



Mechanism analysis of ions interaction in $\text{MgCl}_2/\text{LiCl}$ solution and effect of lithium on ammonia precipitation products

Jin TAN¹, Zheng-ping WU^{1,2}, Yuan-bing SUN¹, Jin-ling ZHANG¹, Zhou-lan YIN^{1,2}, Qi-yuan CHEN^{1,2}

1. School of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China;

2. Key Laboratory of Resource Chemistry of Nonferrous Metals, Ministry of Education, Central South University, Changsha 410083, China;

Received 31 March 2014; accepted 25 July 2014

Abstract: Producing magnesium hydroxide is the basic way to utilize magnesium resources of natural brines. However, the effect of lithium on properties of product is always neglected. The interaction between ions in magnesium chloride solution containing lithium was illustrated based on the experimental results, and the effect of lithium on the crystallization of magnesium was clarified. The results of X-ray diffraction (XRD), scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), thermogravimetry analysis (TGA) and laser particle size analysis indicate that the effect of lithium is not obvious on the crystal phase and morphology of the products. But the XRD relative intensity of (001) surface of magnesium hydroxide declines, the specific surface area reduces apparently and the additive mass of lithium affects the heat loss rates of precipitations obviously. Quantum chemical calculations on the interactional systems of $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ and $\text{Li}(\text{H}_2\text{O})_4^+$ were performed using B3LYP/6-311G basis set. The results show that when the distance of Mg^{2+} and Li^+ is 7–10 Å, the interaction energy is high and the trend of solvation is strong, which would make hydroxide ions easier to combine with hydrogen ions in ammonia precipitation process. And the absolute value of solvation free energy reduces significantly in MgCl_2 solution (1 mol/L) containing lithium ion.

Key words: magnesium hydroxide; lithium; ammonia precipitation; interaction between ions; solvation free energy

1 Introduction

Recently, extracting magnesium hydroxide has been the best way to utilize magnesium resources of natural brines [1–3]. The effects of boron and lithium on ammonia precipitation have not been paid enough attention, especially of lithium impurity, which is ignored at all. Some researchers [4–6] studied the removing impurities before precipitating magnesium hydroxide, but there are no relevant reports about the effect of lithium on the properties of magnesium hydroxide.

There are two main reasons why the effect of lithium on precipitation of magnesium hydroxide was rarely studied. One is that the quantity of lithium in solution is very small; the other is that the solubility of magnesium hydroxide is far less than that of lithium hydroxide. From the point of view of thermodynamic, lithium can only exist in the form of Li^+ in solution. But lithium still could not be neglected due to the diagonal

relationship of the periodic table of the elements: the ionic radii and properties of Mg and Li are similar [7]. It is still questionable to ignore the effect of lithium on the properties of precipitations, even though the possibility of entering the lattice of magnesium hydroxide is very small in terms of lithium ion.

The essential connection between the interaction of components in solution and crystallization process and the properties of product also should be taken into consideration. In the mixed solution of lithium and magnesium chloride, the interaction between Mg^{2+} and Li^+ is existent objectively and it is different from that between the same ions. Impurity ions change the microscopic interactions and the effect on the crystallization process and product is actually existent, but the thermodynamic experiments are difficult to reflect and explain the microscopic information, which may mislead us to ignore some microscopic facts. Combining theoretical calculation with experiment is a feasible way to obtain further data about the microscopic

interactions between ions based on the experimental results. PAVLOV et al [8] studied the coordinated behavior of hydrated magnesium ions using density functional theory, and got the octahedral structure of a magnesium ion and six water molecules. MARKHAM et al [9] investigated the contributions of water molecules in the first and second coordination shells to the overall hydration energy of divalent beryllium and magnesium cations. TURNER et al [10] calculated the interaction energy of ionic liquids, 1-alkyl-3-methylimidazolium halides, by ab initio method using Gaussian 98 at 6-31G* and 6-31+G* basis sets level. The cluster-continuum model was employed to calculate the solvation free energies of $\text{VO}_2^+/\text{VO}^{2+}$ ions and some cations (such as Na^+ and Mg^{2+} , etc) in the aqueous solution by ZHAO and XIE [11], PLIEGO and RIVEROS [12] and WESTPHAL and PLIEGO [13], respectively. BRYANSLAV et al [14] researched the solvation free energy using mixed cluster/continuum models. ZHANG et al [15], GAO et al [16], GHATEE et al [17] and SHUKLA et al [18] focused on different ionic liquids and studied the interactional energy of cation–anion, amino acid–halogen anion, etc. MENG et al [19] and TAWA et al [20] did some quantum chemical calculations about molecular structure and solvation free energy.

In this work, experiments combined with theoretical calculation were carried out to investigate the effect of lithium on the properties of magnesium hydroxide precipitated by using ammonia, which was rarely mentioned experimentally until now. A new path to build structure model of complex inorganic solution was

proposed and the solution structure model of actual magnesium chloride containing lithium was simulated using the quantum calculation results of the electronic spatial extent for the first time. Through theoretical calculation of the microscopic interaction between ions, the effect mechanism of lithium ion on the properties of products was clarified.

2 Experimental

2.1 Experimental procedures

MgCl_2 solution (54 mL, 1 mol/L) was measured 8 times and added to eight volumetric flasks (250 mL) separately. Lithium chloride solutions (125, 62.5, 31.2, 15.6, 6.25, 3.12, 1.56 and 0 mL, 6.0 mol/L) were put in the correspondent volumetric flasks respectively, then the mixed solutions were diluted to 250 mL by distilled water. In these mixtures, the concentration of magnesium chloride was 1 mol/L and the concentrations of lithium chloride were 3.0, 1.5, 0.75, 0.375, 0.15, 0.075, 0.0375 and 0 mol/L (denoted as samples 8, 7, 6, 5, 4, 3, 2, 1, respectively). The flowchart is shown in Fig. 1.

