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Solubility and Stability of Nesquehonite ($MgCO_3 \cdot 3H_2O$) in Mixed NaCl + $MgCl_2$, NH_4Cl + $MgCl_2$, LiCl, and LiCl + $MgCl_2$ Solutions

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The solubility and stability of nesquehonite ($MgCO_3 \cdot 3H_2O$) in mixed solutions (NaCl + $MgCl_2$, NH_4Cl + $MgCl_2$, LiCl, and LiCl + $MgCl_2$) were measured by using a classic isothermal dissolution method over the temperature range of (298 to 308) K. The concentration investigated for all salts was up to 0.2 $mol \cdot dm^{-3}$ NaCl, 1.5 $mol \cdot dm^{-3}$ NH_4Cl, 0.6 $mol \cdot dm^{-3}$ $MgCl_2$, and 1.5 $mol \cdot dm^{-3}$ LiCl at ambient temperature. The solubility of $MgCO_3 \cdot 3H_2O$ phases in all the cases investigated was found to increase with the temperature increment. The comparison of solubility in $MgCl_2$ solutions and NaCl + $MgCl_2$, NH_4Cl + $MgCl_2$, and LiCl + $MgCl_2$ mixed solutions has been investigated. XRD and SEM examination of the equilibrated solids showed that nesquehonite in all cases is stable in the temperature range of (298 to 308) K.

Introduction

Qarham salt lake is well-known for its huge reserves of potassium representing more than 90 % of all potassium deposits in China. However, the brines in Qarham salt lake also contain extremely high Mg content with a Mg/K ratio up to 30 and Mg/Li up to 1000. After the exploitation of potash salts, the waste brine is almost a pure solution of magnesium chloride containing a minor amount of lithium, boron, and other minor constituents.[1] Magnesium chloride cannot be utilized effectively and is discarded back into the lakes. This has caused not only the wasting of valuable magnesium resources but also a serious environmental problem. Therefore, extraction and application of magnesium, lithium, and boron resources that exist in the saline lakes in China is becoming more and more important from economic, environmental, and technological points of view.

Magnesium chloride (or bischofite) has potentially a huge variety of applications in industry. Most importantly, it is a raw material for production of magnesium oxide, magnesium hydroxide, and magnesium metal. Hence a new novel process was proposed by Wang et al.[2] to exploit the extraction and utilization of magnesium resources existing in discarded brine. In this process, magnesium is recovered by precipitation of nesquehonite. This magnesium mineral compound[3] was selected as a target precipitate due to its good filtration properties. Nesquehonite upon calcination yields high-quality magnesium oxide (MgO).[4,5]

The solubility and phase equilibrium of salts in electrolyte aqueous solutions play a significant role in the development, design, optimization, and operation of precipitation processes.[6−8] Solubility is essential to determine phase relationships in a system that includes unstable or metastable solid phases.[9,10] In these cases, solubility determination becomes possible when the equilibrium of unstable and metastable solids in solutions is reached before phase transformation occurs. One example is the solubility of nesquehonite ($MgCO_3 \cdot 3H_2O$)[11] that can be precipitated as $MgCO_3 \cdot 3H_2O$ below 323 K, while $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ precipitates at elevated temperature.[2]

Solubility values of nesquehonite in various aqueous chloride solutions are available in some compilations. It can provide a database for model calculation of the system.[12] However, as we discussed in an earlier paper,[11] most of the previous studies have been limited to reporting only the solubility of $MgCO_3 \cdot 3H_2O$ in single salt solutions at elevated temperatures. There has been limited information on the influence of mixed electrolytes and no information on $MgCO_3 \cdot 3H_2O$ solubility in concentrated chloride electrolytes at elevated temperatures.

The above discussion indicates that there is still a need to systematically investigate the solubility and stability of nesquehonite in mixed chloride electrolyte solutions, and this is done here for the NaCl + $MgCl_2$, NH_4Cl + $MgCl_2$, LiCl, and LiCl + $MgCl_2$ solutions over the temperature range of (298 to 308) K. Additionally, the stability of the corresponding solid phases is examined by XRD and SEM.

Experimental Section

The approaches that determine the solubility of salts in solutions can be categorized as either a dissolution or a precipitation method.[13] The dissolution method is considered to be more reliable and feasible since it avoids the complication of formation of intermediate phases that are commonly encountered in precipitation. In this work, the dissolution method was employed.

Chemicals. All chemical reagents used in the experiments were analytical grade without further purification. All solutions used in this study were prepared by dissolving the relevant chemicals in deionized water (conductivity < 0.1 $\mu S \cdot cm^{-1}$) (Table 1). The solid substance of $MgCO_3 \cdot 3H_2O$ was precipitated by the reaction of $MgCl_2$ with Na_2CO_3 or $(NH_4)_2CO_3$.[2,11] The structure and morphology of the synthesized samples are demonstrated in Figure 1 and Figure 2.

