

SOLID–LIQUID EQUILIBRIA IN THE QUATERNARY SYSTEM Na^+ , Mg^{2+} // Cl^- , SO_4^{2-} – H_2O AT 25 AND 30°C

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(Received February 13, 1999)

Abstract

The isoplethic sections in the diagram of the quaternary system Na^+ , Mg^{2+} // Cl^- , SO_4^{2-} – H_2O were established at 25 and 30°C by analytical and conductometric measurements. Three compounds can be observed in the isoplethic sections: NaCl , Na_2SO_4 and $\text{MgNa}_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. Seven fields are determined, relating to the precipitation of one, two or three salts. The solubility range of $\text{MgNa}_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ is wide, while the liquidus curve of Na_2SO_4 is very short. The compositions, expressed in Jänecke coordinates, at the eutonic and peritonic points, respectively, were:

42.70% Cl^- and 745% H_2O ; 79.47% Cl^- and 787% H_2O ; 71.6% Cl^- and 744% H_2O at 25°C; and
48.80% Cl^- and 715% H_2O ; 80.20% Cl^- and 778% H_2O ; 70.14% Cl^- and 707% H_2O at 30°C.

Keywords: brine, sea water, sodium sulphate, solubility diagram, quaternary system

Introduction

The treatment of sea water and brines is an important problem for the industrial development of Tunisia. The surface areas of the salt lakes ‘Chotts’ and ‘Sebkhat’ in the south of the country are very important. Various research projects were undertaken in the past in order to extract valuable products, but none was completed.

Industrial needs for mineral salts such as sodium sulphate (Na_2SO_4), magnesium sulphate (MgSO_4) and potassium sulphate (K_2SO_4) are constantly increasing world-wide.

NaCl and $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ were the first salts obtained by the evaporation of sea water and a sample of a Tunisian brine [1, 2]. To extract sodium sulphate from these salts, we have focussed in a first step on the determination of the isoplethic sections NaCl – $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ at 25 and 30°C in the quaternary system Na^+ , Mg^{2+} // Cl^- , SO_4^{2-} – H_2O .

Literature background

The quaternary system Na^+ , $\text{Mg}^{2+} // \text{Cl}^-$, $\text{SO}_4^{2-} - \text{H}_2\text{O}$ has been investigated by several authors [3–30], at temperatures between -34.6°C and 189°C , and more than 1500 solubility data are given in the literature. Five compounds are mentioned at 25 and 30°C : NaCl (NC), Na_2SO_4 (NS), $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (NS10), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (MS7), $\text{Na}_2\text{Mg}(\text{SO}_4)_2$ (NMS) and $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (NMS4). However, the solubility ranges of these compounds have not been completely determined at 30°C .

With a view to selecting the best data, we converted the literature data on the system Na^+ , $\text{Mg}^{2+} // \text{Cl}^-$, $\text{SO}_4^{2-} - \text{H}_2\text{O}$ at 25°C into solute mole fractions by percentage of cations or anions (Jänecke coordinates) and plotted them in a diagram (Fig. 1).

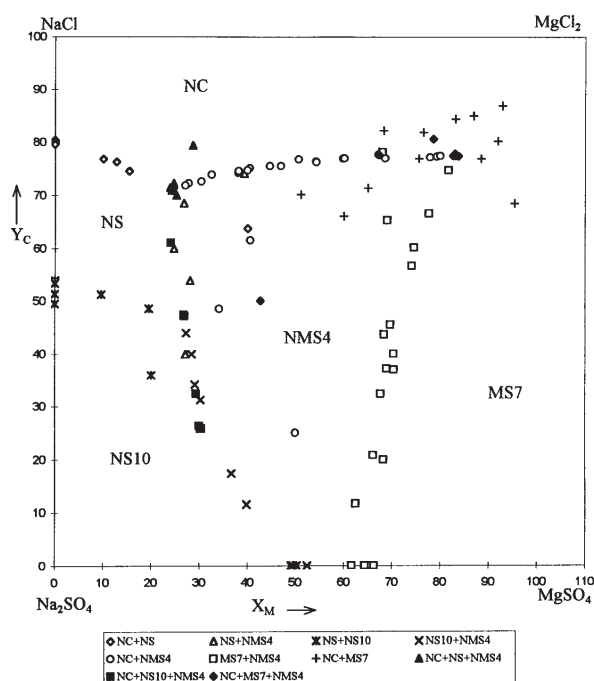


Fig. 1 Quaternary system Na^+ , $\text{Mg}^{2+} // \text{Cl}^-$, $\text{SO}_4^{2-} - \text{H}_2\text{O}$ at 25°C (literature data)

The nature of the compounds in equilibrium with the liquid is sometimes uncertain, since some experimental points are located in regions where other salts are expected.