These solutions were held at the constant temperature of 25 °C and stirred at the speed of 1800 r/min. The ammonia was prepared at the temperature of 60–90 °C with self-made device. Excess ammonia gas was put into the device until the thin film solid on the surface of solution disappeared; the suspension liquid was stirred a few minutes and aged for 30 min, then it was transferred into the reserve container. Eight different samples were prepared followed the above steps. The suspension liquid was separated by means of

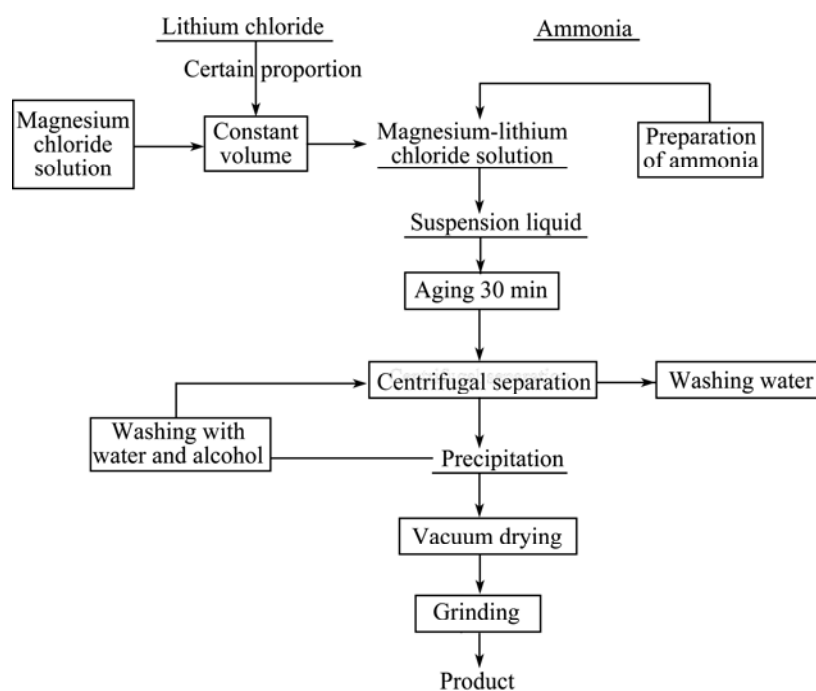


Fig. 1 Flowchart of magnesium hydroxide prepared via ammonia precipitation

centrifugation at 6000 r/min for 5 min; the precipitations were washed 3 times with distilled water and 1 time with alcohol at last. The final products were dried 12 h under 0.08 MPa vacuum degree at 80 °C, then cooled to room temperature and ground in an agate crucible. The white powder was collected finally.

The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku 2500 diffractometer equipped with a sealed Cu tube. SEM images were characterized by Nova Nano SEM 230 scanning electron microscope (SEM). IR spectra were determined at room temperature with Nico LET-6700 FTIR and the thermogravimetric analysis (TGA) data were obtained on Thermo TG/FT-IR in nitrogen atmosphere (70 mL/min) at a constant rate of 5 °C/min from 25 °C to 600 °C. The powder was dispersed with ultrasonic vibrations for 30 min and then the particle size and distribution of the powder were measured using a laser particle size analyzer (Malvern, Mastersizer 2000).

2.2 Computational methods

Firstly, geometry optimization and frequency calculations of $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ and $\text{Li}(\text{H}_2\text{O})_4^+$ were performed at B3LYP/6-311G level respectively. These optimized structures of $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ and $\text{Li}(\text{H}_2\text{O})_4^+$ were initial models. Secondly, the position of Mg^{2+} from $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ was fixed and the other atoms were non-restrictive. At last, $\text{Li}(\text{H}_2\text{O})_4^+$ was put near $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ randomly. The optimized calculation and frequency calculations were implemented on this model using the same basis set.

The distance of Mg^{2+} and Li^+ of the optimized structure of $\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+$ was used as starting point and the straight-line distance of Mg^{2+} and Li^+ was changed by step 5 Å. At the same time, the optimized structure of $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ and $\text{Li}(\text{H}_2\text{O})_4^+$ were maintained respectively. The single-point energy was calculated at the B3LYP/6-311G and B3LYP/6-311G/SCRF=(IEFPCM, solvent=water).

According to the electronic spatial extent calculated by single-point energy calculation, the number of water molecule which could be accommodated in the system of $\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+$ was calculated at different distances of Mg^{2+} and Li^+ one by one. The ratio of Mg^{2+} and H_2O in 1 mol/L MgCl_2 solution was close to 1:54. The experimental solution was simulated based on the calculation result of distances between ions, and the structure models of $\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+$, $\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Mg}(\text{H}_2\text{O})_6^{2+}$ and $\text{Li}(\text{H}_2\text{O})_4^+-\text{Li}(\text{H}_2\text{O})_4^+$ were built respectively. The fixed distance between cations and the optimized structure and solvation energy were implemented. The schematic drawing of calculation model is presented in Fig. 2 and all calculations were performed on the high performance workstation of Central South University.

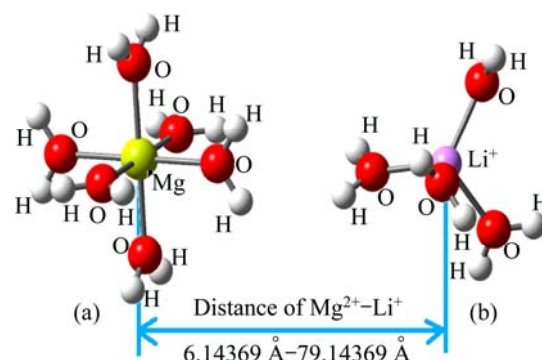


Fig. 2 Schematic drawing of calculation model: (a) $\text{Mg}(\text{H}_2\text{O})_6^{2+}$; (b) $\text{Li}(\text{H}_2\text{O})_4^+$

3 Results and discussion

3.1 X-ray diffraction analysis

X-ray diffraction patterns of the samples are illustrated in Fig. 3. The four patterns are in agreement with the standard JCPDS card (PDF-21-0297), and the narrow diffraction peaks indicate that the precipitations are quite pure. Figure 3 shows that there are no impurity peaks and the effect of lithium on the crystal phase is unobservable. Although Mg and Li are diagonal relationship elements, lithium ion is difficult to replace magnesium ion in $\text{Mg}(\text{OH})_2$ lattice in the process of precipitating magnesium hydroxide.

