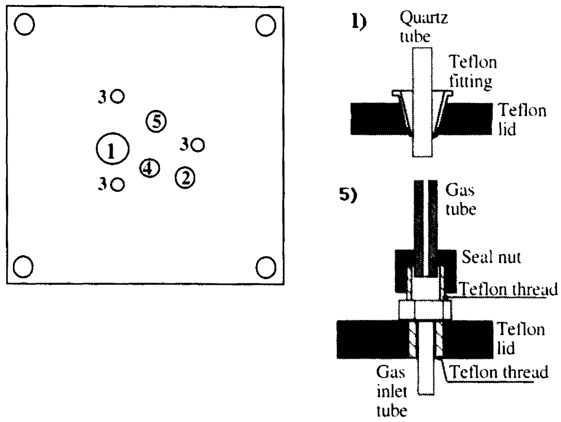

Fig. 2. A sketch of the cell lid seen from above. The cross-section through hole 1 shows the conical arrangement used to guide the sample extraction tube through the lid. The same arrangement was also used for the thermocouple shielding (hole 4) and the radiation shield rods (holes 3). The connection between the gas line outside and the gas tube inside the reaction cell is shown in detail as a cross-section through hole 5. The same arrangement, but without any tube inside the cell, was applied for the gas outlet (hole 2).

inlet tube, the sample extraction tube, and the radiation shield holders. They were held above the crucible by three alumina rods (diameter 3 mm) fastened in the cell lid in the same way as the sample extraction tube (Fig. 2). The holes in the radiation shields had the same positions relative to the centre as the holes in the cell lid. The thermocouple was protected by an alumina tube closed in the lower end. This tube was guided through the cell lid by a conical arrangement preventing direct contact between the atmospheres inside and outside the cell (Fig. 2). The lower end of the thermocouple protection was shielded from contact with the melt by a platinum casing. The gas inlet tube (sintered alumina) extended with a Pt-tube at the lower end. The upper end of the gas inlet tube was attached to a Teflon fitting, which in turn was screwed through the cell lid. The gas line was coupled to the other end of this fitting. See Fig. 2 for details. The platinum part of the gas tube was immersed in the melt, and the gas stream provided the stirring. The sample extraction tube (quartz) had a quartz sinter of porosity 3 (pore size 15–40 μm) at the end to be immersed in the melt just before sampling. This pore size was reported to be suitable for extracting samples from $MgCl_2$–NaCl melts.[26] In some of the experiments the quartz sinter was replaced by a quartz capillary (1 × 3 mm ϕ, 50 mm long) mounted inside the tube. A syringe was attached to the other end of the sample extraction tube through a plastic tube protected from contact with the corrosive gas by a Teflon valve.

Experimental procedure. The salts were crushed and transferred to the crucible inside a glovebox. The experimental cell containing the crucible was closed and positioned inside the furnace, and the salts were slowly heated to 830 °C under constant HCl flow. After 3 h the temperature was lowered to the experimental temperature. The melt was bubbled with a gas mixture consisting of Ar, H_2O and HCl in pre-set ratios. When equilibrium was established in the system a melt sample was sucked into the sample extraction tube, quenched in liquid N_2, and immediately transferred to a glove box. The sample was then prepared and analysed for total oxygen content, n_O^{tot} (carbothermal reduction analysis at about 2100 °C), and for O^{2-} base equivalents, n_O^{bas} (acid consumption method). In the experiments where the system contained NaCl, the samples were also analysed for Na^+ and Mg^{2+} by ICP.

The gas mixture composition was made up by controlling the flow rates of two separate gas streams, dry HCl and humid Ar, independently. The argon stream was humidified by passing it through a bubble flask filled with water saturated with NaCl. This water solution was kept at about 30 °C in a thermostatted water reservoir. The water was saturated with NaCl in order to lower its vapour pressure. The gas tubes between the bubble flask and the experimental cell were heated with a flexible resistance wire in order to prevent condensation.

In the two first experiments reported, the gas streams were measured using ball flow meters with maximum flow capacities of about 100 ml min^{-1} at room temperature and 1 atm. Needle valves mounted at the gas inlets of the flow meters were used to control the gas flow rates. For the last four experiments the Ar and HCl flow rates were measured and controlled independently by two Bronkhorst Hi-Tec F-201C-FA electronic mass flow controllers with maximum flow capacities of 250 and 100 ml min^{-1} for HCl and Ar, respectively, measured at 0 °C and 1 bar. The flow controllers were operated by a four-channel Bronkhorst Hi-Tec E-5500 power supply.