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Table 1. Chemical Reagents Employed

compound name	formula	purpose	provider	purity
magnesium chloride	$MgCl_2 \cdot 6H_2O$	solubility and synthesis	Sinopharm Chemical Reagent Co. Ltd.	≥ 98.0 %
sodium carbonate	Na_2CO_3	synthesis	Chemical Company of Beijing	≥ 99.8 %
ammonium chloride	NH_4Cl	solubility	Chemical Company of Beijing	≥ 99.5 %
sodium chloride	NaCl	solubility	Chemical Company of Beijing	≥ 99.5 %
lithium chloride	LiCl	solubility	Sinopharm Chemical Reagent Co. Ltd.	≥ 97.0 %

Procedure. A typical experimental procedure can be described as follows. A volume of 200 mL of salt solution of known composition was introduced into Erlenmeyer flasks (250 mL volume) which were equipped with a magnetic stirrer and capped with glass stoppers. The flasks were then immersed in a temperature-controlled water bath, allowing the solution to stir continuously for about 0.5 h to establish temperature equilibrium. The temperature was kept constant within 0.1 K. Then, excess solid (3 g of nesquehonite) was quickly added to the solutions in flasks, which were tightly capped again by using glass stoppers to avoid the absorption of CO_2. The standard equilibration time used was 6 h.[11] After solid−liquid equilibrium was attained, stirring was stopped to allow solids to settle. The supernatant solution was then withdrawn and immediately filtered by using 0.22 μm Whatman Puradisc syringe filters. The clear filtrate was added into a 25 mL volumetric flask which was kept in the water bath and then heated to bath temperature for measuring the density of the nesquehonite saturated solution. The solubility (s) of nesquehonite, expressed as moles per kilogram of H_2O, was obtained from C analysis. The content of C was determined by TOC which is used to determine C of organic and inorganic substances in environmental applications. The solid phase was filtered and washed three times with water. The washed solids were dried at 323 K for 12 h and then analyzed by X-ray powder diffraction to determine whether the solid phase had been altered by phase transformation. Additionally, scanning electron microscope (SEM) image techniques were also used for examination of the solid phases.

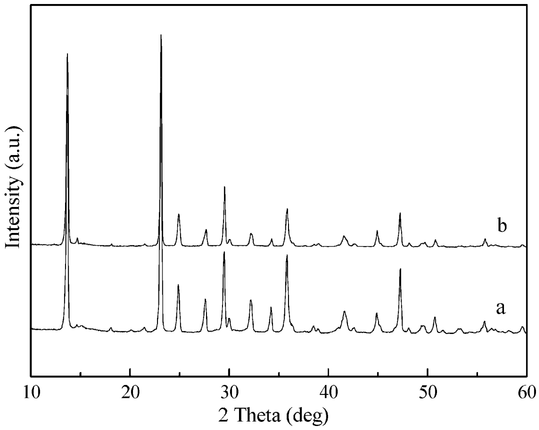

Figure 1. XRD pattern of synthesized $MgCO_3 \cdot 3H_2O$ material compared with literature data. (a) literature value, (b) experimental value.

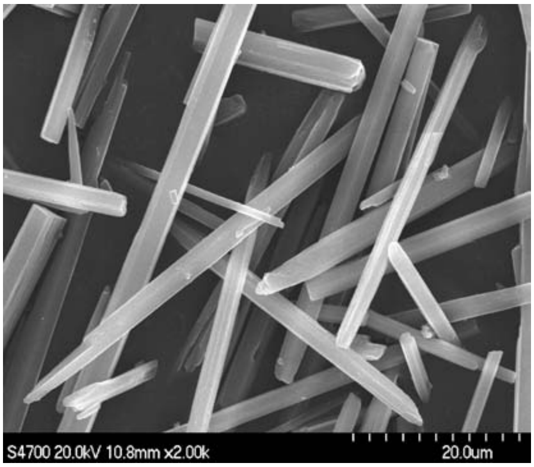

Figure 2. SEM morphology for the synthesized $MgCO_3 \cdot 3H_2O$ material.

Table 2. Solubility of $MgCO_3 \cdot 3H_2O$ (1) in NaCl (2) + $MgCl_2$ (3) + H_2O (4) (Equilibration Time: 6 h)