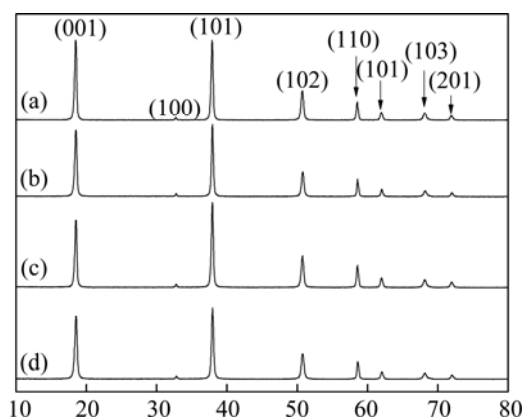


Fig. 3 X-ray diffraction patterns of samples with different LiCl concentrations: (a) Sample 1; (b) Sample 4; (c) Sample 6; (d) Sample 8

The ratios of XRD peak intensity of (001) and (101) planes, $I_{(001)}/I_{(101)}$, are listed in Table 1. Compared with sample 1, with the increasing of concentration of lithium, the values of $I_{(001)}/I_{(101)}$ change greatly, and the XRD peak relative intensity of (001) plane declines, which is a weak polar crystal surface. Furthermore, with increase of lithium content, the crystal size according to Sherrer formula based on (001) plane decreases, while that of (101) is enlarged. Though the effect of lithium on the

magnesium hydroxide crystal phase can not be seen directly in Fig. 3 and lithium ion is difficult to replace magnesium ion of magnesium hydroxide lattice, Table 1 still implies that lithium changes the surface properties in the growth process, and the effect of lithium on the crystal growth should be taken into consideration.

Table 1 Crystal size according to Sherrer formula of ammonia precipitation products and intensity ratios of (001) and (101) planes

Sample No.	Crystal size/nm		$I_{(001)}/I_{(101)}$
	(101)	(001)	
1	274	261	99.3%
4	295	244	91.8%
6	275	257	78.6%
8	268	222	88%

3.2 FTIR analysis

Figure 4 shows the FTIR spectra of the products prepared using 1 mol/L MgCl_2 solution containing LiCl with different concentrations. There are four absorption peaks at least from 1000 cm^{-1} to 4000 cm^{-1} in the FTIR spectra of Samples 1–8: 1) the O—H stretching vibration near 3696 cm^{-1} is the characteristic absorption peak of magnesium hydroxide; 2) the absorption peak at 3420 cm^{-1} is the stretching vibration of association hydroxyl bond; 3) the bending vibration peak of H—O—H bond is at 1639 cm^{-1} ; 4) the skeletal vibration peak of Mg—O is at $500\text{--}840\text{ cm}^{-1}$. The peak at 3420 cm^{-1} denotes the existence of association hydrogen bond. Actually, the products prepared via ammonia precipitation are small and flake powder, the oxygen with strong electronegativity should be easy to combine with exposed proton of other crystal nucleus in a certain direction, which would induce the association of —OH. The H—O—H bond bending vibration peak at 1639 cm^{-1}

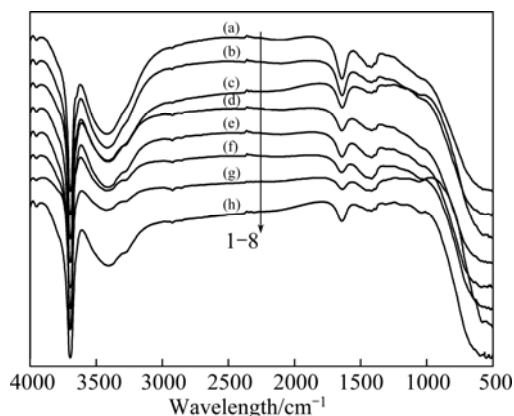


Fig. 4 FTIR spectra of samples with different LiCl concentrations: (a) Sample 1; (b) Sample 2; (c) Sample 3; (d) Sample 4; (e) Sample 5; (f) Sample 6; (g) Sample 7; (h) Sample 8

cm^{-1} and absorption peak at 1419 cm^{-1} , which should be weakened or even disappeared with the decreasing of polarity, are relative to the precipitation polarity.

It can not be confirmed whether lithium exists in the products based on FTIR spectra, because the characteristic absorption peak of LiOH at $(3687\pm 50)\text{ cm}^{-1}$ is close to that of $\text{Mg}(\text{OH})_2$ at 3696 cm^{-1} . Comparing with the absorption peaks of eight samples, it can be found that the peak changes, but the characteristic peaks are in good coherence and the eight FTIR spectra reveal no significant difference.

3.3 SEM analysis

Figure 5 displays SEM images of the samples prepared using 1 mol/L MgCl_2 solution containing 0, 0.75, 3.0 mol/L LiCl respectively via ammonia precipitation. The particles of Sample 1 are unequal and irregular. The agglomeration phenomena could be seen in Figs. 5(b) and (c), and the growth plane and cleavage plane of these two crystals are not observed.