The ball flow meters and the electronic mass flow controllers were calibrated using a soap film flowmeter (Ar flow controller) and by dissolving HCl in a NaOH solution and subsequent titration with 0.1 M HCl (HCl flow controller). The water content of the humidified Ar stream was calibrated after each experiment by passing the stream through a tube filled with P_2O_5, and measuring the weight change as function of time.

The oxide analysis techniques used were carbothermal reduction using a Leco TC-436 oxygen and nitrogen determinator and acid consumption method (iodometric titration). During the carbothermal reduction analysis technique the sample is heated together with graphite powder to a temperature high enough for all oxide to react with the graphite. The CO(g) thus formed is oxidised to CO_2(g) and detected by IR absorption. See Vindstad[27] or Mediaas *et al.*[17,18] for a more thorough description of the carbothermal reduction technique.

Data treatment

The total amount of oxygen and the amount of basic oxide equivalents in a melt sample are given by eqns. (11) and (12), respectively:

$$x_O^{tot} = x_{MgO}^{\circ} + x_{MgOHCl}^{\circ} \tag{11}$$

$$x_O^{bas} = x_{MgO}^{\circ} + \tfrac{1}{2}x_{MgOHCl}^{\circ} \tag{12}$$

The total mole fraction of oxygen in the melt, x_O^{tot}, can be calculated from the carbothermal reduction analysis results, n_O^{tot}, using eqn. (13)

$$x_O^{tot} = n_O^{tot}\frac{x_{NaCl}M_{NaCl} + x_{MgCl_2}M_{MgCl_2}}{16 \times 10^6} \tag{13}$$

where n_O^{tot} is in micrograms per gram sample (ppm O), and x_i and M_i are the mole fraction and molar weight of component i, respectively. The mole fraction of basic oxide equivalents, x_O^{bas}, is calculated from the acid consumption analysis results, n_O^{bas}, in a similar way.

By combining eqns. (11) and (12), the content of both MgO and MgOHCl in the melt could be determined experimentally. It was, however, concluded that due to decomposition of MgOHCl during sample extraction, only the carbothermal reduction analysis results could be trusted.[27] The MgO content has therefore been calculated from thermodynamic data[2] and experimentally determined MgO solubilities in NaCl–$MgCl_2$ melts[16] using the equilibrium constant for reaction (5) and eqns. (8) and (9). In Table 1 thermodynamic data from four different thermochemical tables are given at 727 °C together with the corresponding value of K_3. Reasonable agreement is observed. We have chosen data from Ref. 2, since these data have been carefully evaluated prior to tabulation.

The mole fraction of MgOHCl has been obtained from x_O^{tot} and x_{MgO}° by a simple subtraction:

$$x_{MgOHCl}^{\circ} = x_O^{tot} - x_{MgO}^{\circ} \tag{14}$$

Results

The results from the hydrolysis experiments are presented in Figs. 3 and 4. The quasi-equilibrium constant for eqn. (4), $K_4' = x_{MgOHCl}^{\circ}p_{HCl}/a_{MgCl_2}p_{H_2O}$, can be determined from the plots shown in these figures. In Fig. 3 x_{MgOHCl}° is plotted versus p_{H_2O}/p_{HCl} for pure $MgCl_2$. The equilibrium constant for reaction (4) in pure $MgCl_2$ at 730 °C was calculated using linear regression, and $K_4' = 0.67 \pm 0.07$ is given by the slope of the line. The corresponding results from experiments in the liquid NaCl–$MgCl_2$ ($x_{MgCl_2} \approx 0.62$, $a_{MgCl_2} \approx 0.45$) mixture at

Table 1. Thermodynamic data for reaction (3) at 727 °C.

ΔH_3°/ kJ mol^{-1}	ΔS_3°/ J (K mol)$^{-1}$	ΔG_3°/ kJ mol^{-1}	K_3°	Ref.
47.4	66.7	−19.3	10	2
47.4	66.5	−19.1	9.9	25
52.7	69.2	−16.5	7.3	28
52.1	68.9	−16.8	7.5	29