solution parameters			solubility as $MgCO_3$ in different units		
M_2	M_3	ρ_s	C_1	M_1	m_1
$mol \cdot L^{-1}$	$mol \cdot L^{-1}$	$g \cdot mL^{-1}$	$g \cdot L^{-1}$	$mol \cdot L^{-1}$	$mol \cdot kg^{-1}$ of H_2O
		$T = 298$ K			
0.2	0.05	1.0068	0.5881	0.006975	0.007047
0.2	0.1	1.0116	0.6256	0.007420	0.007497
0.2	0.15	1.0148	0.6710	0.007958	0.008054
0.2	0.2	1.0180	0.7265	0.008617	0.008734
0.2	0.25	1.0224	0.8185	0.009708	0.009845
0.2	0.3	1.0264	0.8909	0.01057	0.01073
0.2	0.35	1.0300	0.9295	0.01103	0.01120
0.2	0.4	1.0332	0.9977	0.01183	0.01205
0.2	0.45	1.0376	1.0356	0.01228	0.01251
0.2	0.5	1.0420	1.0806	0.01282	0.01306
0.2	0.55	1.0452	1.1262	0.01336	0.01363
0.2	0.6	1.0484	1.1789	0.01398	0.01429
		$T = 308$ K			
0.2	0.05	1.0045	0.87965	0.01030	0.01043
0.2	0.1	1.0087	0.87517	0.01024	0.01038
0.2	0.15	1.0113	0.93499	0.01092	0.01109
0.2	0.2	1.0152	0.92789	0.01083	0.01101
0.2	0.25	1.0191	0.98813	0.01152	0.01172
0.2	0.3	1.0239	1.03179	0.01203	0.01224
0.2	0.35	1.0270	1.06583	0.01240	0.01264
0.2	0.4	1.0306	1.11879	0.01300	0.01327
0.2	0.45	1.0347	1.18846	0.01380	0.01410
0.2	0.5	1.0400	1.21794	0.01415	0.01445
0.2	0.55	1.0421	1.25442	0.01453	0.01488
0.2	0.6	1.0458	1.30701	0.01513	0.01550

Results and Discussion

Solubility of $MgCO_3 \cdot 3H_2O$ in Mixed NaCl + $MgCl_2$ Solutions. The solubility of nesquehonite in mixed NaCl (0.2 $mol \cdot dm^{-3}$) + $MgCl_2$ [(0.05 to 0.6) $mol \cdot dm^{-3}$] was obtained at a temperature range of (298 to 308) K. The results of experimentally determined solubility are summarized in Table 2 and demonstrated graphically in Figure 3. In Table 2, the solubility of $MgCO_3 \cdot 3H_2O$ is expressed both in molarity (M/$mol \cdot dm^{-3}$) and molality (m/$mol \cdot kg^{-1}$) for convenient practical and thermodynamic reference.

Figure 3 shows that the solubility of $MgCO_3 \cdot 3H_2O$ increases with increasing concentration of $MgCl_2$ at the same concentration level of NaCl. XRD analysis (Figure 4) shows the solid phase to be stable within the temperature range of (298 to 308) K. The equilibrated solids were examined by SEM. Typical SEM images are presented in Figure 5. It can be clearly seen that the solid phase of $MgCO_3 \cdot 3H_2O$ is needle-shaped at (298 to 308) K.

Solubility of $MgCO_3 \cdot 3H_2O$ in Mixed NH_4Cl + $MgCl_2$ Solutions. The same approach was used to obtain the solubility of $MgCO_3 \cdot 3H_2O$ in mixed $MgCl_2$ (0.2 $mol \cdot dm^{-3}$) + NH_4Cl

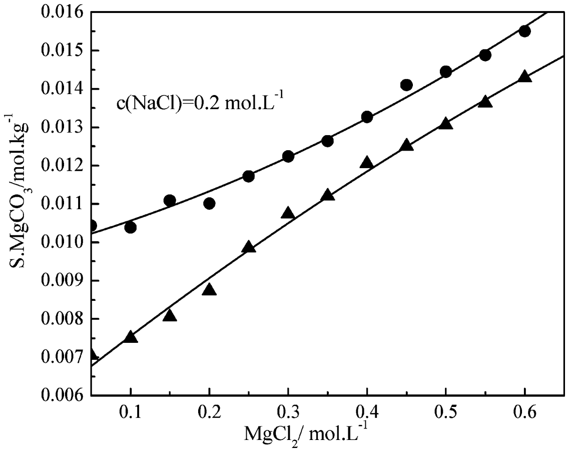

Figure 3. Solubility of $MgCO_3 \cdot 3H_2O$ in mixed solutions (NaCl + $MgCl_2$) at different temperatures: -▲-, 298 K; -●-, 308 K.

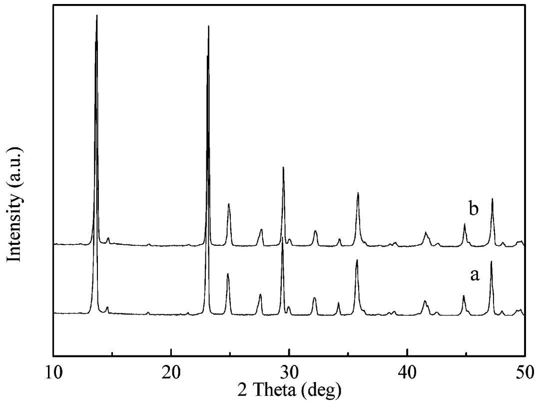

Figure 4. XRD pattern of $MgCO_3 \cdot 3H_2O$ in mixed solutions (NaCl + $MgCl_2$) after 6 h. (a) 298 K, (b) 308 K.

