Monatshefte für Chemie 134, 763–768 (2003)
DOI 10.1007/s00706-002-0589-1

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Experimental Determination of the Isotherm at 15°C of the System Mg^{2+}/Cl^{-}, $SO_4{}^{2-}$–H_2O

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Received October 16, 2002; accepted (revised) December 3, 2002
Published online April 24, 2003

Summary. The diagram of the ternary system Mg^{2+}/Cl^{-}, $SO_4{}^{2-}$–H_2O was established at 15°C by means of analytical and conductimetric measurements. Three compounds were found in this diagram, which are $MgSO_4{\cdot}6H_2O$, $MgSO_4{\cdot}7H_2O$, and $MgCl_2{\cdot}6H_2O$. The solubility field of $MgSO_4{\cdot}7H_2O$ is important whereas those of $MgSO_4{\cdot}6H_2O$ and $MgCl_2{\cdot}6H_2O$ are small. The compositions (mass-%) of the two invariant points determined by the two methods are: $MgSO_4$:$MgCl_2$ = 2.73:33.80 and $MgSO_4$:$MgCl_2$ = 3.38:28.91. Both the measured and the calculated isotherm at 15°C have been used for modelling of the diagram Mg^{2+}/Cl^{-}, $SO_4{}^{2-}$–H_2O between 0 and 35°C. The polythermal invariant point was approximately located between 15 and 10°C.

Keywords. Oceanic salt system; Solubility diagram; Magnesium sulphate hydrates.

Introduction

In the framework of studies of compilations of soluble salts in sea water and in brines, all systems representing these salts have to be evaluated. The major ions to be considered are Na^{+}, K^{+}, Mg^{2+}, Cl^{-}, and $SO_4{}^{2-}$ in H_2O. They form a reciprocal quinary system [1].

Many studies have been undertaken on this system in order to extract the valuable products from brines, but none was complete. Whereas the data concerning this quinary system are available in large numbers, it is not always easy to calculate its diagrams accurately. The discrepancy between the results from distinct authors, the variety of units, the inaccuracy of the data, *etc*. make the modeling difficult. This becomes even more evident for the diagrams in which magnesium is present. Many of these kinds of systems have to be reinvestigated. As a first step of this

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Dedicated to Prof. Dr. *Heinz Gamsjäger* on the occasion of his 70th birthday

reinvestigation, we focused on the establishment of the ternary system Mg^{2+}/Cl^{-}, $SO_4{}^{2-}$–H_2O at 15°C.

Concerning this system, more than 500 solubility data are given in literature and many isotherms were established from 0 to 189°C [2–29], but the experimental points are often non-concordant. For this system fifteen compounds are cited: ice, $MgCl_2{\cdot}nH_2O$ ($n = 2, 4, 6, 8, 12$), and $MgSO_4{\cdot}n'H_2O$ ($n' = 1, 3.77, 3.85, 3.9, 4, 4.1, 5, 6, 7$). But most of the experimental points are in total discrepancy and the coordinates of the invariant equilibrium have not been determined.

Moreover, the hydration number of magnesium sulphate in equilibrium with liquid is sometimes uncertain since some experimental points are located in regions where other salts are expected. These deficiencies make the modeling of the diagram and the localisation of its binary and ternary points difficult. Meanwhile, the ternary point related to $MgSO_4{\cdot}7H_2O$, $MgSO_4{\cdot}6H_2O$, and $MgCl_2{\cdot}6H_2O$ seems to be located between the isotherms at 10 and 20°C. To try to remove the ambiguity and to have a base for calculations, we established the diagram Mg^{2+}/Cl^{-}, $SO_4{}^{2-}$–H_2O at 15°C.

Results and Discussions

The solubility data, obtained by analytical and synthetic methods, are gathered in Tables 1 and 2 and presented in Fig. 1. They are expressed in mass-%.