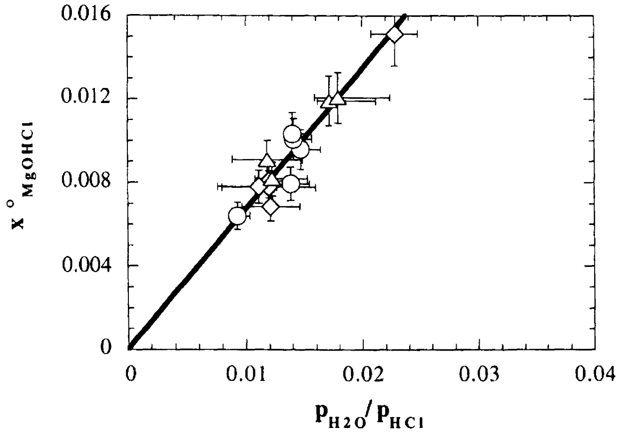

Fig. 3. x°_{MgOHCl} in pure $MgCl_2$ plotted versus p_{H_2O}/p_{HCl} at 730 °C and 1 bar total pressure ($p_{H_2O}+p_{HCl}+p_{Ar}$). Different symbols indicate different experimental runs. 10% uncertainty in n_0^{tot} is indicated in the figure as vertical error bars. Regression line indicates $K_4'=0.67\pm0.07$.

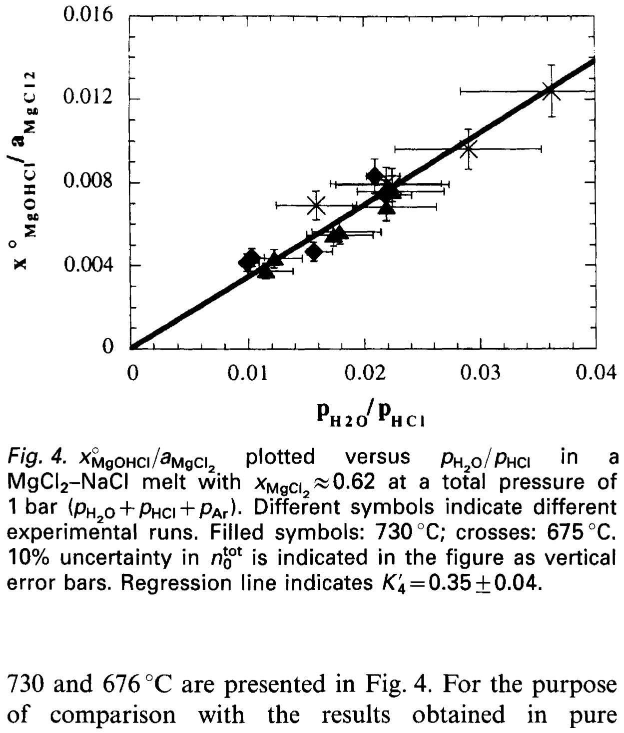

Fig. 4. $x^{\circ}_{MgOHCl}/a_{MgCl_2}$ plotted versus p_{H_2O}/p_{HCl} in a $MgCl_2$–NaCl melt with $x_{MgCl_2}\approx0.62$ at a total pressure of 1 bar ($p_{H_2O}+p_{HCl}+p_{Ar}$). Different symbols indicate different experimental runs. Filled symbols: 730 °C; crosses: 675 °C. 10% uncertainty in n_0^{tot} is indicated in the figure as vertical error bars. Regression line indicates $K_4'=0.35\pm0.04$.

730 and 676 °C are presented in Fig. 4. For the purpose of comparison with the results obtained in pure $MgCl_2(1)$, x°_{MgOHCl} determined in the mixture has been divided by a_{MgCl_2}. Linear regression gives $K_4'=0.35\pm0.04$. An effect of temperature on K_4' was not observed in the temperature range $675<T/°C<730$.

All the experimental results are presented in Table 2.

The equilibrium constants obtained in the present work are plotted together with the corresponding data reported by Savinkova and Lelekova[13] in Fig. 5. For the latter results a_{MgCl_2} has been calculated from at x_{MgCl_2} values given in their paper using eqn. (9) for the activity coefficient of $MgCl_2$.[24] The agreement between the two sets of data is satisfactory. Uncertainties in the data of Savinkova and Lelekova[13] are not given.

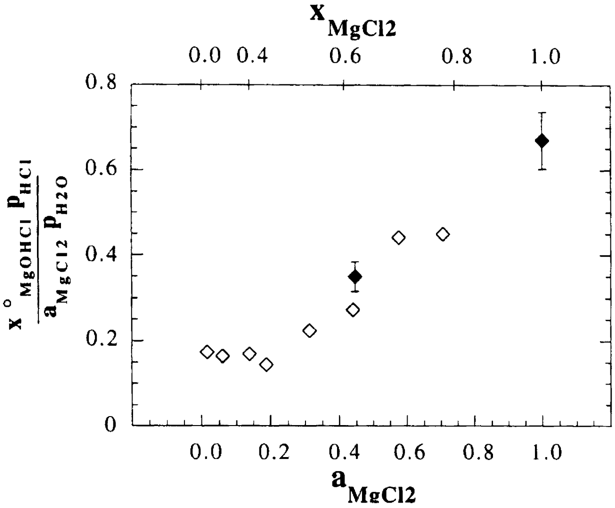

Fig. 5. K_4' plotted versus a_{MgCl_2}. ◇, From Ref. 13 ($600\leqslant T/°C\leqslant700$); ◆, present work ($675\leqslant T/°C\leqslant730$).

