NH$_4^+$-Mg^{2+}-PO$_4^{3-}$-H$^+$-H$_2$O 体系的优势区相图

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摘要: 通过优势区相图的构建对 NH$_4^+$-Mg^{2+}-PO$_4^{3-}$-H$^+$-H$_2$O 体系的热力学平衡关系进行了研究。在不同镁、磷物质的量比和离子强度的条件下绘制了 lg$C_{T,Mg}$-lg$C_{T,P}$ 和 lg$C_{T,P}$-pH 相图, 确定了 MgNH$_4$PO$_4$·6H$_2$O、Mg$_3$(PO$_4$)$_2$·8H$_2$O、MgHPO$_4$·3H$_2$O 和 Mg(OH)$_2$ 的热力学稳定区。结果表明, 在相当广的 pH 范围内, MgNH$_4$PO$_4$·6H$_2$O 和 Mg$_3$(PO$_4$)$_2$·8H$_2$O 都是主要存在的固相; 在较低 pH 和较高磷浓度的条件下, MgNH$_4$PO$_4$·6H$_2$O 和 MgHPO$_4$·3H$_2$O 可以共存; 而 MgNH$_4$PO$_4$·6H$_2$O 和 Mg(OH)$_2$ 在碱性条件下更为稳定。当 MgNH$_4$PO$_4$·6H$_2$O、Mg$_3$(PO$_4$)$_2$·8H$_2$O 与液相共存、pH=9.08~9.52 时, 溶液总氮浓度达到最低值。lg$C_{T,Mg}$-lg$C_{T,P}$ 和 lg$C_{T,P}$-pH 相图可以用于指导磷酸铵镁的沉淀−溶解平衡过程, 有利于废水中氨氮的脱除和回收。

关键词: 氨氮; 磷酸铵镁; 热力学; 优势区相图

Predominance Diagrams for NH$_4^+$-Mg^{2+}-PO$_4^{3-}$-H$^+$-H$_2$O System

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Abstract: The thermodynamics of NH$_4^+$-Mg^{2+}-PO$_4^{3-}$-H$^+$-H$_2$O system was investigated based on the construction of predominance diagrams. The lg$C_{T,Mg}$-lg$C_{T,P}$ and lg$C_{T,P}$-pH diagrams were constructed at an arbitrary Mg/P molar ratio with consideration of the ion strength influence($C_{T,Mg}$: total concentration of magnesium; $C_{T,P}$: total concentration of phosphorus; $C_{T,N}$: total concentration of nitrogen). The thermodynamic stable zones of struvite (MgNH$_4$PO$_4$·6H$_2$O), bobierrite (Mg$_3$(PO$_4$)$_2$·8H$_2$O), newberyite (MgHPO$_4$·3H$_2$O), and magnesium hydroxide (Mg(OH)$_2$) were determined. The results show that struvite and bobierrite are the dominating phases in a wide range of pH value. Struvite and newberyite coexist with solute phase at low pH value and high total concentration of phosphorus while struvite and magnesium hydroxide are more stable at the alkaline condition. The minimum total concentration of nitrogen appears at pH value of 9.08~9.52 while struvite and bobierrite coexist with the solute phase. The predominance diagrams could be used to predict the precipitation-dissolution equilibrium of struvite for ammonia nitrogen removal and recovery from wastewater.

Key words: ammonia nitrogen; struvite; thermodynamics; predominance diagrams

Ammonia nitrogen (NH$_3$-N) is a key cause for water quality deterioration and eutrophication while it is also important for agriculture and industry. Until now, much attention has been paid to the technologies for removal and recovery of NH$_3$-N, such as biological method, struvite precipitation, and ammonia stripping, etc [1-3]. Compare with other methods, struvite precipitation has been considered to be an effective way[4-7] as it is convenient for the recovery of NH$_3$-N as a slow-release fertilizer. The method has the advantages such

as high reaction rate, low residual nitrogen concentration, low energy consumption, and so on.