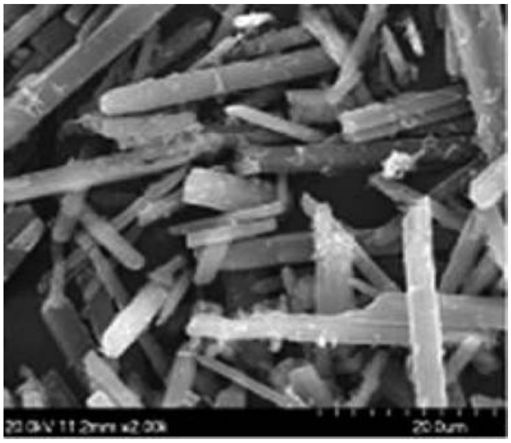

Figure 5. SEM images of $MgCO_3 \cdot 3H_2O$ in mixed solutions (NaCl + $MgCl_2$) at 308 K after 6 h.

[(0.1 to 1.5) $mol \cdot dm^{-3}$] solutions at (298 to 308) K. The results determined in this study are given in Table 3 and graphically in Figure 6. The solubility of $MgCO_3 \cdot 3H_2O$ sharply increases with increasing NH_4Cl concentration and temperature at the same concentration level of $MgCl_2$. XRD patterns (Figure 7) show that $MgCO_3 \cdot 3H_2O$ is stable within the temperature range of (298 to 308) K in mixed NH_4Cl + $MgCl_2$ solutions.

Solubility of $MgCO_3 \cdot 3H_2O$ in Lithium Chloride Solutions. The solubility of $MgCO_3 \cdot 3H_2O$ in lithium chloride solutions with concentrations up to 1.5 $mol \cdot dm^{-3}$ over the temperature range of (298 to 308) K was determined by using the same procedure. The obtained experimental solubility data are shown in Table 4 and Figure 8. Figure 8 illustrates that the solubility of $MgCO_3 \cdot 3H_2O$ increases with the concentration of LiCl. XRD patterns as shown in Figure 9 demonstrate that the solid phase is stable over the temperature range of (298 to 308) K.

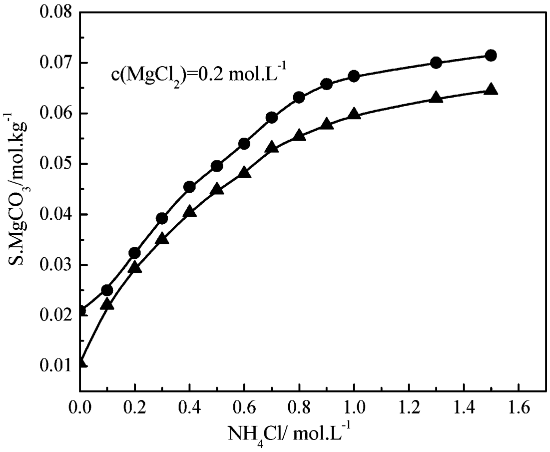

Figure 6. Solubility of $MgCO_3 \cdot 3H_2O$ in mixed solutions (NH_4Cl + $MgCl_2$) at different temperatures. -▲-, 298 K; -●-, 308 K.

Solubility of $MgCO_3 \cdot 3H_2O$ in Mixed LiCl + $MgCl_2$ Solutions. The solubility of nesquehonite in mixed $MgCl_2$ (0.5 $mol \cdot dm^{-3}$) + LiCl [(0.1 to 1.5) $mol \cdot dm^{-3}$] was obtained over the temperature range of (298 to 308) K. The results determined in this study are given in Table 5 and graphically in Figure 10. The solubility of $MgCO_3 \cdot 3H_2O$ sharply increases with increasing LiCl concentration and increases with increasing temperature. XRD patterns (Figure 11) and SEM images (Figure 12) show that $MgCO_3 \cdot 3H_2O$ is stable within the temperature range of (298 to 308) K in mixed $MgCl_2$ + LiCl solutions.

Comparison of Solubility of $MgCO_3 \cdot 3H_2O$ in $MgCl_2$ Solutions and NaCl + $MgCl_2$, NH_4Cl + $MgCl_2$, and LiCl + $MgCl_2$ Mixed Solutions. The comparison of solubility of $MgCO_3 \cdot 3H_2O$ in $MgCl_2$ solutions and NaCl + $MgCl_2$, NH_4Cl + $MgCl_2$, and

Table 3. Solubility of $MgCO_3 \cdot 3H_2O$ (1) in $MgCl_2$ (2) + NH_4Cl (3) + H_2O (4) (Equilibration time: 6 h)