Discussion

The uncertainties associated with the carbothermal reduction analyses of hygroscopic melt samples add up to about 10% (our best estimate, based on experience). This is considered the most important error source related to determining x°_{MgOHCl}. This uncertainty is indicated in Figs. 3–5 as vertical error bars. The most important additional source of error in the determination of x°_{MgOHCl} is considered to be the composition of the gas phase. Estimated uncertainties in the gas composition are indicated in Figs. 3 and 4 as horizontal error bars. These estimates are based on the relative variations between different calibration parallels, and on the difference between their mean value and the equilibrium water pressure as calculated from thermodynamic data available in the literature.[30,31] In some instances the calibration procedure was problematic since the absorption medium for water clogged in the absorption tube, and large variations in water pressure were determined at a given gas flow rate and temperature. This problem is the major reason for the large horizontal error bars shown in Fig. 4. Other error sources, such as those in the thermodynamic data utilised for calculating x°_{MgO} and the presence of oxygen-containing impurities in the melt, are probably less important.

In our calculation of x°_{MgO} we assumed that $a_{MgO}=x^{\circ}_{MgO}$. Another possible error source in the calculation of x°_{MgOHCl} is therefore deviations from Henry's law for $MgO(1)$ close to saturation. Despite the fact that the saturation mole fraction for MgO in pure $MgCl_2$ is as low as 0.0036,[16] MgO may exhibit deviations from Henryan ideality at concentrations close to saturation. It is not possible to test this hypothesis on the basis of the available data, and we have therefore assumed that MgO obeys Henry's law in the whole concentration range.

The fact that our results can be plotted as straight

Table 2. Hydrolysis data. a_{MgCl_2} is calculated using eqn. (9).[a]

No.	x_{MgCl_2}	a_{MgCl_2}	T/°C	p_{HCl}/bar	p_{H_2O}/bar	n_O^{tot}/ppm O^{2-}	x_{MgO}	x_{MgOHCl}
[b]	1	1	730	0.83	0	181	0	0.0011
1	1	1	730	0.71	0.0085	1465	0.00063	0.0081
2	1	1	730	0.71	0.0085	1413	0.00063	0.0078
3	1	1	730	0.57	0.013	2794	0.0015	0.0151
4	1	1	730	0.73	0.0081	1407	0.00057	0.0078
5	1	1	730	0.71	0.0086	1260	0.00064	0.0069
[b]	1	1	730	0.80	0	251	0	0.0015
6	1	1	730	0.71	0.0084	1634	0.00062	0.0091
7	1	1	730	0.63	0.0108	2175	0.0010	0.0119
8	1	1	731	0.62	0.0111	2214	0.0011	0.0121
9	1	1	730	0.71	0.0087	1482	0.00065	0.0082
[b]	1	1	727	1	0	210	0	0.0012
10	1	1	729	0.64	0.0089	1471	0.00080	0.0079
11	1	1	729	0.64	0.0094	1842	0.00085	0.0096
12	1	1	734	0.73	0.0067	1210	0.00049	0.0064
13	1	1	725	0.64	0.0090	1909	0.00080	0.0101
14	1	1	733	0.64	0.0090	1963	0.00083	0.0103
[b]	0.62	0.45	729	1	0	193	0	0.00098
15	0.62	0.45	729	0.73	0.0075	408	0.00012	0.00196
16	0.62	0.45	726	0.73	0.0072	385	0.00010	0.00185
17	0.62	0.45	728	0.64	0.010	447	0.00018	0.00209
18	0.62	0.45	729	0.57	0.012	785	0.00028	0.00371
19	0.62	0.45	726	0.57	0.013	706	0.00028	0.00330
[b]	0.63	0.46	730	1	0	71	0	0.00036
20	0.63	0.46	732	0.73	0.0084	361	0.00013	0.00171
21	0.63	0.46	740	0.73	0.0089	419	0.00014	0.00199
22	0.63	0.46	735	0.64	0.011	550	0.00023	0.00257
23	0.63	0.46	736	0.64	0.011	537	0.00022	0.00251
24	0.63	0.46	738	0.57	0.013	678	0.00032	0.00313
25	0.63	0.46	737	0.57	0.013	746	0.00033	0.00347
[b]	0.62	0.43	676	1	0	90	0	0.00046
26	0.62	0.43	676	0.64	0.010	614	0.00013	0.00299
27	0.62	0.43	675	0.57	0.013	714	0.00020	0.00343
28	0.62	0.43	676	0.57	0.013	712	0.00020	0.00341
29	0.62	0.43	676	0.52	0.015	876	0.00029	0.00415
30	0.62	0.43	679	0.47	0.017	1136	0.00040	0.00536

