

## THE STABILITY OF THE CHLORO COMPLEXES OF MAGNESIUM AND OF THE ALKALINE EARTH METALS AT ELEVATED TEMPERATURES

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The stability of the chloro complexes,  $\text{MgCl}^+$ ,  $\text{CaCl}^+$ ,  $\text{SrCl}^+$  and  $\text{BaCl}^+$ , has been determined potentiometrically in an aqueous medium in the temperature range, 15–60°C, at an ionic strength of  $I = 1.0$  ( $\text{NaNO}_3$ ), using a silver chloride electrode and an ion-sensitive electrode selective to chloride ions. The stability of the chloro complexes decreases in the order,  $\text{Mg} > \text{Ca} \cong \text{Sr} > \text{Ba}$  and increases with increasing temperature of the solution.

The divalent ions of the alkaline earth metals and of magnesium have a very low tendency to form chloro complexes, as follows from the results of previous works dealing with this topic, summarized in Table I.

TABLE I

Published Data on the Stability of Chloro complexes  $\text{MCl}^+$  in Aqueous Solutions  
M represents Mg, Ca, Sr, or Ba.

$\text{M}^{2+}$	$T, ^\circ\text{C}$	$I$	Medium	Complex stability	Method	Ref.
$\text{Mg}^{2+}$	18	var	$\text{MgCl}_2$	no complex found	cond.	1
	25	var	$\text{MgCl}_2$	no complex found	part. pressures	2
	25	var	$\text{MgCl}_2$	very low	activity coeff.	3
	25	var	HCl	very low	cat. ex.	4
	0		$\text{KClO}_4$ (sat.)	$\beta_1 = 4.2$	cryosc.	5
	0		$\text{KClO}_3$ (sat.)	$\beta_1 = 1.2$	cryosc.	5
	0	0		$\beta_1 = 8.3$	cryosc.	5
$\text{Ca}^{2+}$	18	var	$\text{CaCl}_2$	no complex found	cond.	1
	25	var	$\text{CaCl}_2$	very low	activity coeff.	3
$\text{Sr}^{2+}$	18	var	$\text{SrCl}_2$	no complex found	cond.	1
	25	var	$\text{SrCl}_2$	very low	activity coeff.	3
$\text{Ba}^{2+}$	18	var	$\text{BaCl}_2$	no complex found	cond.	1
	18	0		$\beta_1 = 0.74$	cond.	6
	25	var	$\text{BaCl}_2$	very low	activity coeff.	3

However, during geochemical study of metal transfer in hydrothermal solutions, even the existence of poorly stable complexes, which may play a significant role in the transfer of metals in the earth's crust<sup>7</sup>, should be considered. As these processes often take place at an elevated temperature, we decided to study the stability of the chloro complexes of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  at temperatures up to 60°C. Since the stability of these complexes is low, it may justly be assumed that virtually only the  $\text{MCl}^+$  complexes are formed in the  $\text{M}^{2+}-\text{Cl}^-$  complexation systems ( $\text{M}^{2+}$  representing  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  or  $\text{Ba}^{2+}$ ) and the stability constants,  $\beta_{\text{MCl}} = \beta_1$ , can be calculated from the relationship

$$\beta_1 = \frac{(\text{MCl})}{(\text{M}) \cdot (\text{Cl})} = \frac{m_{\text{Cl}} - (\text{Cl})}{[m_{\text{M}} - m_{\text{Cl}} + (\text{Cl})] \cdot (\text{Cl})} \quad (1)$$

holding in the presence of excess metal M, *i.e.* for  $m_{\text{M}} > m_{\text{Cl}}$ . Symbols (MCl), (M) and (Cl) denote equilibrium concentrations and symbols  $m_{\text{M}}$  and  $m_{\text{Cl}}$  the overall molalities of the respective components of the studied system (the charges are omitted for the sake of simplicity). The overall molalities of the metal and the ligand are known and the value of (Cl) can be determined by direct potentiometry.

## EXPERIMENTAL

### Instruments and Chemicals

The ion-sensitive "chloride" electrode Orion 94-17, a silver chloride electrode, a reference calomel electrode (Radiometer K-401) with a liquid bridge (1*m*- $\text{NaNO}_3$ ), a glass electrode (Radiometer G-202), a digital pH-meter (Radiometer PHM-52) and an ultrathermostat were employed.

Sodium chloride and barium, magnesium, sodium, strontium and calcium nitrates, used for the preparation of stock solutions and ionic strength adjustment, were of *p.a.* purity. Their purity was checked by determining the impurity content by flame photometry. The solutions were standardized gravimetrically and their pH was within 4–5.5 and was not further adjusted. Traces of foreign cations were removed from the  $\text{NaNO}_3$  solution using a strongly acidic cation exchanger (Dowex 50 W) in the  $\text{Na}^+$ -cycle. All solutions were prepared using water redistilled in a quartz apparatus. The absence of chloride ions in all the solutions used (except for the NaCl solution) was checked by reaction with a 5% silver nitrate solution.

### Measuring Procedure

In 100 ml polyethylene vessels, previously leached with steam, solutions containing 0.00100 mol/kg  $\text{Cl}^-$  and 0.100 or 0.200 mol/kg  $\text{M}^{2+}$  were prepared. The ionic strength of the mixtures was adjusted to  $I = 1.00$  using a calculated amount of sodium nitrate solution. Each solution was prepared in triplicate. Further, standard chloride solutions were prepared, containing  $1.00 \cdot 10^{-3}$  and  $1.00 \cdot 10^{-4}$  mol/kg NaCl. The solutions were thermostatted at 15, 25, 35, 45 and 60°C and the potentials of the silver chloride and the selective "chloride" electrode were measured alternately in the standard NaCl solutions and in the studied mixtures.