solution parameters			solubility as $MgCO_3$ in different units		
M_2	M_3	ρ_s	C_1	M_1	m_1
$mol \cdot L^{-1}$	$mol \cdot L^{-1}$	$g \cdot mL^{-1}$	$g \cdot L^{-1}$	$mol \cdot L^{-1}$	$mol \cdot kg^{-1}$ of H_2O
			$T = 298$ K		
0.2	0.1	1.0128	1.8347	0.02176	0.02206
0.2	0.2	1.0160	2.4350	0.02888	0.02935
0.2	0.3	1.0160	2.8852	0.03422	0.03499
0.2	0.4	1.0196	3.3211	0.03939	0.04037
0.2	0.5	1.0212	3.6718	0.04355	0.04482
0.2	0.6	1.0236	3.9231	0.04653	0.04804
0.2	0.7	1.0244	4.3143	0.05117	0.05310
0.2	0.8	1.0260	4.4838	0.05318	0.05542
0.2	0.9	1.0280	4.6507	0.05516	0.05769
0.2	1.0	1.0292	4.7915	0.05683	0.05970
0.2	1.3	1.0336	4.9863	0.05914	0.06292
0.2	1.5	1.0372	5.0731	0.06017	0.06450
			$T = 308$ K		
0.2	0.1	1.0100	2.0724	0.02458	0.02499
0.2	0.2	1.0132	2.6753	0.03173	0.03235
0.2	0.3	1.0140	3.2233	0.03823	0.03919
0.2	0.4	1.0152	3.7207	0.04413	0.04544
0.2	0.5	1.0184	4.0462	0.04799	0.04955
0.2	0.6	1.0212	4.3952	0.05213	0.05399
0.2	0.7	1.0208	4.7864	0.05677	0.05916
0.2	0.8	1.0240	5.0967	0.06045	0.06316
0.2	0.9	1.0252	5.2847	0.06268	0.06579
0.2	1.0	1.0272	5.3901	0.06393	0.06735
0.2	1.3	1.0304	5.5276	0.06556	0.07002
0.2	1.5	1.0344	5.5984	0.06640	0.07144

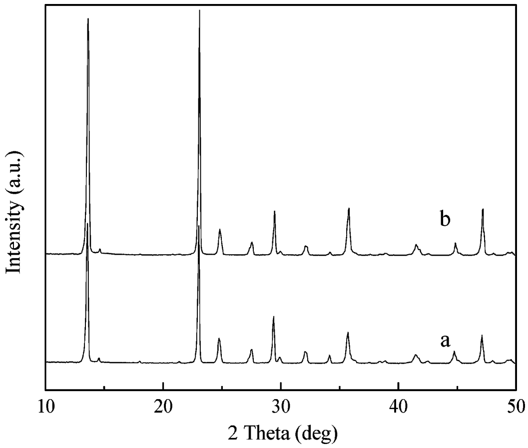

Figure 7. XRD pattern of $MgCO_3 \cdot 3H_2O$ in mixed solutions (NH_4Cl + $MgCl_2$) after 6 h. (a) 298 K, (b) 308 K.

Table 4. Solubility of $MgCO_3 \cdot 3H_2O$ (1) in LiCl (2) + H_2O (3) (Equilibration time: 6 h)

solution parameters		Solubility as $MgCO_3$ in different units		
M_2	ρ_s	C_1	M_1	m_1
$mol \cdot L^{-1}$	$g \cdot mL^{-1}$	$g \cdot L^{-1}$	$mol \cdot L^{-1}$	$mol \cdot kg^{-1}$ of H_2O
		$T = 298$ K		
0.1	0.9988	1.2284	0.01457	0.01466
0.2	1.0000	1.4460	0.01715	0.01732
0.3	1.0040	1.6154	0.01916	0.01936
0.4	1.0064	1.7689	0.02098	0.02125
0.5	1.0108	1.8962	0.02249	0.02277
0.6	1.0112	2.0303	0.02408	0.02448
0.7	1.0136	2.1053	0.02497	0.02543
0.8	1.0144	2.2554	0.02675	0.02735
0.9	1.0204	2.3287	0.02762	0.02818
1.0	1.0204	2.4004	0.02847	0.02918
1.3	1.0268	2.6145	0.03101	0.03200
1.5	1.0320	2.7486	0.03260	0.03376
		$T = 308$ K		
0.1	0.9948	1.3364	0.01585	0.01602
0.2	0.9976	1.7014	0.02018	0.02043
0.3	1.0004	1.7857	0.02118	0.02149
0.4	1.0036	2.1517	0.02552	0.02592
0.5	1.0052	2.2141	0.02626	0.02675
0.6	1.0072	2.5884	0.03070	0.03135
0.7	1.0104	2.6651	0.03161	0.03232
0.8	1.0128	2.9670	0.03519	0.03606
0.9	1.0152	3.0732	0.03645	0.03743
1.0	1.0172	3.2309	0.03832	0.03944
1.3	1.024	3.3042	0.03919	0.04059
1.5	1.0304	3.5142	0.04168	0.04327

LiCl + $MgCl_2$ mixed solutions has been demonstrated graphically in Figure 13. Figure 13 illustrates that the solubility of $MgCO_3 \cdot 3H_2O$ in $MgCl_2$ solutions is larger than that in mixed NaCl + $MgCl_2$ and mixed LiCl + $MgCl_2$ solutions. In NH_4Cl + $MgCl_2$ solutions, the solubility is larger than that in $MgCl_2$ solutions because of the hydrolysis of NH_4^+.