Experimental

The isopleth sections $\text{NaCl} - \text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ at 25 and 30°C in the Na^+ , $\text{Mg}^{2+} // \text{Cl}^-$, $\text{SO}_4^{2-} - \text{H}_2\text{O}$ system were established by two methods:

Synthetic method

This is based on the variation in the electric conductivity of electrolyte solutions with composition: small amounts of water are progressively added to a saturated solution of given formal composition, containing an excess of solid. After each addition, the conductance is measured when equilibrium is reached (i.e. when there is no change with time in the conductivity). The curve of conductance versus added water volume is plotted. This 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 is controlled by means of a thermostate jacket maintained at 25 or $30^{\circ}\text{C}\pm 0.02^{\circ}\text{C}$ by the circulation of water.

Analytical method

The classical 'ensemble' [31] and 'wet residue' [32] methods were used. The mixtures were stirred during 15 days at constant temperature to attain equilibrium and then allowed to settle. The liquid and solid were next separated and analysed for Na^+ , Mg^{2+} , SO_4^{2-} and Cl^- . The sodium content was determined by flame photometry [33]. The magnesium concentration was obtained by titration with ethylenediamine-tetraacetic acid disodium salt (EDTA) [34] with eriochromeT black as indicator in buffered ammoniacal solution (pH=10). A potentiometric method [35] was used to determine chloride ion concentration. The concentration of sulphate ion was determined by gravimetry [36].

In order to identify the solid phases, X-ray diffraction was applied. Diffractograms were recorded on a Philips PW 1050/70 diffractometer. CuK_{α} radiation was utilized. Diffraction measurements were carried out at a rate of $(1/8)^{\circ}\text{min}^{-1}$ per 2θ .

Compounds

Analytical reagents (99% purity): NaCl , Na_2SO_4 and $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ were supplied by Merck.

Astrakanite, $\text{Na}_2\text{Mg}(\text{SO}_4)_2\cdot 4\text{H}_2\text{O}$, was prepared by adding water under mechanical stirring to Na_2SO_4 and $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ in stoichiometric proportions at 25°C . The stirring was maintained for 1 day and the resulting precipitate was filtered off and dried at room temperature.

Results

The solubility data are presented in Figs 2 and 3 and Tables 1 and 2. They are expressed in mole fraction % (X_M , Y_C and Z_H are the data for Mg^{2+} , Cl^- and H_2O , respectively).

X_M , Y_C and Z_H are given by the following equations:

$$X_M = 100 \frac{2[Mg^{2+}]}{2[Mg^{2+}] + [Na^+]}$$

$$Y_C = 100 \frac{[Cl^-]}{2[Mg^{2+}] + [Na^+]}$$

$$Z_H = 100 \frac{[H_2O]}{2[Mg^{2+}] + [Na^+]}$$

All the values listed in Tables 1 and 2 were determined with an error in Jänecke coordinates of ± 0.02 .

Table 1 Quaternary system Na^+ , Mg^{2+}/Cl^- , $SO_4^{2-}-H_2O$ at 25°C;
Isoplethic section $NaCl-Na_2Mg(SO_4)_2 \cdot 4H_2O$

Composition of liquid phase*			Composition of wet residue**			Solid phase
XM	YC	ZH	XM	YC	ZH	
0.00	100.00	905	0.00	100.00	0	NC
4.52	90.96	880	0.00	100.00	0	NC
7.30	85.40	840	0.25	99.50	22	NC
10.27	79.47	787	0.50	99.00	6	NC+NS
12.20	75.60	770	0.00	100.00	0	NC+NS
13.50	73.00	839				NS
18.60	62.80	860				NS
13.98	72.04	744	39.60	20.80	54	NC+NS+NMS4
14.00	72.00	754	38.20	83.60	22	NC+NS+NMS4
14.15	71.70	736	33.59	32.81	76	NC+NS+NMS4
14.25	71.50	748	18.00	64.00	56	NC+NS+NMS4
14.50	71.00	736	22.95	54.10	60	NC+NS+NMS4
16.65	66.70	764	49.15	1.70	65	NS+NMS4
18.10	63.80	770	48.56	2.87	85	NS+NMS4
19.53	60.93	780	48.68	2.63	83	NS+NMS4
22.60	54.80	781	49.18	0.74	86	NS+NMS4
28.65	42.70	745	48.73	2.53	94	NS+NMS4
34.10	31.80	862	49.53	0.93	98	NMS4
38.84	22.31	893	49.42	1.15	105	NMS4
48.22	3.56	740	49.51	0.97	100	NMS4
50.00	0.00	670	50.00	0.00	102	NMS4