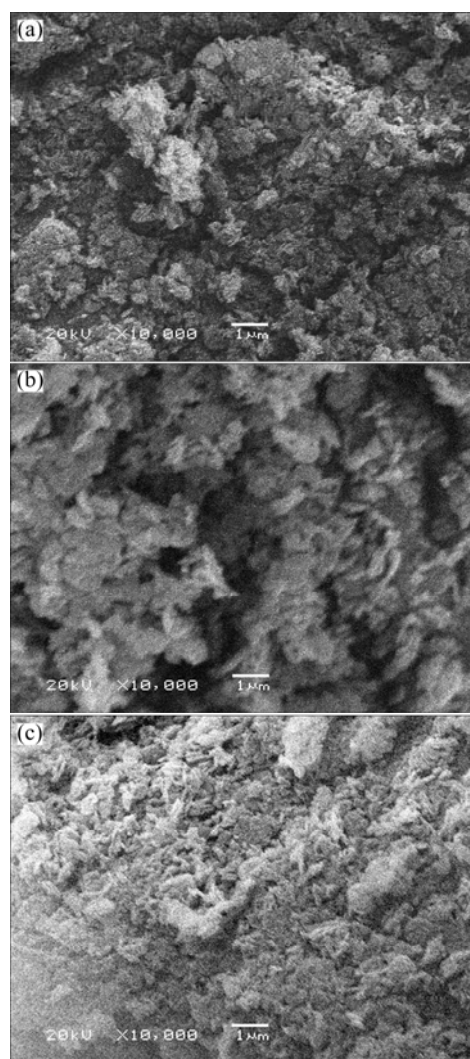


Fig. 5 SEM images of samples with different LiCl concentrations: (a) Sample 1; (b) Sample 6; (c) Sample 8

3.4 Laser particle size analysis

The particle size distribution and relative parameters are shown in Fig. 6 and Table 2, which are in coincidence with the SEM results. The $d(0.5)$ of Sample 1 is less than 1 μm and the particles are small and dispersive with poor uniformity. Moreover, the strong peak in the large particle orientation implies the existence of agglomeration phenomena. Because of the existence of lithium that affects the crystal growth process, the particle sizes of Samples 4, 6 and 8 are larger than that of Sample 1. Combining with the results of XRD analysis, it can be confirmed that lithium acts as a certain role in promoting crystal growth and increases the sizes of some crystal surface. From the distributions of $d(0.5)$ (2.7–3.7 μm), it is obvious that the particle sizes of Samples 4, 6 and 8 are uniform, and the quantity of lithium impurity does not affect the particle size.

In addition, the specific surface areas of Samples 4, 6 and 8 are far less than that of Sample 1, which suggests that the larger the specific surface areas, the more obvious the agglomeration phenomena, thereby the dispersion property is poor. Because the growth of weak polar faces of Samples 4, 6 and 8 is slower than that of Sample 1, the agglomeration phenomena occur, and the particle size of the products increases.

3.5 Thermogravimetric analysis

TGA curves and the parameters of TGA are illustrated in Fig. 7 and Table 3. The results demonstrate that the mass loss rates of precipitations change with the increase of concentration of LiCl. Firstly, the mass loss rates of precipitations in Samples 4, 6 and 8 are about 27.5% and close to that of Sample 1. Secondly, the peak values of Samples 4, 6 and 8 in the range of 358–380 $^{\circ}\text{C}$ are higher than that of Sample 1 and this should be related to particle size and agglomeration situation. Thirdly, the mass loss rates of Samples 5–8 increase to about 30.0%. However, the peak temperature of TG decreases apparently with the increase of concentration of LiCl. It can be concluded that lithium does not change the composition of precipitation, but it has an effect on the crystallization process. On the one hand, the effect of lithium on the formation of growth units of magnesium hydroxide is to change the growth habit plane in the initial nucleation stage, thereby the particle size becomes small and the mass loss rate increases; on the other hand, the existence of lithium might deform the structure of growth units of magnesium hydroxide and rise the crystallization defects that would become the active sites in the later thermal decomposition stage and the factors of accelerating thermal decomposition reaction.