The thermodynamics about precipitation-dissolution equilibrium of struvite has been reported by many researchers. The solubility constants or conditional solubility constants for struvite were determined under different conditions[8-13]. The effects of ion concentration and pH value on struvite precipitation were investigated, and the optimal conditions for struvite formation were obtained [14-18]. However, the thermodynamic studies mentioned above were concentrated in the two-phase equilibrium between struvite and solute phase. Little attention has been paid to the cases while two or more solid phases among struvite, bobierrite, newberyite, and magnesium hydroxide coexist with solute phase. In fact, struvite is not stable and can transform into other forms of precipitates under certain conditions. Babic′-Ivancˇic et al [19] found that both struvite and newberyite could precipitate simultaneously at 37 ℃ and an initial pH value of 7.4, and struvite readily transformed into newberyite at pH<6. Golubev and Savenko[20] found that struvite in seawater transforms to bobierrite, and newberyite was stable in seawater at pH value <7. Dempsy [21] found that newberyite was the predominant solid phase at pH value of 5~7.

In order to obtain ion concentrations in struvite precipitation process, it is critical to build the stable zones and coexistence conditions of the four possible solid phases, including struvite, bobierrite, newberyite, and magnesium hydroxide in NH_4^+-Mg^{2+}-PO_4^{3-}-H^+-H_2O system. On this basis, the $lgC_{T,Mg}$-pH, $lgC_{T,N}$-$lgC_{T,Mg}$, and $lgC_{T,N}$-pH diagrams have been drawn at Mg/P molar ratio of 11 in our previous work[22]. The effect of ion strength on the equilibrium, however, was ignored and Mg/P molar ratio was confined. The aims of this study were to investigate the struvite stability at arbitrary Mg/P molar ratio with consideration to the influence of ion strength. The predominance diagrams, that is, $lgC_{T,Mg}$-$lgC_{T,P}$ and $lgC_{T,P}$-pH diagrams for NH_4^+-Mg^{2+}-PO_4^{3-}-H^+-H_2O system were drawn.

1　Thermodynamics modeling

The possible species in the system mainly include Mg^{2+}, PO_4^{3-}, NH_4^+, H^+, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, $MgPO_4^+$, $MgHPO_4(aq)$, $MgH_2PO_4^+$, $MgOH^+$, $NH_3 \cdot H_2O$ (aq), $MgNH_4PO_4$, $MgHPO_4$, $Mg_3(PO_4)_2$, and $Mg(OH)_2$. The equilibrium relations between the ion species and stability constants of the solid phases are listed in Table 1.

The total concentration of magnesium, nitrogen, and phosphorus, denoted as $C_{T,Mg}$, $C_{T,N}$, and $C_{T,P}$, is the sum of the concentrations of their complexes and free ions as illustrated in equations (13) ~(15). Charge

Table 1　Thermodynamic Data for NH_4^+-Mg^{2+}-PO_4^{3-}-H^+-H_2O System (25 ℃)