## RESULTS AND DISCUSSION

The stability constant values,  $\beta_1$ , of the studied complexes were calculated from equation (1), into which the  $(\text{Cl})_x$  value was substituted for the free chloride ion

molality, found from the relationship

$$\Delta E_{\text{cor.}} = S \log \frac{(\text{Cl})_s}{(\text{Cl})_x}, \quad (2)$$

where  $\Delta E_{\text{cor.}}$  is the difference of the measuring electrode potentials in the studied mixture and in the standard,  $1.00 \cdot 10^{-3}$  mol/kg NaCl, corrected for the liquid-junction potential, calculated from the Henderson equation<sup>8</sup>. The measured  $\Delta E$  values amounted to 0.0 to 5.7 mV, the correction for the liquid-junction potential being up to 0.5 mV, depending on the kind of ions present and on the temperature. The value of quantity  $S$ , representing the Nernstian slope for the measuring electrode potential in a solution of chloride ions, was determined experimentally using both the standard NaCl solutions. Quantity  $S$  changed by about 1 mV/pCl in 6 hours. The effect of this variation was virtually eliminated in the measuring procedure used. Changes in the activity coefficient,  $\gamma_{\text{Cl}}$ , were suppressed to a minimum by maintaining a constant ionic strength.

The measured data were handled on the IBM 1410 computer. The program in FORTRAN IV language contained algorithms for computation of the concentration of free chloride ion,  $a$ , and of  $\beta_1$  values for individual measurements, for computation of the mean value,  $\bar{\beta}_1$ , for each system  $\text{M}^{2+}-\text{Cl}^-$  at individual temperatures and for

TABLE II

The Stability Constant Values for the Studied Chlorocomplexes  $\text{MCl}^+$  ( $I = 0.1$  ( $\text{NaNO}_3$ ))  
The concentration constants are valid for the given ionic strength; molalities were used.

$\text{M}^{2+}$	Method <sup>a</sup>	Temperature, °C				
		15	25	35	45	60
$\text{Mg}^{2+}$	A	0.88	0.83	0.88	1.0	1.1
	B	0.74	0.77	0.86	1.0	1.2
$\text{Ca}^{2+}$	A	0.66	0.76	0.81	0.89	0.92
	B	0.64	0.77	0.75	0.86	0.95
$\text{Sr}^{2+}$	A	0.87	0.68	0.67	0.79	0.93
	B	0.60	0.57	0.66	0.75	0.95
$\text{Ba}^{2+}$	A	0.46	0.40	0.51	0.66	0.75
	B	0.33	0.36	0.47	0.65	0.75

<sup>a</sup> Method A measurement with the Orion ion-selective electrode; method B measurement with silver chloride electrode. Each constant is the average of six measured results (see the text). The reproducibility of the constants: method A the standard deviation of the constant,  $s = 0.10$  to  $0.30$ ; method B  $s = 0.15$  to  $0.30$ .

TABLE III

The Standard Enthalpies and Entropies of Reactions  $M^{2+} + Cl^- \rightleftharpoons MCl^+$  (at 25°C)

The  $\Delta H^\circ$  and  $\Delta S^\circ$  values were calculated from the shape of the  $\beta_1 = f(T)$  dependences in a temperature range of 15–35°C.

$M^{2+}$	$\Delta H^\circ$ cal/mol	$\Delta S^\circ$ cal/mol . K
$Mg^{2+}$	$-1\,296 \pm 1\,259$	$-4.9 \pm 4.2$
$Ca^{2+}$	$-1\,719 \pm 1\,044$	$-6.3 \pm 3.5$
$Sr^{2+}$	$-2\,275 \pm 998$	$8.9 \pm 3.4$
$Ba^{2+}$	$-2\,708 \pm 1\,908$	$-11.1 \pm 6.4$

computation of the standard deviations. Further, standard enthalpies,  $\Delta H^\circ$ , and entropies,  $\Delta S^\circ$ , with the corresponding standard deviations were calculated for a temperature of 25°C. The results are given in Tables II and III. The dependence of the stability constants on temperature can be expressed by the relationships:

$$MgCl^+: (\beta_1)_T = 17.5 - 0.113 T + 0.000192 T^2,$$

$$CaCl^+: (\beta_1)_T = -9.48 + 0.0607 T - 0.0000885 T^2,$$

$$SrCl^+: (\beta_1)_T = 39.2 - 0.25 T + 0.000407 T^2,$$

$$BaCl^+: (\beta_1)_T = 9.97 - 0.0683 T + 0.000122 T^2.$$

The stability of the studied chloro complexes decreases in the series,  $MgCl^+ > CaCl^+ > SrCl^+ > BaCl^+$ , *i.e.* in the order of increasing ionic radii (and decreasing ionic potential,  $Z/r$ ). Hence, the chloro complexes of magnesium and the alkaline earths can be considered as ion-associates, analogous to associates  $MOH^+$ ,  $MF^+$ ,  $MSO_4$  *etc.* Only the values for the  $Mg^{2+}$  and  $Ba^{2+}$  complexes can be compared with the literature data; our values are lower than those given in the literature<sup>5,6</sup> for somewhat different conditions (Table I). It follows from the stability constants found,  $\beta_{MCl}$ , that complexes  $MCl^+$  start to appear in aqueous solutions under the given conditions (about 5% fraction) at  $(Cl) = 0.1$  mol/kg; at a concentration of 1.0 mol/kg  $Cl^-$ , the amount of the chloro complex of barium is about 25%, that of magnesium almost 50% and at a molality of 10 mol/kg, 80–90% of the metal M exists as the  $MCl^+$  complex in solution.

The  $\Delta H^\circ$  and  $\Delta S^\circ$  values are of poor precision and thus have only orientative significance.

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