Table 1. Ternary system Mg^{2+}/Cl^{-}, $SO_4{}^{2-}$–H_2O at 15°C (Analytical method)

Density/gcm^{-3}	Saturated solution composition/mass-%			Solid phases
	$MgCl_2$	$MgSO_4$	H_2O	
1.2525	0.00	24.87	75.13	*MS*7
1.2090	2.54	20.68	76.78	,,
1.1917	6.22	16.13	77.65	,,
1.1754	9.90	12.60	77.50	,,
1.1764	12.53	10.47	77.00	,,
1.1805	16.20	7.12	76.68	,,
1.1892	18.69	5.78	75.53	,,
1.1986	22.00	4.57	73.43	,,
1.2245	25.33	3.80	70.87	,,
1.2571	27.05	3.14	69.81	,,
1.2780	30.89	3.01	66.10	*MS*7 + *MS*6
1.3058	33.87	2.69	63.44	,,
1.3129	33.69	2.81	63.50	*MC*6 + *MS*6
1.2957	33.74	2.74	63.52	,,
1.3142	34.02	2.70	63.28	,,
1.3131	33.68	2.71	63.61	,,
1.2959	35.21	1.22	63.57	*MC*6
1.2787	35.17	0.00	64.83	,,

Table 2. Ternary system $Mg^{2+}/Cl^-, SO_4^{2-}$–H_2O at 15°C (Synthesis method)

Density/gcm^{-3}	Saturated solution composition/mass-%			Solid phases
	$MgCl_2$	$MgSO_4$	H_2O	
1.2525	0.00	24.84	75.16	*MS*7
1.2090	2.26	21.00	76.74	,,
1.1917	4.32	17.62	78.06	,,
1.1754	6.53	15.72	77.75	,,
1.1764	8.44	13.82	77.74	,,
1.1805	10.82	11.28	77.90	,,
1.1892	13.29	9.22	77.49	,,
1.1986	16.13	7.20	76.67	,,
1.2245	19.32	5.02	75.66	,,
1.2571	22.38	4.11	73.51	,,
1.2780	28.91	3.38	67.71	*MS*7 + *MS*6
1.3058	34.15	1.97	63.88	*MC*6
1.3129	35.36	0.00	64.64	,,

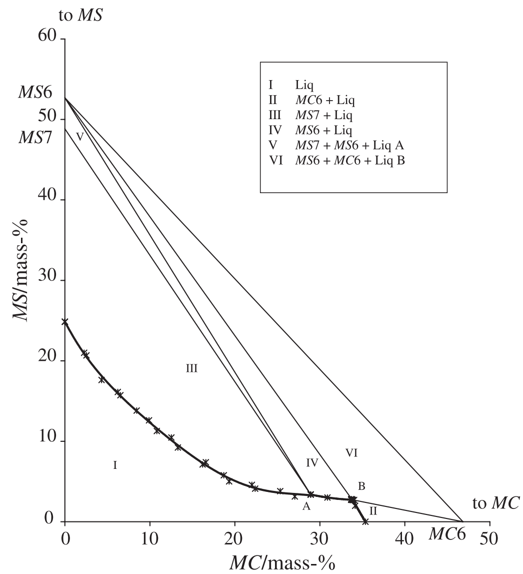

Fig. 1. System $MgCl_2$–$MgSO_4$–H_2O at 15°C

Three solid phases, $MgCl_2 \cdot 6H_2O$ (*MC*6), $MgSO_4 \cdot 6H_2O$ (*MS*6), and $MgSO_4 \cdot 7H_2O$ (*MS*7), were observed. This proves that the temperature of the polythermal invariant point must be less than 15°C. In fact at 10°C only $MgSO_4 \cdot 7H_2O$ and $MgCl_2 \cdot 6H_2O$ are stable. $MgSO_4 \cdot 6H_2O$ appears at 15°C. The solubility field of $MgSO_4 \cdot 7H_2O$ is important, whereas the liquidus curves of $MgCl_2 \cdot 6H_2O$ and $MgSO_4 \cdot 6H_2O$ are very small. The compositions of the isothermal invariant points determined by the two methods are given in Table 3.