NO.	Equilibrium reaction	Equilibrium equation	pK	Ref.
(1)	$Mg^{2+}+PO_4^{3-}+NH_4^++6H_2O \rightleftharpoons MgNH_4PO_4 \cdot 6H_2O(s)$	$C_{Mg^{2+}}C_{NH_4^+}C_{PO_4^{3-}}=K_{MgNH_4PO_4(S)}$	13.26	[11]
(2)	$Mg^{2+}+HPO_4^{2-}+3H_2O \rightleftharpoons MgHPO_4 \cdot 3H_2O(s)$	$C_{Mg^{2+}}C_{HPO_4^{2-}}=K_{MgHPO_4 \cdot 2H_2O(S)}$	5.51	[23]
(3)	$3Mg^{2+}+2PO_4^{3-}+22H_2O \rightleftharpoons Mg_3(PO_4)_2 \cdot 22H_2O(s)$	$C_{Mg^{2+}}^3 C_{PO_4^{3-}}^2=K_{Mg_3(PO_4)_2 \cdot 22H_2O(S)}$	25.2	[24]
(4)	$Mg^{2+}+2OH^- \rightleftharpoons Mg(OH)_2(s)$	$C_{Mg^{2+}}C_{OH^-}^2=K_{Mg(OH)_2(S)}$	11.16	[24]
(5)	$H_3PO_4 \rightleftharpoons H^++HPO_4^{2-}$	$C_{H^+}C_{H_2PO_4^-}=K_{H_2PO_4}C_{H_3PO_4}$	2.15	[14]
(6)	$H_2PO_4^- \rightleftharpoons H^++HPO_4^{2-}$	$C_{H^+}C_{HPO_4^{2-}}=K_{H_2PO_4^-}C_{H_2PO_4^-}$	7.2	[14]
(7)	$HPO_4^{2-} \rightleftharpoons H^++PO_4^{3-}$	$C_{H^+}C_{HPO_4^{2-}}=K_{HPO_4^{2-}}C_{HPO_4^{2-}}$	12.35	[14]
(8)	$MgPO_4^- \rightleftharpoons Mg^{2+}+PO_4^{3-}$	$C_{Mg^{2+}}C_{PO_4^{3-}}=K_{MgPO_4^-}C_{MgPO_4^-}$	4.80	[14]
(9)	$MgHPO_4(aq) \rightleftharpoons Mg^{2+}+HPO_4^{2-}$	$C_{Mg^{2+}}C_{HPO_4^{2-}}=K_{MgHPO_4(aq)}C_{(MgHPO_4)aq}$	2.428	[23]
(10)	$MgH_2PO_4^+ \rightleftharpoons Mg^{2+}+H_2PO_4^-$	$C_{Mg^{2+}}C_{H_2PO_4^-}=K_{MgH_2PO_4}C_{MgH_2PO_4^+}$	0.45	[14]
(11)	$MgOH^+ \rightleftharpoons Mg^{2+}+OH^-$	$C_{Mg^{2+}}C_{OH^-}=K_{MgOH}C_{MgOH^-}$	2.56	[14]
(12)	$NH_4^++H_2O \rightleftharpoons NH_3 \cdot H_2O(aq)+H^+$	$C_{(NH_3H_2O)aq}C_{H^+}=K_{NH_4^+}C_{NH_4^+}$	9.24	[24]

balance equation is given by equation (**16**).

$$C_{T,Mg}=C_{Mg^{2+}}+C_{MgPO_4^-}+C_{MgHPO_4(aq)}+C_{MgH_2PO_4^+}+C_{MgOH^+} \quad (13)$$

$$C_{T,P}=C_{H_3PO_4}+C_{H_2PO_4^-}+C_{HPO_4^{2-}}+C_{PO_4^{3-}}+C_{MgPO_4^-}+$$
$$C_{MgHPO_4(aq)}+C_{MgH_2PO_4^+} \quad (14)$$

$$C_{T,N}=C_{NH_3 \cdot H_2O(aq)}+C_{NH_4^+} \quad (15)$$

$$C_{H_2PO_4^-}+2C_{HPO_4^{2-}}+3C_{PO_4^{3-}}+C_{MgPO_4^-}+C_{OH^-}+C_{Cl^-}=$$
$$C_{NH_4^+}+2C_{Mg^{2+}}+C_{MgH_2PO_4^+}+C_{MgOH^+}+C_{Na^+}+C_{H^+} \quad (16)$$

The described thermodynamic equations incorporate pH value of the solution due to the presence of H⁺ and OH⁻ when equilibrium constant of water ($K_w=10^{-14}$) is known (equation (**17**)).

$$C_{H^+}C_{OH^-}=K_w \quad (17)$$

Equations (**19**) and (**20**) are used to calculate ionic strength (I) and activity coefficient (γ_i), respectively[12].

$$I=\frac{1}{2}\sum C_iZ_i^2 \quad (18)$$

$$-\lg\gamma_i=AZ_i^2(\frac{I^{1/2}}{1+I^{1/2}}-0.3I) \quad (19)$$

where C_i is the concentration of each component, Z_i is the valency of the corresponding component, and A is the DeBye-Hückel constant, 0.509, at 25 ℃.