Stability of $MgCO_3 \cdot 3H_2O$ in Na−Mg−NH_4−Li−Cl Brines. The stability of $MgCO_3 \cdot 3H_2O$ in Na−Mg−NH_4−Li−Cl brines was also determined along with solubility measurements. The results are summarized in Table 6. It can be observed that $MgCO_3 \cdot 3H_2O$ is stable in mixed NaCl (0.2 $mol \cdot dm^{-3}$) + $MgCl_2$ [(0.05 to 0.6) $mol \cdot dm^{-3}$] solutions. In mixed $MgCl_2$ + NH_4Cl, it is stable within the concentration of 0.2 $mol \cdot dm^{-3}$ $MgCl_2$ and 0.6 $mol \cdot dm^{-3}$ NH_4Cl at the temperature of (298 and 308) K, while in LiCl solutions it is stable at (298 to 308) K. $MgCO_3 \cdot 3H_2O$ was found to be stable in mixed $MgCl_2$ + LiCl concentrations up to 0.5 $mol \cdot dm^{-3}$ $MgCl_2$ and 1.5 $mol \cdot dm^{-3}$ LiCl.

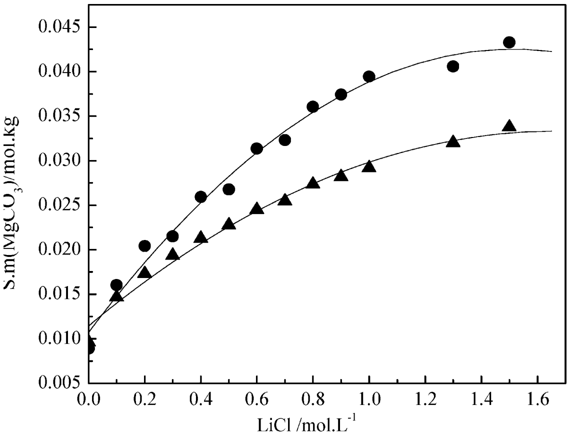

Figure 8. Solubility of $MgCO_3 \cdot 3H_2O$ in LiCl solutions at different temperatures. -▲-, 298 K; -●-, 308 K.

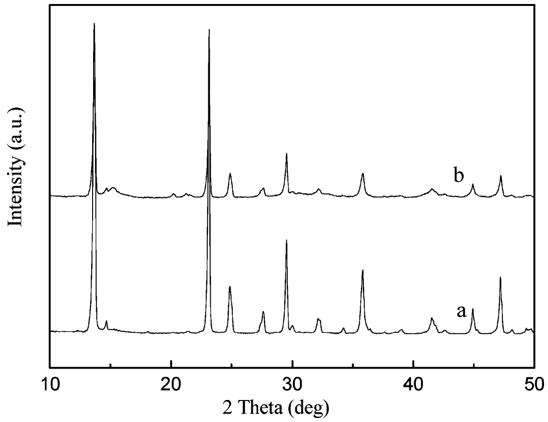

Figure 9. XRD pattern of $MgCO_3 \cdot 3H_2O$ in LiCl solutions after 6 h. (a) 298 K, (b) 308 K.

Thermodynamic Interpretation

The observed behavior of $MgCO_3 \cdot 3H_2O$ solubility in $MgCl_2$ solutions may be explained by considering various equilibria. As an earlier paper discussed, the solubility equilibrium for $MgCO_3 \cdot 3H_2O$ solids in aqueous electrolytes is expressed as follows[11]

$$MgCO_3 \cdot 3H_2O(s) \leftrightarrow Mg^{2+} + CO_3^{\ 2-} + 3H_2O \qquad (1)$$

The solubility of $MgCO_3 \cdot 3H_2O$ is complicated in electrolyte solutions due to the formation of the bicarbonate (HCO_3^-) ion.

$$H^+ + CO_3^{\ 2-} \leftrightarrow HCO_3^{\ -} \qquad (2)$$

The solubility of $MgCO_3 \cdot 3H_2O$ in magnesium chloride solutions increases with an increasing concentration of magnesium chloride because of the formation of $MgHCO_3^+$. The complexation reaction is expressed as follows[14]

$$Mg^{2+} + HCO_3^{\ -} \leftrightarrow MgHCO_3^{\ +} \qquad (3)$$

When the concentration of magnesium chloride increases, Mg^{2+} can be transformed to $MgHCO_3^+$. This is the reason by which the solubility of $MgCO_3 \cdot 3H_2O$ in magnesium chloride media consistently increases with increasing concentration of magnesium chloride.