[a] n_O^{tot} is obtained from the carbothermal reduction analyses, x_{MgO} has been calculated from tabulated thermodynamic data,[2] and x_{MgOHCl} is calculated from n_O^{tot} and x_{MgO} using eqns. (13) and (14). [b] Samples taken after the melt had been purged with HCl for 12–48 h.

lines as shown in Figs. 3 and 4 is an indication that MgOHCl obeys Henry's law in the concentration ranges studied. This is further illustrated in Fig. 6, where K'_4 is plotted versus p_{H_2O}/p_{HCl}. No significant variation of K'_4 with p_{H_2O}/p_{HCl} can be observed.

The decrease observed in K'_4 from pure $MgCl_2$ to the NaCl–$MgCl_2$ mixture as shown in Fig. 6, however, shows that K'_4 is not a true equilibrium constant. A thermodynamic equilibrium constant where the activity of MgOHCl is Raoultian rather than Henryan will not be a function of the melt composition. This equilibrium constant is given by

$$K_4^\circ = \frac{a^R_{MgOHCl}p_{HCl}}{a_{MgCl_2}p_{H_2O}} = \frac{x^\circ_{MgOHCl}\gamma^R_{MgOHCl}p_{HCl}}{a_{MgCl_2}p_{H_2O}} = K'_4\gamma^R_{MgOHCl} \tag{15}$$

where K'_4 and K_4° are quasi-Henryan and Raoultian based

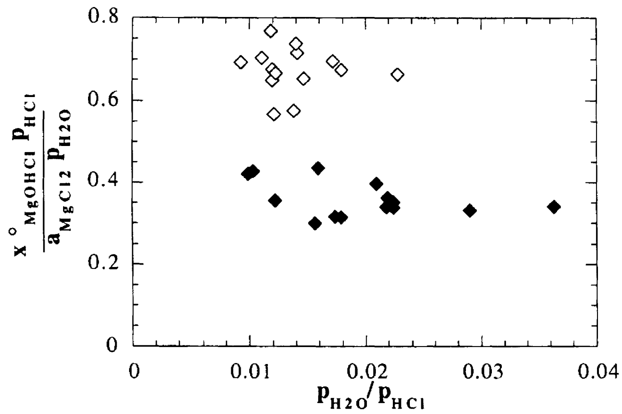

Fig. 6. K'_4 plotted versus p_{H_2O}/p_{HCl}. Open symbols: pure $MgCl_2$; filled symbols: $x_{MgCl_2} \approx 0.62$.

equilibrium constants, respectively. The above equation implies that a decrease in K'_4 owing to a dilution of the melt with NaCl, will result in a corresponding increase in γ^R_{MgOHCl}. Similar behaviour has been observed for γ^R_{MgO} in the same melts.[16] The equilibrium constant for the dissolution of MgO in a molten salt, eqn. (6), is given by $K^\circ_6 = a^R_{MgO} = x^\circ_{MgO}\gamma^R_{MgO}$. Since $a^R_{MgO} = 1$ for a MgO-saturated melt, γ^R_{MgO} (at 730 °C) is given by

$$\gamma^R_{MgO} = \frac{1}{x^{sat}_{MgO}} \approx \frac{1}{-1.55 \times 10^{-4} + 4.00 \times 10^{-3} a_{MgCl_2}} \qquad (16)$$

In pure $MgCl_2$ at 730 °C, $\gamma^R_{MgO} \approx 280$. It is important to keep in mind that this value is referred to pure, solid MgO. This large, positive value is in agreement with the low solubility of MgO in $MgCl_2$, $x_{MgO} = 0.0036$ at 730 °C.[16] Using pure, liquid MgO as standard state we would obtain an activity coefficient less than one. Taking the value for $\Delta_{fus}G^\circ(MgO) = 50$ kJ mol^{-1}, as listed in Ref. 2, gives $a_{MgO} = 0.0024$ at 730 °C, corresponding to $\gamma_{MgO} = 0.68$. We have chosen to use the solid standard state for MgO. The reason is the large uncertainty in the free energy of fusion for MgO.