2　Results and discussion

Based on equations (**1**)~(**19**), the thermodynamic

equilibrium relationship for NH₄⁺-Mg²⁺-PO₄³⁻-H⁺-H₂O system was calculated at room temperature (25 ℃) and atmospheric pressure. According to the Gibbs Phase Rule, when the temperature and pressure keep constant, the relation between freedom (F), phase number (P), and independence component number (C) is $F=C-P$. For NH₄⁺-Mg²⁺-PO₄³⁻-H⁺-H₂O system, $F=5-P$. It is supposed that Na⁺ or Cl⁻ can coexist in order to balance electric charge of the system. The five variables of $C_{Mg^{2+}}$, $C_{NH_4^+}$, $C_{PO_4^{3-}}$, C_{H^+}, C_{Na^+} or C_{Cl^-} are confined by equilibrium equation (**1**) (or (**2**), (**3**), (**4**)) and conservation equations (**14**)~(**17**). If $C_{T,P}$, $C_{T,N}$, pH value, C_{NaCl}, and equilibrium solid phases are given, the five variables can be calculated. The $\lg C_{T,Mg}$-$\lg C_{T,P}$ and $\lg C_{T,P}$ - pH diagrams can be drawn.

2.1　Predominance diagrams at fixed pH value without inert salts

In the absence of inert salts such as NaCl, Na₂SO₄ and so on, it is supposed that only one of Na⁺ and Cl⁻ can coexist to balance electric charge of the system. The plots of $\lg C_{T,Mg}$ against $\lg C_{T,P}$ at pH value of 7.0, 8.0, 9.0, 10.0, and 11.0 are shown in Fig.1((a)~(e)), respectively.

An invariant phase equilibrium requires the coexistence of four phases at a fixed pH value ($F=4-P$).
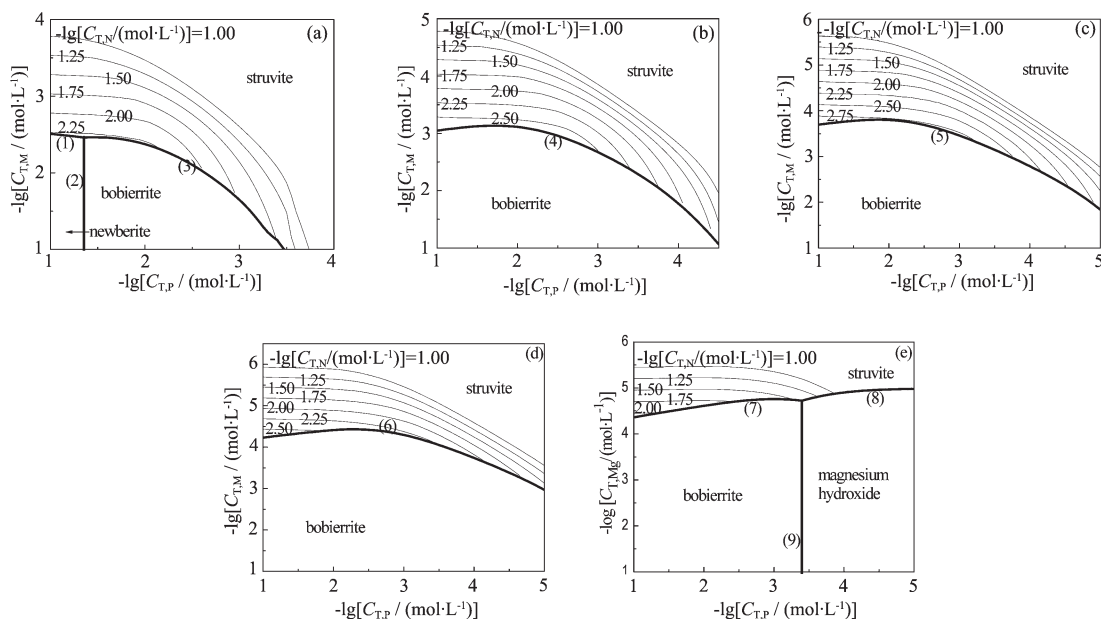
(a) pH=7.0; (b) pH=8.0; (c) pH=9.0; (d) pH=10.0; (e) pH=11.0