The observed behavior of $MgCO_3 \cdot 3H_2O$ solubility in NH_4Cl solutions may be explained by the following hydrolysis reaction of NH_4^+

Table 5. Solubility of $MgCO_3 \cdot 3H_2O$ (1) in $MgCl_2$ (2) + LiCl (3) + H_2O (4) (Equilibration time: 6 h)

solution parameters			solubility as $MgCO_3$ in different units		
M_2	M_3	ρ_s	C_1	M_1	m_1
$mol \cdot L^{-1}$	$mol \cdot L^{-1}$	$g \cdot mL^{-1}$	$g \cdot L^{-1}$	$mol \cdot L^{-1}$	$mol \cdot kg^{-1}$ of H_2O
		$T = 298$ K			
0.5	0.1	1.0356	1.1188	0.01327	0.01288
0.5	0.2	1.0372	1.1256	0.01335	0.01299
0.5	0.3	1.0392	1.1332	0.01344	0.01311
0.5	0.4	1.0424	1.1374	0.01349	0.01317
0.5	0.5	1.0440	1.1416	0.01354	0.01326
0.5	0.6	1.0472	1.1509	0.01365	0.01337
0.5	0.7	1.0492	1.1601	0.01376	0.01351
0.5	0.8	1.0516	1.1551	0.01370	0.01348
0.5	0.9	1.0528	1.1703	0.01388	0.01370
0.5	1.0	1.0552	1.1913	0.01413	0.01396
0.5	1.3	1.0620	1.2040	0.01428	0.01420
0.5	1.5	1.0676	1.2183	0.01445	0.01441
		$T = 308$ K			
0.5	0.1	1.0324	1.1871	0.01408	0.01371
0.5	0.2	1.0344	1.2107	0.01436	0.01401
0.5	0.3	1.0368	1.2234	0.01451	0.01418
0.5	0.4	1.0392	1.2419	0.01473	0.01442
0.5	0.5	1.0420	1.2529	0.01486	0.01457
0.5	0.6	1.0440	1.2773	0.01515	0.01489
0.5	0.7	1.0464	1.2967	0.01538	0.01514
0.5	0.8	1.0484	1.2993	0.01541	0.01521
0.5	0.9	1.0500	1.3178	0.01563	0.01547
0.5	1.0	1.0520	1.3288	0.01576	0.01563
0.5	1.3	1.0580	1.3431	0.01593	0.01590
0.5	1.5	1.0648	1.3574	0.01610	0.01610

$$NH_4{}^+ + H_2O \leftrightarrow NH_4OH + H^+ \tag{4}$$

The pH of solution decreases with the increasing concentration of ammonium chloride, and H^+ can increase the solubility of $MgCO_3 \cdot 3H_2O$.[11] Therefore, the solubility of $MgCO_3 \cdot 3H_2O$ in ammonium chloride media consistently increases with increasing concentration of ammonium chloride.

Conclusions

The solubility of $MgCO_3 \cdot 3H_2O$ in mixed NaCl + $MgCl_2$, NH_4Cl + $MgCl_2$, LiCl, and LiCl + $MgCl_2$ solutions has been measured for a wide range of conditions up to 0.2 $mol \cdot dm^{-3}$ NaCl, 0.6 $mol \cdot dm^{-3}$ $MgCl_2$, 1.5 $mol \cdot dm^{-3}$ NH_4Cl, and 1.5 $mol \cdot dm^{-3}$ LiCl and (298 to 308) K. The solubility of $MgCO_3 \cdot 3H_2O$ in mixed NaCl 0.2 $mol \cdot dm^{-3}$ + $MgCl_2$ increases with increasing concentration of $MgCl_2$ and temperature. In mixed 0.2 $mol \cdot dm^{-3}$ $MgCl_2$ + NH_4Cl solutions, it increases with increasing concentration of NH_4Cl and temperature. The solubility of $MgCO_3 \cdot 3H_2O$ in LiCl increases with increasing salt concentration and temperature. The solubility of $MgCO_3 \cdot 3H_2O$ in mixed $MgCl_2$ + LiCl also increases with increasing salt concentration at (298 to 308) K. The comparison of solubility of $MgCO_3 \cdot 3H_2O$ in $MgCl_2$ solutions and mixed NaCl + $MgCl_2$, NH_4Cl + $MgCl_2$, and LiCl + $MgCl_2$ solutions has been investigated. The solubility of $MgCO_3 \cdot 3H_2O$ in $MgCl_2$ solutions is larger than that in mixed NaCl + $MgCl_2$ and mixed

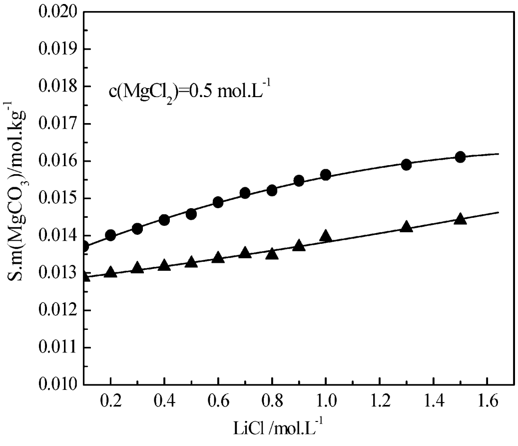

Figure 10. Solubility of $MgCO_3 \cdot 3H_2O$ in mixed solutions (LiCl + $MgCl_2$) at different temperatures. -▲-, 298 K; -●-, 308 K.