Since magnesium oxide is complexed as $Mg_2OCl_x^{2-x}$ in $MgCl_2$–NaCl melts,[16,32] and the complex formation reaction

$$MgO(l) + MgCl_2(l) = Mg_2OCl_2(l) \qquad (17)$$

has a large equilibrium constant, the system MgO–$MgCl_2$ exhibit negative deviations from ideality when liquid standard states are used for both components. Furthermore, we observe from eqn. (16) that γ^R_{MgO} increases as a_{MgCl_2} decreases. This is also in accordance with the proposed complexation reaction (17).

As mentioned above γ^R_{MgOHCl} is also changing with the $MgCl_2$ concentration, but a numerical value of γ^R_{MgOHCl} cannot be obtained owing to the unknown Raoultian standard state of MgOHCl. It is, however, possible to give some comments on the variations observed in the Raoultian MgOHCl activity coefficient. Let us begin by observing from Fig. 5 that, just like γ^R_{MgO}, γ^R_{MgOHCl} decreases with increasing a_{MgCl_2} [eqn. (15)]. This apparently similar behaviour of the two solutes may be a key to understanding the chemistry of dissolution of MgOHCl in $MgCl_2$-containing melts.

A closer look at the $MgOH^+$ ion tells us that it is likely to be bent, much like water where one H^+ has been substituted by Mg^{2+}. This is due to the two lone pairs on the oxygen atom, and it implies that this ion must be considered a dipole. When pure liquid $MgCl_2$ is hydrolysed, interactions between the positive Mg^{2+} ions and the negative end of the $MgOH^+$ dipole are likely to occur, like in the Mg_2O^{2+} ion formed when MgO is dissolved in $MgCl_2$. Such interactions may be exemplified by the reaction

$$MgOHCl(l) + MgCl_2(l) = Mg_2OHCl_3(l) \qquad (18)$$

having a quasi-equilibrium constant equal to

$$K'_{18} = \frac{x_{Mg_2OHCl_3}}{x_{MgOHCl}a_{MgCl_2}}$$

x_{MgOHCl} denotes the mole fraction of 'free' MgOHCl species in the melt. They are taken as free in the sense that if $x_{MgOHCl} = x^\circ_{MgOHCl}$ the solution behaves ideally. The larger K'_{18}, the larger the negative deviation from ideality for MgOHCl. A rough estimate of γ^R_{MgOHCl}, given that reaction (18) is the only complex forming reaction involving MgOHCl established in the melt, would be that given by

$$\gamma^R_{MgOHCl} = \frac{x_{MgOHCl}}{x^\circ_{MgOHCl}} = \frac{x_{MgOHCl}}{x_{MgOHCl} + x_{Mg_2OHCl_3}} \qquad (19)$$

It is easy to see from eqns. (18) and (19) that increasing a_{MgCl_2} implies decreasing γ^R_{MgOHCl}. This is again in agreement with our data and the data of Savinkova and Lelekova[13] shown in Fig. 5. It is, however, important to note that the activity of MgOHCl will increase with increasing a_{MgCl_2} [eqn. (4)].

Let us compare briefly the two complex forming reactions (17) and (18). The Mg–O bond must be weaker in the $(Mg–OH–Mg)^{3+}$ than in the $(Mg–O–Mg)^{2+}$ complex owing to the presence of H^+. This implies that $K_{18} < K_{17}$. Our experimental data confirm this argument. Boghosian *et al.*[16] found that when pure $MgCl_2$ was diluted with NaCl until $x_{MgCl_2} = 0.62$, γ^R_{MgO} increased by a factor of 2.2. Our data show that γ^R_{MgOHCl} increases by a factor of 1.9 for the same change in $MgCl_2$ concentration. This means that the equilibrium constant of equilibrium (17) is larger than for equilibrium (18).

A consequence of the above interpretation of the change observed in γ^R_{MgOHCl} [eqn. (18)] is that MgOHCl exhibits negative deviation from ideality at least in pure $MgCl_2(l)$. This means that γ^R_{MgOHCl} has to be less than one in this melt, implying that K°_4 is less in magnitude than K'_4 as determined in pure $MgCl_2(l)$. K°_4 must therefore at least be less than 0.67, and $\Delta G^\circ_4 > 0$.

