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Effect of permanent magnetic field on water association in circulating water

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ABSTRACT

Orthogonal experiments of $L_{16}(4^5)$ were conducted to study the effect of permanent magnetic field on water association in circulating water. The operation parameters include the magnetic field intensity, initial concentration of Ca^{2+} and Mg^{2+}, magnetic treatment time, temperature and water flow velocity. The chemical shift, alkalinity, relative variation of activation energy and concentrations of Ca^{2+} and Mg^{2+} were used as the optimization objectives. Applying the relevant analysis method, the dominance degrees of influence factors for four objectives were analyzed, and the optimum condition was obtained. Furthermore, the effects of ion concentration and magnetic field intensity on water association were analyzed. The optimum condition was obtained as 900 mg/L of initial concentration, 0.5 T of magnetic field intensity, 303 K of temperature, 54 h of time and 0.17 m/s of water flow velocity. The results show that the operation parameters have different effects on water association. Water association increases with increase of magnetic field intensity. High concentration Ca^{2+} and Mg^{2+} can strengthen water association, and the effect of Mg^{2+} on water association is greater than that of Ca^{2+}. High concentration of HCO_3^- and CO_3^{2-} can break water clusters and decrease water association.

Keywords: Permanent magnetic field; Calcium carbonate; Water association; Chemical shift

1. Introduction

In many industrial processes, scale formation is a common and costly problem. Scale deposits can increase operation and maintenance costs by lowering flow capacity and increasing pump energy consumption in cool water systems. Moreover, scale formation resists the heat transfer between hot water systems and heat exchangers. Normally, chemical reagents, such as scale inhibitor and chemical inhibitors by means of chelation [1], dispersion [2] and inhibition [3–6], can effectively control scale formation. Especially for desalination processes, the use of scale inhibitor is the most commonly technique [7,8]. However, chemical method is expensive and can change the chemical property of circulating water. Furthermore, polyphosphate has long-term negative effect on the environment. The magnetic treatment technique has been widely employed to prevent scale formation in the industrial system, particularly in heat exchangers and domestic equipment. Such a physical treatment method is advantageous where it does not involve chemicals. Thus, magnetic treatment is playing an increasing and important role in regards to scale control and amelioration of dispersion separation [9,10].

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The first patent of magnetic water treatment was registered in Belgium by Vermeiren in 1945 [11]. Magnetic treatment devices of different configurations are currently available in the European market. Despite the practical use has been for several decades, the mechanism explanation of effects still remains unclear due to incomplete understanding of how the magnetic treatment device affects circulating water. Alimi et al. found that the magnetic treatment for hard water increased the number of precipitates in bulk water and favored homogeneous nucleation [12]. J.M.D. Coey and S. Cass concluded that the solution pH value, flow rate and residence time were important parameters for precipitation [13]. Glushchenko et al. proposed a "design module" expressed as $M = Bvt$ (M is design module, $T\cdot m$; v is liquid velocity, m/s; t is exposure time, s), and showed the magnetic treatment effect was closely related to the flow velocity, time and magnetic field intensity [14]. They recommended the design module of 300–400 $T\cdot m$. Lili Jiang et al. studied the effect of permanent magnetic field on calcium carbonate scale formation in circulating water. Their results revealed an optimal water velocity of 1.2 m/s and magnetic flux intensity of 0.7 T [15]. Toledo et al. compared experimental data of water viscosity, enthalpy and surface tension with theoretical values. The results showed that external magnetic field affected the hydrogen bond networks [16]. The competition between intra- and inter-molecular hydrogen bond networks weakened the intra-cluster hydrogen bonds, broke large clusters into smaller clusters. Kronenberg found an optimum flow velocity for his magnetic configuration and suggested that breakage of hydrogen bond by resonant vibration was involved [17]. However, Chang and Weng investigated the effect of magnetic field on the hydrogen bond structure of water and found that the number of hydrogen bonds increased by 0.34% when magnetic field intensity increased from 1 to 10 T [18]. The explanation may be rooted in changes of ion distributions and hydration near the dispersed particle surfaces. Higashitani and Oshitani investigated the effect of magnetic field on the stability of non-magnetic colloid particles and suggested that colloid stability may be influenced by magnetic field through alterations of water molecule structure and ions either adsorbed on the particle surface or in the medium [19]. The mechanism of effect has not been clearly understood and various contradictory results have been reported [20]. Arulmozhi et al. analyzed the relationship between chemical shift and line width and showed that cations promoted water association but anions destroyed water association [21]. Horne et al. studied the relationship between the structure of water clusters and the coefficient of viscosity [22]. Ruihua Li et al. investigated the effects of alkali metals and alkaline earth metal chlorides on liquid water structure [23]. Their results showed that chemical shift reflected the effects of ions on water association. Waskylishen et al. measured the sizes of water clusters with ^{17}O-Nuclear magnetic resonances before and after water treatment [24]. They analyzed the line width and noted that the average cluster size in bulk water decreased and the number of water molecules per cluster also decreased.