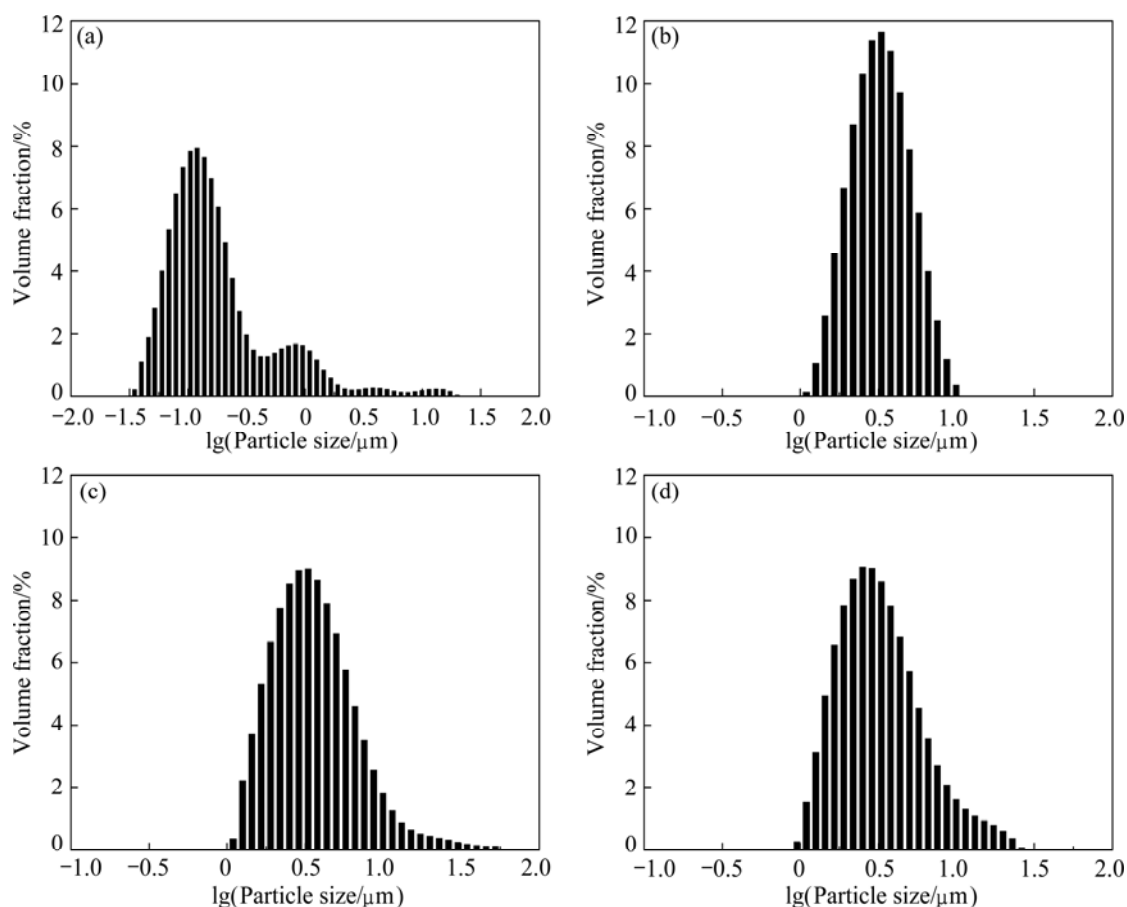


Fig. 6 Particle size distributions of products prepared using MgCl_2 solution containing lithium: (a) Sample 1; (b) Sample 4; (c) Sample 6; (d) Sample 8

Table 2 Particle size distribution parameters of products prepared using MgCl_2 solution containing lithium

Sample No.	$D[4,3]/\mu\text{m}$	$D[3,2]/\mu\text{m}$	$d(0.5)/\mu\text{m}$	SSA/ $(\text{m}^2\cdot\text{g}^{-1})$
1	0.551	0.131	0.15	45.9
4	3.86	3.194	3.486	1.88
6	5.038	3.283	3.653	1.83
8	4.408	2.956	3.255	2.03

$D[4,3]$: the volume weighted average particle size; $D[3,2]$: the surface weighted average particle size; $d(0.5)$: the average grain size with 50% volume fraction; SSA: the specific surface area

3.6 Interaction between ions in magnesium chloride solution containing lithium

The results of experiments reveal that lithium has an effect on the properties of products. Intrinsically, the existence of lithium ion should be considered and it changes the interaction between ions and the micro-environment of crystallization process. Those variations are difficult to perceive and distinguish by experimental methods, but the effects indeed exist. Quantum chemical calculation is a real effective way to explore the interaction between ions at present.

With the initial models of optimized structures of $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ and $\text{Li}(\text{H}_2\text{O})_4^+$, the position of Mg^{2+} from

$\text{Mg}(\text{H}_2\text{O})_6^{2+}$ is fixed and $\text{Li}(\text{H}_2\text{O})_4^+$ is placed near $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ randomly. The optimized calculation on $\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+$ is performed and the optimized results are found that the optimized distance between Mg^{2+} and Li^+ is 69.1414396 Å. The energy of $\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+$ is the lowest and the repulsive force is the smallest only when the distance between Mg^{2+} and Li^+ is very far, which suggests that the effect of Li^+ in the MgCl_2 solution should be ignored when the concentration of lithium is extremely low. But the distance between Mg^{2+} and Li^+ in actual solution is far less than 69.1414396 Å. Therefore, 69.1414396 Å is decreased by step 5 Å and the total energy, solvation free energy $\Delta G(\text{solv})$, dipole moment and electronic spatial extent of $\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+$ with different distances of $\text{Mg}^{2+}-\text{Li}^+$ are calculated in vacuum and water, respectively.

The interaction energy of $\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+$ is defined as follows:

$$E_{\text{Interaction}(\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+)} = E_{\text{Total}(\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+)} - E_{\text{Total}(\text{Mg}(\text{H}_2\text{O})_6^{2+})} - E_{\text{Total}(\text{Li}(\text{H}_2\text{O})_4^+)} \quad (1)$$

where $E_{\text{Interaction}(\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+)}$ is the interaction energy

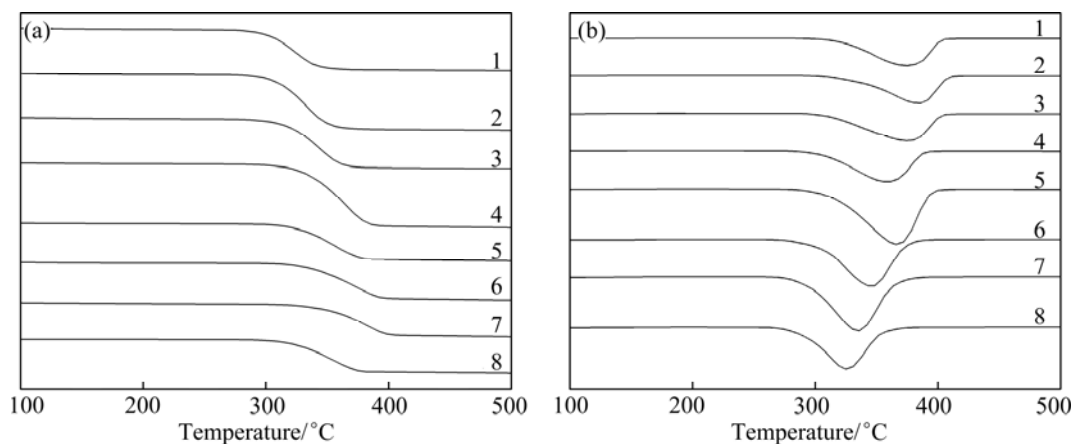


Fig. 7 TG-DTG curves of products prepared using MgCl_2 solution containing lithium: (a) TG curve; (b) DTG curve (1—Sample 1; 2—Sample 2; 3—Sample 3; 4—Sample 4; 5—Sample 5; 6—Sample 6; 7—Sample 7; 8—Sample 8)