If we consider reaction (4) from a hard–soft Lewis acid–base point of view, the Lewis bases involved in the exchange reaction may be taken as OH^- and Cl^-, and the Lewis acids as H^+ and $MgCl^+$. The acids and bases are arranged in order of what we consider to be increasing softness. Since the same number of gas and liquid molecules are consumed and produced during the reaction, the entropy change, ΔS°_4, is expected to be small. Reaction (4) may be re-expressed as

$$ClMg^+–Cl^-(l) + H^+–OH^-(g)$$
$$= ClMg^+–OH^-(l) + H^+–Cl^-$$

From this rearrangement and the above considerations we can see that reaction (4) proceeds from predominantly hard–hard and soft–soft interactions towards mixed hard–soft interactions. On this basis we expect ΔH°_4 to be positive. These arguments therefore also lead us to a positive G°_4, in accordance with what we deduced from our complexation model [eqn. (18)].

The similarity in dissolution behaviour for MgO and MgOHCl is further emphasised by the changing slope of the K'_4 versus a_{MgCl_2} plot around $x_{MgCl_2}=0.33$ shown in Fig. 5. Boghosian *et al.*[16] observed the same behaviour for the solubility of MgO in the same solvent system, and ascribed this change to the significant thermodynamic and structural changes occurring in the NaCl–$MgCl_2$ melt at this composition.

Positive deviation from ideality for $MgCl_2$ in hydrolysed NaCl–$MgCl_2$ melts have been reported by Savinkova and Lelekova.[13] However, it is not likely that a strong negative deviation from ideality, as observed in anhydrous NaCl–$MgCl_2$ melts, is reversed by addition of as little as 2 mol% MgOHCl to the melt. Savinkova and Lelekova[13] do not indicate the uncertainties in their data, and it is therefore difficult to evaluate their results. It should be noted that our qualitative dissolution model [eqn. (18)] is supported by the data of Savinkova and Lelekova.

Two alternative interpretations of the observed increase in γ^R_{MgOHCl} when NaCl is added to the melt are possible. If MgOHCl was present in the chloride melt in a partly dissociated form, i.e. as Mg^{2+}, OH^-, $MgOH^+$ and Cl^- ions, the change in γ^R_{MgOHCl} observed could be explained by the increased strength of the Mg^{2+}–OH^- interactions when the next nearest neighbours of Mg^{2+} were Na^+ rather than Mg^{2+} ions. This would be due to the lower ionic potential of Na^+ than of Mg^{2+}. A larger fraction of the OH^- ions would then be complexed with Mg^{2+} in melts containing NaCl than in pure $MgCl_2$. Consequently, γ^R_{MgOHCl} would be larger in NaCl–$MgCl_2$ melts than in pure $MgCl_2$. However, the fact that pure alkali chlorides do not undergo hydrolysis to any significant degree indicates that OH^- do not exist as free ions in chloride melts.[33] This means that practically all the OH^- ions are bonded to Mg^{2+} in hydrolysed $MgCl_2$. A strengthening of the Mg–OH bond, therefore, cannot lead to increased Mg–OH^+ complex formation. The second alternative interpretation is based on data by Schenin-King and Picard.[34] Their results indicate that magnesium hydroxychloride is present in the melt as $(MgOH)_2{}^{2+}$ and Cl^- ions. The hydrolysis equilibrium [eqn. (4)] should then be replaced by the reaction

$$2MgCl_2 + 2H_2O = (MgOHCl)_2 + 2HCl \qquad (20)$$

with an equilibrium constant

$$K'_{20} = \frac{x_{dimer} p^2_{HCl}}{a^2_{MgCl_2} p^2_{H_2O}} \qquad (21)$$

where $x_{dimer} = x_{(MgOHCl)_2} = 0.5 x^\circ_{MgOHCl}$ may be calculated from x°_{MgOHCl} given in Table 2. The ratio $x_{dimer}/a^2_{MgCl_2}$ is plotted versus $(p_{H_2O}/p_{HCl})^2$ in Fig. 7. Within experimental error K'_{20} is the same in $MgCl_2$ and in the $MgCl_2$–NaCl mixture. The regression line, however, does not pass through the origin. In principle this could be due to oxygen-containing impurities present in the melt. However, ICP analyses of some of the melt samples revealed no indication of impurity metals in the melt.