Fig.1　Predominance diagrams for NH₄⁺−Mg²⁺-PO₄³⁻-H⁺-H₂O system at pH value of 7.0-11.0 in the absence of inert salts

The invariant point for coexistence of struvite, newberyite, bobierrite, and solute phase is found at pH value of 7.0, $\lg C_{T,P}=-1.35$, $\lg C_{T,Mg}=-2.46$, and $\lg C_{T,N}=-2.30$ (Fig.1(a)). The invariant point for coexistence of struvite, bobierrite, magnesium hydroxide, and solute phase phases is found at pH value of 11.0, $\lg C_{T,P}=-3.40$, $\lg C_{T,Mg}=-4.72$, and $\lg C_{T,N}=-1.47$ (Fig.1(e)).

The coexistence of three phases causes univariant phase equilibrium as shown by the broad solid lines (1) ~(9) in Fig.1. At pH value of 7.0, the three-phase equilibrium line of newberyite, struvite, and solute phase (line (1)), line of newberyite, bobierrite, and solute phase (line (2)), line of bobierrite, struvite, and solute phase (line (3)) are observed, respectively. At pH value of 8.0, 9.0, and 10.0, only the three-phase equilibrium lines of bobierrite, struvite, and solute phase are observed (lines (4~6)). At pH value of 11.0, the three-phase equilibrium line of bobierrite, struvite, and solute phase (line (7)), line of bobierrite, magnesium hydroxide, and solute phase (line (8)), line of magnesium hydroxide, struvite, and solute phase (line (9)) are observed, respectively. Once one of $C_{T,N}$, $C_{T,Mg}$, $C_{T,P}$ is determined on the three-phase equilibrium lines, other two parameters can be obtained.

Under the conditions of two-phase equilibrium between struvite and the solute phase, phase equilibrium relationship is surfaces with three variants ($C_{T,P}$, $C_{T,Mg}$, and $C_{T,N}$), which are shown by thin isoline of $C_{T,N}$. The figure on every line shows the value of $C_{T,N}$ in equilibrium. The solid line parts of the isoline represent stable equilibrium between struvite and solute phase.

2.2 Predominance diagram at variable pH values without inert salts

The plot of $\lg C_{T,P}$ against pH value in the absence of inert salts is shown in Fig.2.

An invariant phase equilibrium requires the coexistence of five phases at variable pH values. No invariant points can be observed in Fig.2. It means that equilibrium between five phases cannot arise for NH_4^+-Mg^{2+}-PO_4^{3-}-H^+-H_2O system.