Table 3 Analyzed parameters of TG of products prepared using MgCl_2 solution containing lithium

Sample No.	$t_s/^\circ\text{C}$	m_s/mg	$t_l/^\circ\text{C}$	m_l/mg	$t_e/^\circ\text{C}$	m_e/mg	$\omega/\%$
1	272.05	12.30	356.22	10.05	390.98	8.91	27.56
2	302.03	12.11	380.31	9.99	408.65	8.79	27.46
3	283.89	13.44	374.05	10.91	402.44	9.74	27.53
4	277.68	13.61	358.64	11.14	396.62	9.85	27.61
5	265.66	22.94	365.92	18.45	408.48	16.35	28.74
6	265.97	17.21	345.72	13.86	396.87	12.03	30.12
7	259.79	19.40	335.96	15.65	396.80	13.61	29.84
8	259.77	14.18	324.96	11.72	384.95	9.96	29.75

t_s is the initial temperature; t_e is the final temperature; m_s is the initial mass; m_e is the final mass; t_l and m_l are the corresponding temperature and mass of the point with the greatest rate of change on mass loss curve; ω is the mass loss rate.

of $\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+$; $E_{\text{Total}}(\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+)$, $E_{\text{Total}}(\text{Mg}(\text{H}_2\text{O})_6^{2+})$ and $E_{\text{Total}}(\text{Li}(\text{H}_2\text{O})_4^+)$ are the total energies of $\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+$, $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ and $\text{Li}(\text{H}_2\text{O})_4^+$, respectively.

Figure 8 shows the interaction energy curves of $\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+$ in vacuum and solution separately. The interaction energy of $\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+$ in solution is nearly 15 times less than that in vacuum, which means that the repulsive force of $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ and $\text{Li}(\text{H}_2\text{O})_4^+$ in solution is smaller than that in vacuum. In solution, the interaction energy between groups is large when the distance is less than 10 Å, and it is 5 times as large as the energy between groups when the distance is 15–20 Å. The interaction energy is constantly low when the distance is more than 20 Å. It indicates that the interaction energy is high and the effect of interaction between ions is obvious when the distance of Mg^{2+} and Li^+ is less than 10 Å in the mixed solution.

The $\Delta G(\text{solv})$ curve of $\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+$ is illustrated in Fig. 9. With the increasing of the distance, the absolute value of solvation energy of $\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+$ decreases and the value has a tendency to be stabilized, which implies that the solvation trend also declines gradually. When the distance is less than 15 Å, $\Delta G(\text{solv})$ becomes large, so that the shorter the distance,

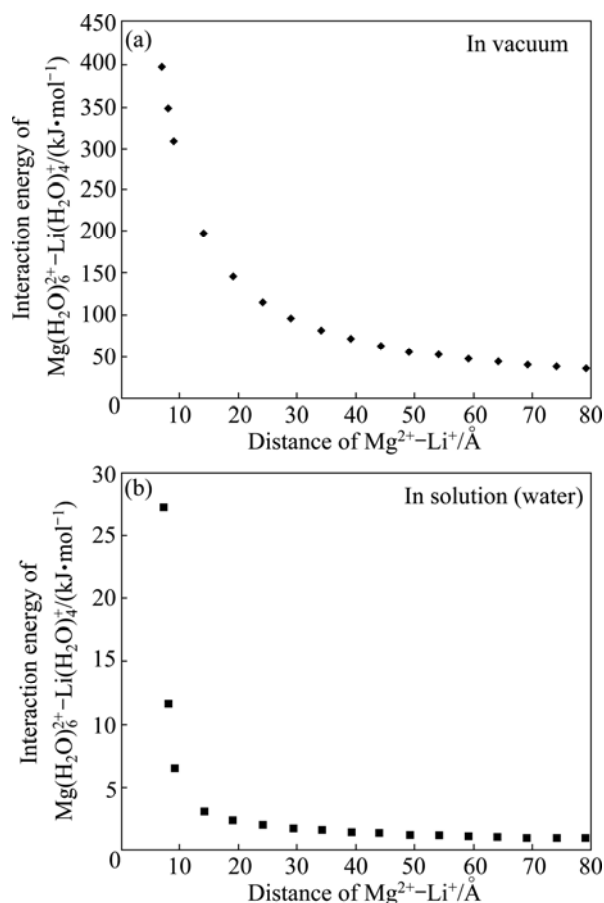


Fig. 8 Interaction energy curves of $\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+$

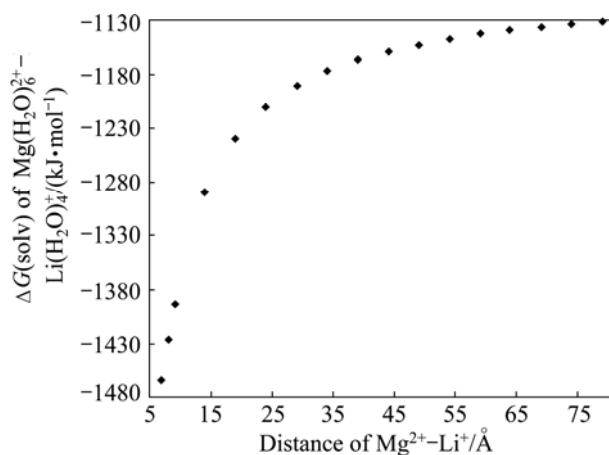


Fig. 9 $\Delta G(\text{solv})$ curve of $\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+$

the more distinct the solvation effect is. Furthermore, in actual solution, the effect of $\text{Mg}^{2+}-\text{Li}^+$ distance on the solvation trend could change the precipitation environment of $\text{Mg}(\text{H}_2\text{O})_6^{2+}$, and when this distance is less than 10 Å, the solvation trend comes to be more obvious. For the solute $\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+$, the dynamic properties (such as conductivity) and static properties (such as the activity coefficient) change because the number of free water molecule decreases in solution. For solvent, due to the rising trend of solvation, the tetrahedron of water layers surrounding solute is damaged more easily, and then the ion directional action of $\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+$ is enhanced because of the dipole of water. The simple conclusions are that the higher the concentration of solution is, the larger the absolute value of solvation energy is; when the distance is 7–10 Å, the solvation trend in concentrated solution is far more obvious than that in dilute solution. Consequently, OH^- can capture H^+ more easily in the ammonia precipitation process.