Table 3. The isothermal invariant points compositions

$MgCl_2$/mass-%	$MgSO_4$/mass-%	H_2O/mass-%	Solid phases
28.91	3.38	67.71	*MS*7 + *MS*6
33.69	2.81	63.49	*MS*6 + *MC*6

Modelling of the Phase Diagram $MgCl_2$–$MgSO_4$–H_2O (Mg^{2+}/Cl^-, SO_4^{2-}–H_2O)

The isotherm at 15°C was recalculated (Fig. 2). Considering this curve as a reference we recalculated the whole diagram. The solubility field of a compound in the ternary system can be calculated according to the general Eq. (1) [1] where U is the logarithm of the solubility product of the species in equilibrium with the liquid, m is an adjustable coefficient of the solid-phase solubility field, and X, Y, U, V, W are the *Jänecke* coordinates of ions present in the solution. This relation includes the solubility fields of all the subsystems.

$$U = \sum_i \sum_j X_i Y_j \left(m^{ij} + \sum_n \sum_k U_k^n \left(m_n^{ijk} + \sum_p \sum_l V_l^p \left(m_{np}^{ijkl} + \sum_q W_m^q m_{npq}^{ijklm} \right) \right) \right) \quad (1)$$

The calculated ternary system is presented in Fig. 2. In this diagram, the experimental data and the calculated curves are in good agreement. Thus, the

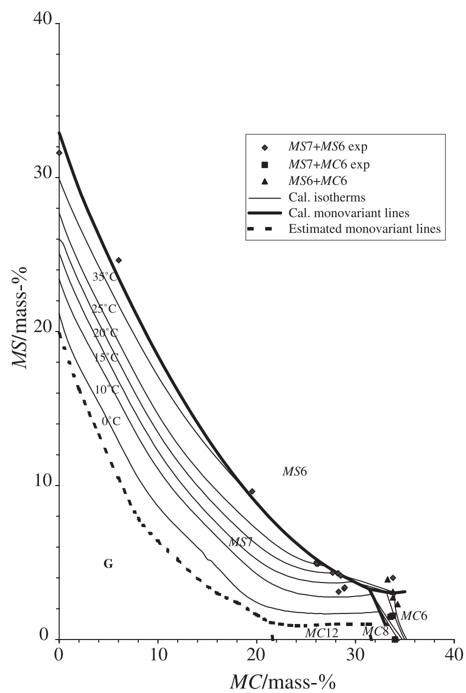

Fig. 2. The calculated ternary system $MgCl_2$–$MgSO_4$–H_2O

determination of the isotherm at 15°C gave evidence for the existence of the two isothermal isobar invariant points and it allowed to define without ambiguity the nature of the three solids which can be observed between 0 and 35°C. It also facilitates the modeling of the diagram $MgCl_2$–$MgSO_4$–H_2O between 0 and 35°C.

Experimental

This isothermal section Mg^{2+}/Cl^{-}, SO_4^{2-}–H_2O at 15°C was established using several methods.

Analytical Methods

The mixtures [30] and the wet residues [31] methods were used. The mixtures were stirred during three days at constant temperature to attain equilibrium and then allowed to settle. The liquid and solid were next separated and analysed for Mg^{2+}, Cl^{-}, and SO_4^{2-}. The Mg content was determined by titration with ethylendiamine-tetraacetic acid disodium salt. A potentiometric method was used to determine the chloride ion concentration. The concentration of SO_4^{2-} was measured by gravimetry and potentiometry.

Synthesis Method

This method is based on the electric conductivity variation of an electrolyte solution with composition. Small amounts of H_2O are progressively added to a saturated solution of a given formal composition, concerning an excess of solid. After each addition, the resistance is measured when equilibrium is reached (*i.e.* when there is no change with time in resistance). The curve of resistance versus added H_2O volume is plotted. It presents a break at each phase change, the last one corresponding to the dissolution of the last crystal of salt. An invariant equilibrium is characterized by a plateau in the curve. The temperature was controlled by means of a thermostat jacket maintained at 15±0.2°C by circulation of H_2O. In order to identify the solid phases, X-ray diffraction was used.

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