The equilibria of four phases causes the univariant lines as shown by the broad solid line (10) and line (11). The line (10) shows the four-phase equilibrium between
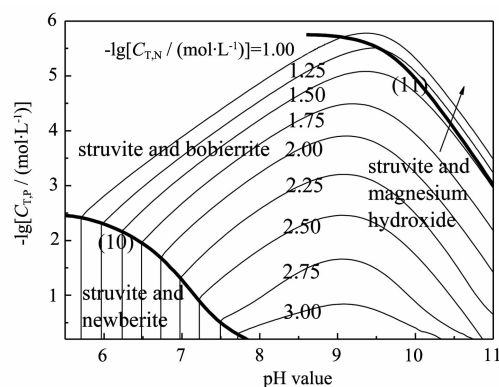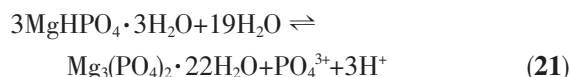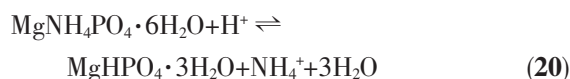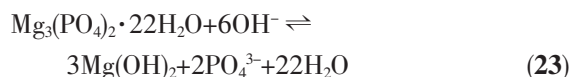

Fig.2 Predominance diagram for NH_4^+-Mg^{2+}-PO_4^{3-}-H^+-H_2O system when two solid phases coexist with solute phase in the absence of inert salts

struvite, newberyite, bobierrite, and solute phase by equations (1), (2), and (3), which can be reformed into equations (20) and (21).

$$MgNH_4PO_4\cdot 6H_2O+H^+ \rightleftharpoons$$
$$MgHPO_4\cdot 3H_2O+NH_4^++3H_2O \tag{20}$$
$$3MgHPO_4\cdot 3H_2O+19H_2O \rightleftharpoons$$
$$Mg_3(PO_4)_2\cdot 22H_2O+PO_4^{3+}+3H^+ \tag{21}$$

The line (11) shows the four-phase equilibrium between struvite, bobierrite, magnesium hydroxide, and solute phase by equations (1), (2), and (4), which can be reformed into equations (22) and (23).

$$2MgNH_4PO_4\cdot 6H_2O+Mg(OH)_2+8H_2O+2H^+ \rightleftharpoons$$
$$Mg_3(PO_4)_2\cdot 22H_2O+2NH_4^+ \tag{22}$$
$$Mg_3(PO_4)_2\cdot 22H_2O+6OH^- \rightleftharpoons$$
$$3Mg(OH)_2+2PO_4^{3+}+22H_2O \tag{23}$$
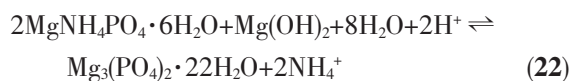
From Fig.2, it can be observed that there are three stable zones with different solid phases: struvite-newberyite zone at lower pH value and higher $\lg C_{T,P}$, struvite-bobierrite zone at middle pH value and middle $\lg C_{T,P}$, and struvite-magnesium hydroxide zone at higher pH value and lower $\lg C_{T,P}$. These results are in agreement with experimental results reported by the previous investigations[14, 19, 21, 25].

The equilibria of three phases causes divariant surfaces, which are shown by thin isoline of $C_{T,N}$ in Fig. 2. At struvite-newberyite zone, the isoline of $\lg C_{T,N}$ is determined by equations (1), (2), which can be combined into equation (20). At struvite-bobierrite zone, the isoline of $\lg C_{T,N}$ is determined by equations (1), (3), which can be combined into equation (24). At

Table 2　Optimal pH Values for Nitrogen Removal at Different Equilibrium Total Concentrations of Phosphorus

$C_{T,P}$ / (mol·L^{-1})	Optimal pH value	Minimum $C_{T,N}$ / (mol·L^{-1})
1.66×10^{-6}	9.38	1.00×10^{-1}
2.95×10^{-6}	9.52	5.62×10^{-2}
8.32×10^{-6}	9.35	3.16×10^{-2}
3.24×10^{-5}	9.22	1.78×10^{-2}
1.26×10^{-4}	9.12	1.00×10^{-2}
6.31×10^{-4}	9.06	5.62×10^{-3}
3.47×10^{-3}	9.08	3.16×10^{-3}
2.19×10^{-2}	9.08	1.78×10^{-3}
1.45×10^{-1}	9.08	1.00×10^{-3}