Generally speaking, a liquid can be treated as homogeneous system. However, ionic liquids can show unique spatial heterogeneity due to their inherent separation features of polar or nonpolar nanophase [25–27]. The presence of a co-solvent can reduce the electrostatic attraction among ions and decrease the overall cohesive energy. In addition, water affects both translational and rotational dynamics of ionic liquids, thereby enhances the relaxation rate [28,29]. Hydrated ions show strong interactions with water molecules and increase water structuring which produces higher viscosity than pure water. Therefore, these ions are referred to as structure makers. However, some ions are only marginally hydrated in aqueous solutions. These ions show weak interactions with water and decrease water structuring and thereby lower solution viscosity. This effect is referred to as negative hydration, and these ions are often referred to structure breakers [30]. The most common criticism of magnetic treatment effects is whether or not magnetic field can strengthen liquid water association. In the light of above views, the present work chooses orthogonal experiments to deal with these issues. It is well known that orthogonal experiments can efficiently correlate various factors for parameter optimization. The method can identify the most influential factors based on high consistency and reproducibility. According to the orthogonal table, one can select the representative experiments, and satisfactory results can be obtained [31].

The objective of the present study is to investigate the effect of a permanent magnetic field on water association in circulating water. The process optimization of magnetic treatment was based on the water structure changes under different operation conditions. All operating conditions, including the magnetic field intensity, initial concentrations of Ca^{2+} and Mg^{2+}, magnetic treatment time, temperature, and water flow velocity, were studied. The orthogonal experiments were carried out and the results were analyzed via range analysis in reference to the chemical shift, alkalinity, relative variation of activation energy and Ca^{2+} and Mg^{2+} concentrations. The dominance degrees for influencing factors and the optimum condition were determined. The effects of magnetic field intensity and ion concentration on water association were analyzed.

2. Experimental equipment and methods

2.1. Experimental equipment and water quality index analysis

The magnetic treatment equipment is shown in Fig. 1. The closed loop is composed of a water tank, a water pump, a valve, a water-heating tank, permanent magnetic adjustable equipment, and a water meter. The flow velocity was controlled by adjusting the valve and water meter within a range of 0–0.68 m/s. The circulating water was heated by passing through the water heating tank, which was adjusted with a temperature controller. The adjustable permanent magnetic equipment was produced by Shenzhen Yitian Magnetic & Devices Co., Ltd, China, and a range of 0–0.8 T was measured with a digital teslameter (HT100, Ningbo Bestway Magnet Co., Ltd., China). Ultra-pure water was used to prevent side effects from foreign ions during magnetic treatment process. Artificial hard water was prepared by dissolving Na_2CO_3, $CaCl_2$ and $MgCl_2\cdot 6H_2O$ in the circulating water. According to the experimental conditions, an orthogonal table of L_{16} (4^5) was applied. These selected factors and levels are listed in Table 1. The chemical shift, alkalinity, relative variation of activation energy and Ca^{2+} and Mg^{2+} concentrations were selected as the objectives.

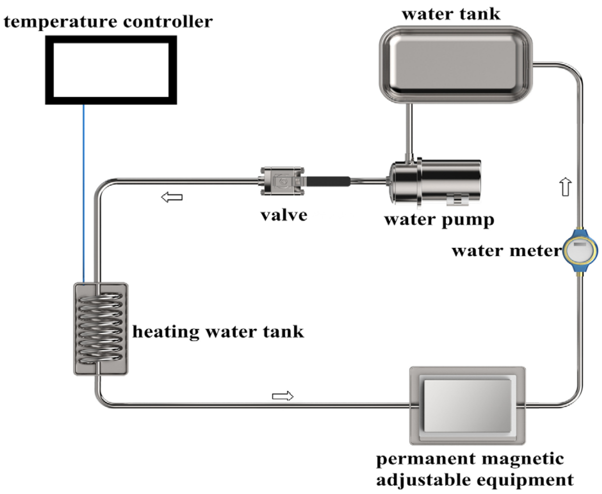

Fig. 1. Magnetic treatment equipment for circulating water.