In experiments, the concentration of MgCl_2 solution is 1 mol/L, so that the ratio of molecule number of Mg^{2+} and H_2O is 1:54. The calculated strategy is to estimate the occupied space of molecule group according to the calculation result of electronic spatial extent, and the number of water can be calculated using the formula as follows:

$$N_{\text{H}_2\text{O}} = 0.3401 \times \{ \varphi_{(\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Mg}(\text{H}_2\text{O})_6^{2+})} - [\varphi_{(\text{Mg}(\text{H}_2\text{O})_6^{2+})} + \varphi_{(\text{Li}(\text{H}_2\text{O})_4^+)}] / 0.3401 \} / \varphi_{(\text{H}_2\text{O})} \quad (2)$$

where $N_{\text{H}_2\text{O}}$ is the number of H_2O molecule, 0.3401 is the space utilization factor, φ is the electronic spatial extent. According to the calculation results of H_2O number (see Table 4), the distance is 8–9 Å when the number of water molecule is about 54. As a result, the distance between two cations is frozen at 8.14 Å. The calculation models

of $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ – $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ and $\text{Li}(\text{H}_2\text{O})_4^+$ – $\text{Li}(\text{H}_2\text{O})_4^+$ are built (see Fig. 10) and the optimized calculations are carried out.

Table 4 Estimates of H_2O number of $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ – $\text{Li}(\text{H}_2\text{O})_4^+$

Distance/ Å	In vacuum		In solution	
	φ	$N_{\text{H}_2\text{O}}$	φ	$N_{\text{H}_2\text{O}}$
79.14369	589601.44	10176.96	589599.5	10177.03
74.14369	517710.25	8925.28	517708.4	8925.35
69.14396	450506.11	7755.21	450504.3	7755.27
64.14396	387989.01	6666.74	387987.3	6666.80
59.14396	330158.94	5659.87	330157.3	5659.94
54.14369	277015.90	4734.61	277014.4	4734.68
49.14369	228559.90	3890.95	228558.5	3891.03
44.14369	184790.92	3128.90	184789.7	3128.98
39.14369	145708.96	2448.45	145707.9	2448.54
34.14369	111314.01	1849.61	111313.1	1849.70
29.14369	81606.04	1332.37	81605.4	1332.46
24.14369	56585.03	896.74	56584.74	896.83
19.14369	36250.88	542.70	36251.12	542.81
14.14369	20603.40	270.27	20604.54	270.39
9.14369	9641.89	79.42	9644.884	79.576
8.14369	8011.58	51.03	8015.07	51.20
7.14369	6568.49	25.91	6572.283	26.08
6.14369	5313.8126	4.06	5317.586	4.23

The results of the solvation free energy $\Delta G(\text{solv})$, solvation stable energy $\Delta E(\text{solv})$ and the dipole moments are recorded in Table 5. $\Delta E(\text{solv})$ is defined as

$$\Delta E(\text{solv}) = -(E_{\text{tol}(\text{in solution})} - E_{\text{tol}(\text{in vacuum})}) \quad (3)$$

Table 5 Calculation results of $\Delta G(\text{solv})$, $\Delta E(\text{solv})$ and dipole moment

System	$\Delta G(\text{solv})/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta E(\text{solv})/(\text{kJ}\cdot\text{mol}^{-1})$	Dipole moment/(C·m)
$\text{Mg}(\text{H}_2\text{O})_6^{2+}$ – $\text{Li}(\text{H}_2\text{O})_4^+$	–1380.6122	1444.739265	2.5035
$\text{Mg}(\text{H}_2\text{O})_6^{2+}$ – $\text{Mg}(\text{H}_2\text{O})_6^{2+}$	–2273.6693	2342.844105	0.1001
$\text{Li}(\text{H}_2\text{O})_4^+$ – $\text{Li}(\text{H}_2\text{O})_4^+$	–666.5428	726.1994767	0.4973

Figure 10 and Table 5 show that the optimized structures of $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ – $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ and $\text{Li}(\text{H}_2\text{O})_4^+$ – $\text{Li}(\text{H}_2\text{O})_4^+$ are cross-symmetric and their dipole moments are 0.1001 and 0.4973, respectively, which are close to zero. Instead, the dipole moment of $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ – $\text{Li}(\text{H}_2\text{O})_4^+$ is 2.5035, far larger than that of $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ – $\text{Mg}(\text{H}_2\text{O})_6^{2+}$. Additionally, the tetrahedron