(a) C_{NaCl}=0.1 mol·L^{-1}; (b) C_{NaCl}=0.3 mol·L^{-1}; (c) C_{NaCl}=0.5 mol·L^{-1}; (d); C_{NaCl}=1.0 mol·L^{-1}
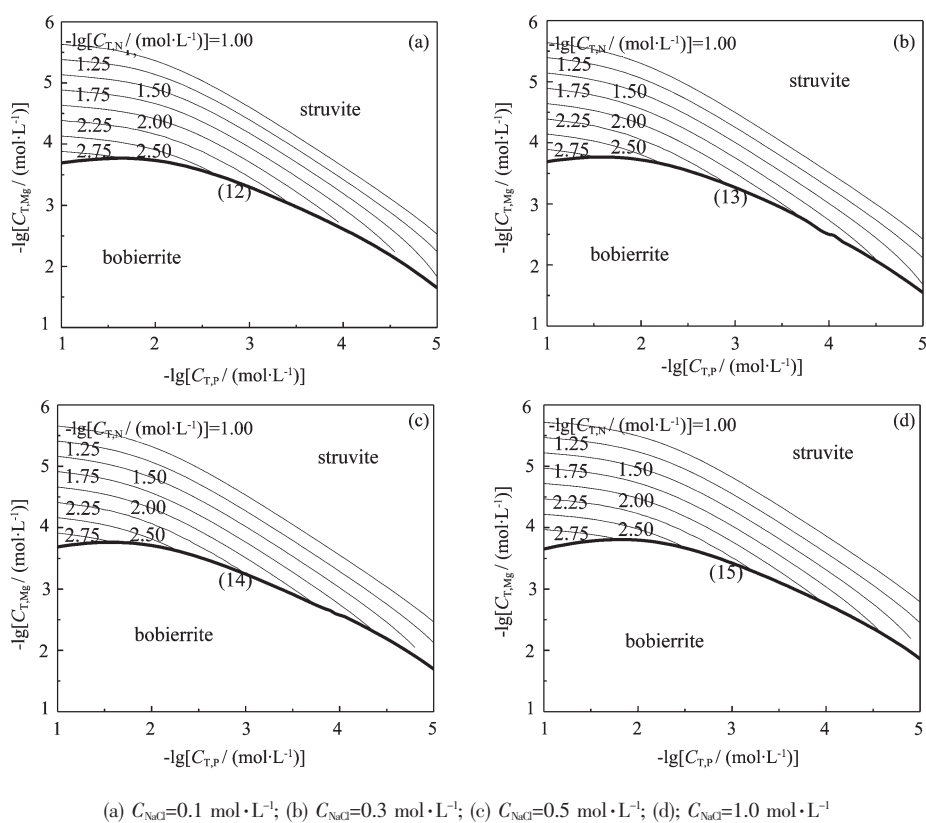
Fig.3　Predominance diagams for NH_4^+-Mg^{2+}-PO_4^{3-}-H^+-H_2O system at pH value of 9.0 and NaCl concentration of 0.1~1.0 mol·L^{-1}

struvite-magnesium hydroxide zone, the isoline of lg$C_{T,N}$ is determined by equations (**1**), (**4**), which can be combined into equation (**25**). From equations (**12**), (**20**), (**24**) and (**25**), it can be seen that $C_{T,N}$ can be represented as a function of pH value and $C_{T,P}$ under the condition of three-phase equilibria.

$$3MgNH_4PO_4·6H_2O+4H_2O \rightleftharpoons$$
$$Mg_3(PO_4)_2·22H_2O+PO_4^{3-}+3NH_4^+ \qquad (24)$$

$$MgNH_4PO_4·6H_2O+3OH^- \rightleftharpoons$$
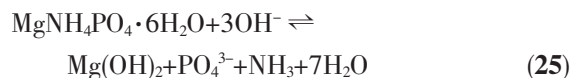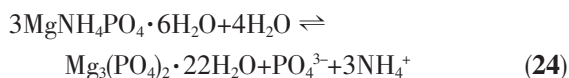$$Mg(OH)_2+PO_4^{3-}+NH_3+7H_2O \qquad (25)$$