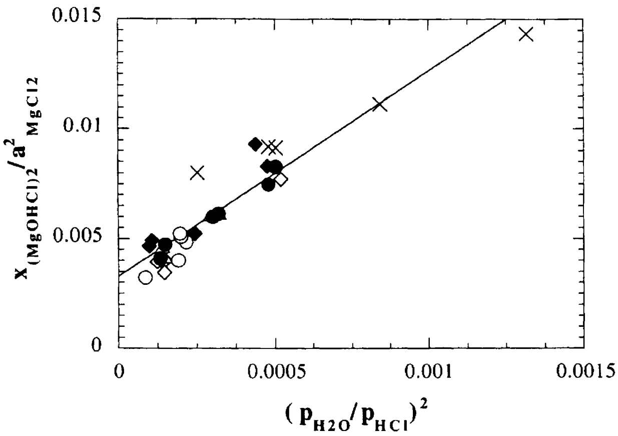

Fig. 7. $x_{dimer}/a^2_{MgCl_2}$ versus $(p_{H_2O}/p_{HCl})^2$. Different symbols represent different experimental runs. Open symbols: pure $MgCl_2$, $T/°C=730$; filled symbols: $x_{MgCl_2}\approx 0.62$, $T/°C=730$; crosses: $x_{MgCl_2}\approx 0.62$, $T/°C=675$. Regression line represents $x_{dimer}/a^2_{MgCl_2} = 0.0031 + 11.6(p_{H_2O}/p_{HCl})^2$.

The oxide contents detected in non-hydrolysed melts (numbered 'i' in Table 2) are not high enough to account for the above observations. This indicates that the $(MgOHCl)_2$ dimer is not an important complex in NaCl–$MgCl_2$ melts, at least not for the solvent compositions and solute concentrations studied in this work.

It should be mentioned that Schenin-King and Picard performed their experiments in the ternary system $MgCl_2$(20%)–LiCl(40%)–KCl(40%) (mol %) at 450 °C. In this system the magnesium ions are to a large extent expected to be present as $MgCl_4{}^{2-}$ ions. This means a much lower activity of $MgCl_2$ than in the present study, and complex formation according to eqn. (18) may be suppressed in favour of reaction (20) in the more basic melts of Schenin-King and Picard.[34]

The results of Savinkova and Lelekova[13] have been recalculated in terms of dimer formation and the recalculated data are plotted in Fig. 8 together with our results. We observe that the ranges of pressure ratios do not

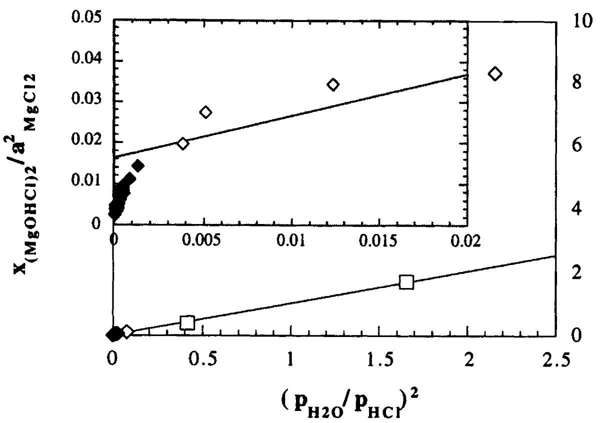

Fig. 8. $x_{dimer}/a^2_{MgCl_2}$ versus $(p_{H_2O}/p_{HCl})^2$. □, (600 °C),[13] ◇, (700 °C),[13] ◆, this work. Details at low pressure ratios are shown as an insert. Regression line based on data from Ref. 13.

overlap. However, there seems to be good agreement between the two sets of data. It is observed that the dimer exhibits positive deviations from Henryan behaviour when its concentration is increased. This may be an indication that the magnesium hydroxychloride is present in the melt as monomers in the very dilute region, and that the dimer becomes increasingly important at higher hydroxide concentrations.

Concluding remarks

The hydrolysis studies turned out to be experimentally difficult. First of all, $MgCl_2$ is very hygroscopic and should preferably be kept and handled inside of a glovebox. This was not possible as hydrolysis involves reactions with water. Furthermore, the corrosive nature of a gas mixture containing both HCl and H_2O at 730 °C introduced serious material problems. The fact that the acid consumption technique could not be used due to decomposition of MgOHCl introduced unforeseen problems. A new analytical technique to measure the sum of oxide and hydroxide in hygroscopic melt samples involving carbothermal reduction of the oxygen-containing species had to be developed. This was in itself difficult and time-consuming. Nevertheless we feel that our data and the interpretation of these data give some new insight into the complex chemistry of hydrolysed melt systems.

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