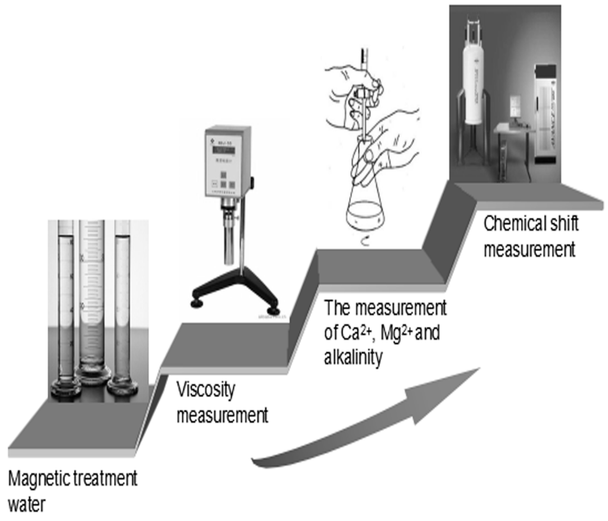

Fig. 2. Diagram of water quality index analysis.

Table 1
Factors and levels of L_{16} (4^5) experiments

Factors	Levels
Magnetic field intensity (T)	0, 0.2, 0.5, 0.8
Initial concentration (mg/L, $Ca^{2+} = Mg^{2+} = CO_3^{2-}$)	0, 300, 600, 900
Time (h)	18, 36, 54, 72
Temperature (K)	298, 303, 308, 313
Flow velocity (m/s)	0.17, 0.34, 0.51, 0.68

Fig. 2 shows the analyzing process of water quality indexes including the concentrations of Ca^{2+} and Mg^{2+}, alkalinity, viscosity and chemical shift. The concentrations of Ca^{2+} and Mg^{2+} can be obtained from hardness. The hardness refers to the existence of dissolved minerals such as calcium and magnesium ions in water solution. It is determined by the titration of EDTA-Na_2 with chrome black T as an indicator. The related calculation equation is shown in Eq. (1). The Ca^{2+} and Mg^{2+} concentrations can be calculated with EDTA-Na_2 titration and the equations are shown in Eqs. (2), (3). The alkalinity can be calculated with Eq. (4).

$$\text{Hardness} = \frac{C_{EDTA\text{-}Na_2} V_1 \times M_{CaO} \times 10^3}{V_{water}} \tag{1}$$

$$C_{Ca} = \frac{C_{EDTA\text{-}Na_2} V_2 \times M_{Ca} \times 10^3}{V_{water}} \tag{2}$$

$$C_{Mg} = \frac{C_{EDTA-Na_2}(V_1 - V_2) \times M_{Ca} \times 10^3}{V_{water}} \tag{3}$$

$$\text{Alkalinity} = \frac{p \times C_{HCl} \times M_{CaCO_3} \times 10^3}{V_{water}} \tag{4}$$

where $C_{\text{EDTA-Na}_2}$ is the concentration of EDTA-Na_2 (mol/L); m is the quantity of $MgCl_2 \cdot 6H_2O$ (g); M is the molecular weight of $MgCl_2 \cdot 6H_2O$ (g/mol); $V_{\text{EDTA-Na}_2}$, V_1 and V_2 denote the volume of EDTA-Na_2 (L); M_{CaO}, M_{Ca} and M_{Mg} are molar weights of CaO, Ca^{2+} and Mg^{2+} (g/mol), respectively; V_{water} is the volume of water (L), C_{Ca} and C_{Mg} are the concentration of Ca^{2+} and Mg^{2+} (mol/L), respectively; p is the volume of HCl when phenolphthalein is fading (L); C_{HCl} is the concentration of hydrochloric acid standard solution (mol/L); M_{CaCO3} is the molar weight of $CaCO_3$ (g/mol); and V_{water} is the volume of water (L).