Fig.2 also shows that the minimum $C_{T,N}$ appears in the range of pH 9.08~9.52 at struvite-bobierrite zone. The optimal pH values at different $C_{T,P}$ are listed in Table 2. These results agree with the experimental results reported in struvite precipitation investigations[26-30].

2.3 Predominance diagrams at different ion strength

In an actual process, NaCl or Na_2SO_4 usually coexists with other ions in $NH_4{}^+$-Mg^{2+}-$PO_4{}^{3-}$-H^+-H_2O system, and it will influence the activities of various ions. For simplicity, the $lgC_{T,Mg}$-$lgC_{T,P}$ diagrams at pH value of 9.0 with NaCl concentration (0, 0.1, 0.3, 0.5, or 1.0) mol·L^{-1} have been conducted in Fig.1(c), and Fig. 3.

It can be observed that only three-phase equilibrium lines of bobierrite, struvite, and solute phase are observed (lines (5, 12~15) at C_{NaCl} 0~1.0 mol·L^{-1} and pH value of 9.0. Solid lines of the thin isoline represent the same meanings as in Fig.1.

In order to investigate the effect of C_{NaCl} on ion strength, $lgC_{T,Mg}$-$lgC_{T,P}$ diagram at $lgC_{T,N}$=−1.00 is drawn in Fig.4.
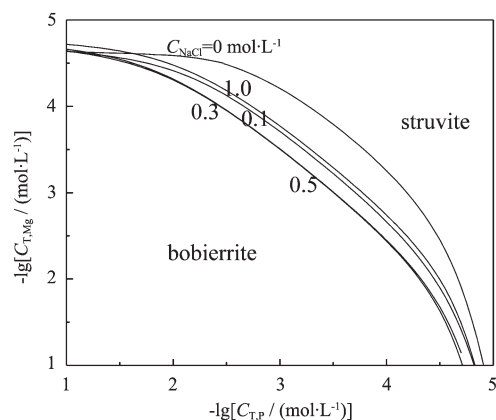

Fig.4　Predominance diagram for $NH_4{}^+$-Mg^{2+}-$PO_4{}^{3-}$-H^+-H_2O system at pH value of 9.0, total nitrogen concentration of 0.1 mol·L^{-1}, and NaCl concentration of 0.1 mol·L^{-1}

The solid thin lines represent the equilibrium between struvite, bobierrite, and solute phase at given C_{NaCl}. It can be observed that C_{NaCl} has important influence on struvite precipitation. With the increasing C_{NaCl}, the solubility of struvite increases at the first, reaches the highest at C_{NaCl} 0.3~0.5 mol·L^{-1}, and then decreases.

3 Conclusions

Total concentration of the components (magnesium, nitrogen and phosphorus), pH value, and ion strength in $NH_4{}^+$-Mg^{2+}-$PO_4{}^{3-}$-H^+-H_2O system are important factors

influencing the stable zones of solid phases. Struvite and newberyite coexist with solute phase at lower pH value and higher $lgC_{T,P}$, struvite and bobierrite coexist with solute phase at middle pH value and middle $lgC_{T,P}$, struvite and magnesium hydroxide are more stable at higher pH value and lower $lgC_{T,P}$. The minimum total concentration of nitrogen appears at pH 9.08~9.52 while struvite and bobierrite coexist with solute phase.

The predominance diagrams of $lgC_{T,Mg}$-$lgC_{T,P}$ and $lgC_{T,P}$-pH can be used to predict the struvite precipitation process for removal and recovery of ammonia nitrogen from wastewater.

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