* determined by synthetic and analytical methods

** determined by analytical method

At 25 and 30°C, three solid phases were observed: $NaCl$, Na_2SO_4 and $Na_2Mg(SO_4)_2 \cdot 4H_2O$. The range of saturation for $Na_2Mg(SO_4)_2 \cdot 4H_2O$ is very large, while the liquidus curve of Na_2SO_4 is short. Two eutonic and one peritonic points were observed. The following compositions were determined:

– Eutonic point E_1 (Figs 2 and 3) is the intercept of the liquidus curves of $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ and Na_2SO_4 .

– Eutonic point E_2 (Figs 2 and 3) is the intercept of the liquidus curves of NaCl and Na_2SO_4 .

– Peritonic point P (Figs 2 and 3) is the intercept of the curves relating to the coprecipitation of two solid phases: $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ – Na_2SO_4 and NaCl – Na_2SO_4 . Its composition is also given by application of the ‘ensemble’ and the wet residue methods to mixtures located in the four-phase area of the diagram NaCl – Na_2SO_4 – $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ –liquid P .

Table 2 Quaternary system Na^+ , $\text{Mg}^{2+}/\text{Cl}^-$, SO_4^{2-} – H_2O at 30°C ;
Isopleth section NaCl – $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$

Composition of liquid phase*			Composition of wet residue			Solid phases
XM	YC	ZH	XM	YC	ZH	
0.00	100.00	900	0.00	100.00	0	NC
1.85	96.30	889	0.00	100.00	0	NC
6.10	87.80	832	0.00	100.00	0	NC
9.90	80.20	778	0.90	98.20	0.37	NC+NS
11.65	76.70	754	0.55	98.90	16	NC+NS
13.70	72.60	730	5.18	89.61	5	NC+NS
14.10	71.80	822				NS
19.00	62.00	815				NS
14.75	70.50	702	13.42	73.16	18	NC+NS+NMS4
14.75	70.50	714	48.70	2.60	89	NC+NS+NMS4
15.05	69.90	708	30.75	38.50	56	NC+NS+NMS4
15.05	69.90	702	11.27	77.46	14	NC+NS+NMS4
15.05	69.90	710	41.43	17.14	71	NC+NS+NMS4
17.48	65.03	734	46.77	2.46	104	NS+NMS4
21.90	56.20	730	48.93	2.14	86	NS+NMS4
25.60	48.80	715	49.12	1.76	96	NS+NMS4
27.25	45.50	744	49.45	1.10	93	NMS4
31.52	36.95	780	48.78	2.52	103	NMS4
35.80	28.39	778	49.36	1.28	102	NMS4
39.04	21.92	760	48.88	2.24	103	NMS4
43.72	12.57	689	49.45	1.10	100	NMS4
46.81	6.38	644	50.00	0.00	101	NMS4
50.00	0.00	598	50.00	0.00	100	NMS4