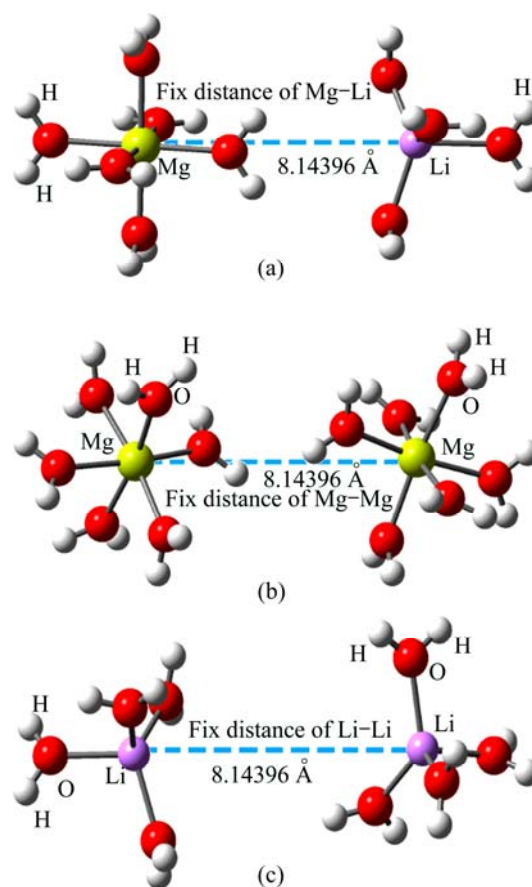


Fig. 10 Optimized structure models of $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ – $\text{Li}(\text{H}_2\text{O})_4^+$, $2\text{Mg}(\text{H}_2\text{O})_6^{2+}$ and $2\text{Li}(\text{H}_2\text{O})_4^+$: (a) $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ – $\text{Li}(\text{H}_2\text{O})_4^+$ optimized model (Mg^{2+} – Li^+ =8.14369 Å); (b) $2\text{Mg}(\text{H}_2\text{O})_6^{2+}$ optimized model (Mg^{2+} – Mg^{2+} =8.14369 Å); (c) $2\text{Li}(\text{H}_2\text{O})_4^+$ optimized model (Li^+ – Li^+ =8.14369 Å)

of $\text{Li}(\text{H}_2\text{O})_4^+$ in $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ – $\text{Li}(\text{H}_2\text{O})_4^+$ is distorted clearly and the direction of —OH in three hydration groups close to the side of $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ is distorted apparently. Furthermore, the absolute value of solvation free energy and solvation stable energy of $\text{Li}(\text{H}_2\text{O})_4^+$ – $\text{Li}(\text{H}_2\text{O})_4^+$ are far less than those of the other systems, and the absolute value of solvation free energy and the solvation stable energy of $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ – $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ are all the largest, which is also far larger than those of $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ – $\text{Li}(\text{H}_2\text{O})_4^+$. It can make a conclusion that the absolute value of solvation free energy would decrease as a result of lithium impurity in solution. Although lithium is difficult to precipitate in the ammonia precipitation process, the effects of lithium on the properties of MgCl_2 solution should not be ignored at all. Reducing of the absolute value of solvation free energy would change the precipitation process and the properties of product. Microscopically, the effect of lithium impurity on the interaction between ions could change the dynamic and static properties, then would make solvation property different, and consequently,

affecting the formation and transformation of crystal unit. Thereby, characteristic of crystallization should be changed in some degree eventually.

4 Conclusions

1) The results of XRD, FTIR, SEM, TGA and laser particle size analysis show that the effect of lithium on the crystal phase and morphology of $\text{Mg}(\text{OH})_2$ is not very obvious, but the relative intensity of the (001) surface of $\text{Mg}(\text{OH})_2$ declines and the average specific surface area of the precipitates decreases. Apparently, the quantity of lithium affects the heat loss rate.

2) The interaction of ions in 1 mol/L MgCl_2 solution is simulated. The dipole moment calculation results imply that the tetrahedron of $\text{Li}(\text{H}_2\text{O})_4^+$ from $\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+$ is distorted and the direction of $-\text{OH}$ in three hydration groups close to the side of $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ is twisted. The absolute values of solvation free energy of $\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Mg}(\text{H}_2\text{O})_6^{2+}$, $\text{Li}(\text{H}_2\text{O})_4^+-\text{Li}(\text{H}_2\text{O})_4^+$ and $\text{Mg}(\text{H}_2\text{O})_6^{2+}-\text{Li}(\text{H}_2\text{O})_4^+$ are -2273.6693 , -666.5428 and -1380.6122 kJ/mol, respectively, which suggests that the effects of lithium on the properties of MgCl_2 solution should be considered. Lithium impurity could change the dynamic and static properties of the solution, and the formation and transformation of crystal unit and crystallization properties in some degree.

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含锂氯化镁溶液离子间作用解析及 锂对氨沉产物性质的影响

谈进¹, 吴争平^{1,2}, 孙元兵¹, 张锦玲¹, 尹周澜^{1,2}, 陈启元^{1,2}

1. 中南大学 化学化工学院, 长沙 410083;

2. 中南大学 教育部有色金属资源化学重点实验室, 长沙 410083

摘 要: 氨法沉镁是盐湖镁资源综合利用的基本途径, 而溶液中少量杂质锂对产品性质的影响一直被忽略。从含锂氯化镁溶液中离子间作用的角度阐述杂质锂对氨法沉镁产物性质影响机制。采用 XRD、SEM、FTIR、TGA 和激光粒度分析等研究锂杂质对氨法制备氢氧化镁过程及其产物性质的影响规律; 在 6-311G/B3LYP 基组水平对 $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ 和 $\text{Li}(\text{H}_2\text{O})_4^+$ 体系进行量子化学计算, 解析镁锂离子间的作用机制。结果表明: 锂的存在对氨沉产物的晶相、形貌和红外吸收影响较小, 但在含锂杂质条件下制备的氢氧化镁产物, (001)弱极性晶面的相对强度有所下降, 产物的比表面积明显变小, 热失重率随制备过程中锂添加量的变化发生了较为显著的改变。在含锂氯化镁水溶液中, 当溶液中 Mg^{2+} 和 Li^+ 间距离小于 10 Å 时作用能较大; 当 Mg^{2+} - Li^+ 间距离在 7~10 Å 时, 溶剂化趋势远大于稀溶液, 氨沉时 OH^- 更易定向夺氢; 首次用电子空间范围计算结果模拟了 1 mol/L 溶液中离子间作用模型, 发现锂离子的存在会使溶剂化自由能的 $\Delta G(\text{solv})$ 绝对值大幅减小。

关键词: 氢氧化镁; 锂; 氨法沉镁; 离子间作用力; 溶剂化自由能

(Edited by Yun-bin HE)