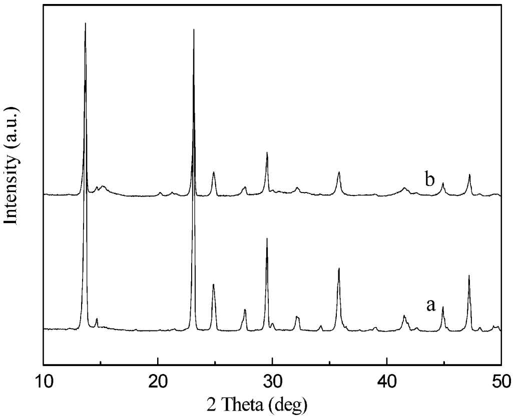

Figure 11. XRD pattern of $MgCO_3 \cdot 3H_2O$ in mixed solutions (LiCl + $MgCl_2$) after 6 h. (a) 298 K, (b) 308 K.

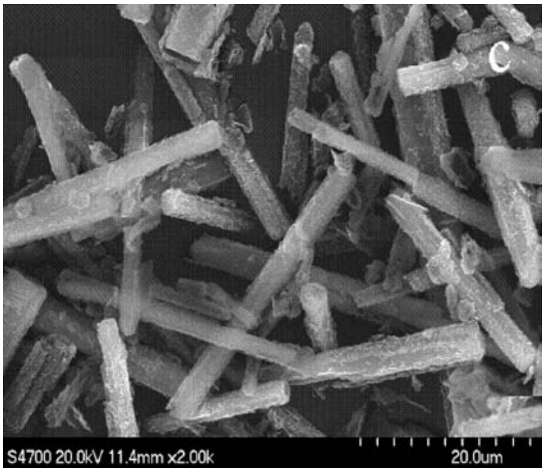

Figure 12. SEM images of $MgCO_3 \cdot 3H_2O$ in mixed solutions (LiCl + $MgCl_2$) at 308 K after 6 h.

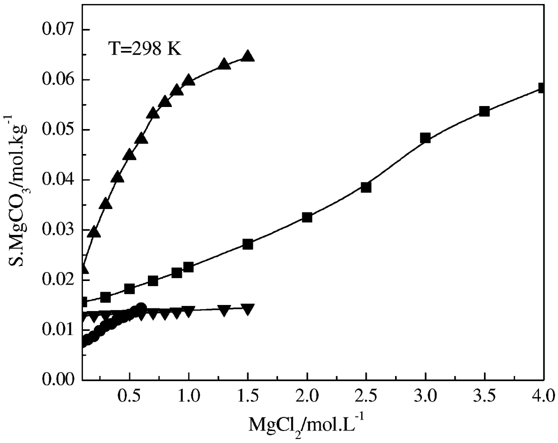

Figure 13. Comparison of solubility of $MgCO_3 \cdot 3H_2O$ in $MgCl_2$ solutions and mixed NaCl + $MgCl_2$, NH_4Cl + $MgCl_2$, and LiCl + $MgCl_2$ solutions. -■-, $MgCl_2$ solutions; -▲-, 0.2 $mol \cdot dm^{-3}$ $MgCl_2$ + NH_4C; -●-, 0.2 $mol \cdot dm^{-3}$ NaCl + $MgCl_2$; -▼-, 0.5 $mol \cdot dm^{-3}$ $MgCl_2$ + LiCl.

Table 6. Stability of $MgCO_3 \cdot 3H_2O$ in Mixed NaCl + $MgCl_2$, NH_4Cl + $MgCl_2$, LiCl, and LiCl + $MgCl_2$ Brines

T / K	M / $mol \cdot L^{-1}$	t / h	equilibrated solid phase(s)
298 to 308	mixed NaCl 0.2 $mol \cdot dm^{-3}$ + $MgCl_2$	6	$MgCO_3 \cdot 3H_2O$
298 to 308	mixed $MgCl_2$ 0.2 $mol \cdot dm^{-3}$ + NH_4Cl	6	$MgCO_3 \cdot 3H_2O$
298 to 308	(0.1 to 1.5) $mol \cdot dm^{-3}$ (LiCl)	6	$MgCO_3 \cdot 3H_2O$
298 to 308	mixed $MgCl_2$ 0.5 $mol \cdot dm^{-3}$ + LiCl	6	$MgCO_3 \cdot 3H_2O$

LiCl + $MgCl_2$ solutions but lower than that in mixed NH_4Cl + $MgCl_2$ solutions because of the hydrolysis of NH_4^+. The behavior of the solubility of $MgCO_3 \cdot 3H_2O$ in $MgCl_2$ solutions was partially explained by thermodynamic interpretation considering $MgHCO_3^+$ formation. XRD results and SEM micrographs indicate that the nesquehonite crystals are stable in mixed solutions (NaCl + $MgCl_2$, NH_4Cl + $MgCl_2$, LiCl, and LiCl + $MgCl_2$) over the temperature range of (298 to 308) K.

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