* determined by synthetic and analytical methods

** determined by analytical method

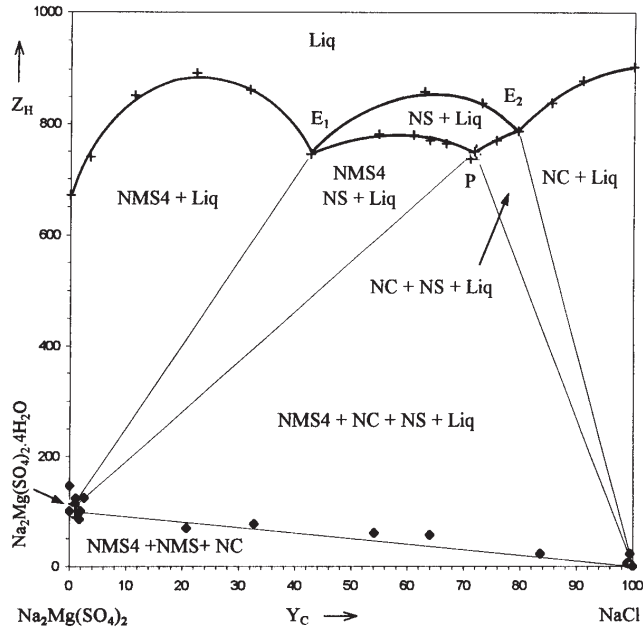


Fig. 2 Quaternary system Na^+ , $\text{Mg}^{2+} // \text{Cl}^-$, $\text{SO}_4^{2-} - \text{H}_2\text{O}$ at 25°C , isoplethic section $\text{NaCl} - \text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$

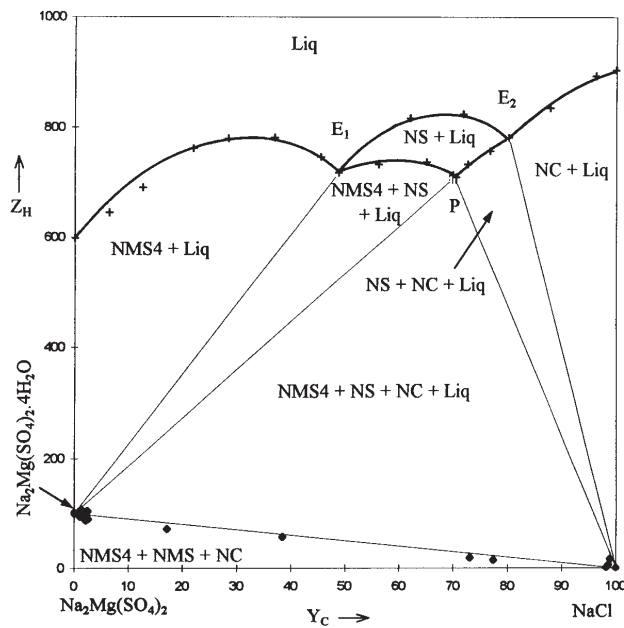


Fig. 3 Quaternary system Na^+ , $\text{Mg}^{2+} // \text{Cl}^-$, $\text{SO}_4^{2-} - \text{H}_2\text{O}$ at 30°C , isoplethic section $\text{NaCl} - \text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$

The compositions, expressed in Jänecke coordinates, of the eutonic and peritonic points were as follows:

at 25°C:

- liquid \rightarrow $\langle \text{Na}_2\text{SO}_4 \rangle + \langle \text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} \rangle$
42.70% Cl^- and 745% H_2O .
- liquid \rightarrow $\langle \text{Na}_2\text{SO}_4 \rangle + \langle \text{NaCl} \rangle$
79.47% Cl^- and 787% H_2O .
- liquid + $\langle \text{Na}_2\text{SO}_4 \rangle \rightarrow \langle \text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} \rangle + \langle \text{NaCl} \rangle$
71.6% Cl^- and 744% H_2O .

at 30°C:

- liquid \rightarrow $\langle \text{Na}_2\text{SO}_4 \rangle + \langle \text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} \rangle$
48.80% Cl^- and 715% H_2O .
- liquid \rightarrow $\langle \text{Na}_2\text{SO}_4 \rangle + \langle \text{NaCl} \rangle$
80.20% Cl^- and 778% H_2O .
- liquid + $\langle \text{Na}_2\text{SO}_4 \rangle \rightarrow \langle \text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} \rangle + \langle \text{NaCl} \rangle$
70.14% Cl^- and 707% H_2O .

Conclusions

The isoplethic sections in the diagram of the quaternary system Na^+ , $\text{Mg}^{2+} // \text{Cl}^-$, $\text{SO}_4^{2-} - \text{H}_2\text{O}$ were established at 25 and 30°C by analytical and conductometric measurements.

Three compounds can be observed in the isoplethic sections: NaCl , Na_2SO_4 and $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. Seven fields are determined, relating to the precipitation of one, two or three salts. The solubility range of $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ is wide, while the liquidus curve of Na_2SO_4 is very short.

The compositions, expressed in Jänecke coordinates, of the eutonic and peritonic points, were determined by two methods.

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