The chemical shift was measured from the residual protons in the D_2O solvent. Nuclear magnetic resonances of water samples were prepared in D_2O. Nuclear magnetic resonance spectrometer experiments were carried out on a Bruker Avance AVIII 400 equipped with a standard 5 mm probe at 400 MHz. The sample was set to 298 K and kept constant within ±0.1 K. Viscosity is a physical parameter of water which was measured by a viscometer which produced by Shanghai Fangrui Devices Co., Ltd. According to the Eyring theory of liquid viscosity, the liquid viscosity η (mPa·s) can be used to calculate the relative variation of activation energy (Eq. (5)) [32].

$$\frac{\Delta E}{E_0} = \frac{E - E_0}{E_0} = \frac{\ln \eta - \ln \eta_0}{\ln \eta_0 - \ln \dfrac{hN_A}{V_m}} \tag{5}$$

where $\frac{\Delta E}{E_0}$ is the relative variation of activation energy; E and E_0 denote the activation energy of experimental water and ultra-pure water (kJ/mol), respectively; h is the Planck constant ($h = 6.626 \times 10^{-34}$ J·s); N_A is the Avogadro′s number ($N_A = 6.02 \times 10^{23}$/mol); V_m is the molar volume of liquid (L/mol); η and η_0 are the viscosities of experiment water and ultra-pure water (mPa·s), respectively.

2.2. Water preparation and experimental method

First, according to Table 1 and the orthogonal experiment table of L_{16} (4^5), the appropriate magnetic field intensity and water velocity were adjusted. Second, artificial hard water was prepared with $CaCl_2$, $MgCl_2{\cdot}6H_2O$ and Na_2CO_3. It should be noted that the initial water chemistry (time = 0 h) was the same for all of the experiments. This meant that no other chemicals were added throughout the process. Then, 10 L artificial hard water was circulated in an enclosed pipeline. Finally 10 mL water was sampled from water tank at definite time intervals and the corresponding water quality indexes were measured. All experiments were repeated three times and the average values were calculated. After each experiment, the pipeline was thoroughly cleaned, first circulating with low concentration acid solution for 1 h and then by deionized water for 12 h.

3. Results and discussion

3.1. Analysis of water quality indexes

The chemical shift, alkalinity, relative variation of activation energy and Ca^{2+} and Mg^{2+} concentrations can be obtained through orthogonal experiments based on the table of L_{16} (4^5). The orthogonal experiment results were analyzed through the range analysis as shown in Fig. 3. The parameter k_i is the average value of the objective variable, where i denotes the level of a certain factor. R is the range which calculated from the difference between maximum and minimum of k_i for a certain factor. By comparing the R values, the dominance degree of each factor can be determined.

Fig. 3 shows the relationships between different factors and an index. And the results of range were analyzed. Normally, the factor which has the greatest effect on an objective index is the key factor for this index, which can be obtained by comparing the R values. Similarly, by comparing k_i values, the optimum factor levels can be obtained. The optimum factors are different for the four objectives. In terms of calcium ion concentration, the remaining concentration reached its maximum at an initial concentration of 900 mg/L (k_4). So the initial concentration of 900 mg/L is the optimization condition for calcium ions concentration. In the same way, the other optimum factors levels can be obtained, which include the magnetic field intensity of 0.5 T, temperature of 303 K, time of 54 h and flow velocity of 0.17 m/s. The dominance degrees of the five influencing factors are in the order of $R_c > R_T > R_v > R_M > R_{Time}$ for Ca^{2+} concentration. In addition, the analysis method of Mg^{2+} concentration is the same as that of Ca^{2+} and shown in Fig. 3b. The calculated results of alkalinity are similar with that of Ca^{2+} and Mg^{2+} (Fig. 3c). The optimum factor levels and the dominance degree of factors for chemical shift and $\Delta E/E_0$ can be obtained from Figs. 3d,e. The main cause of the chemical shift change is the change of inter-molecular hydrogen bond structures. The chemical shift of nuclear magnetic resonance offers important information on individual atom and reflects inter- and intra-molecular interactions, such as the electrostatic interaction of hydrogen bonds and the Van der Waals' force. As the chemical shift increases with the increase of frequency, the degree of water association is enhanced. By comprehensive analysis, the optimum condition is obtained as initial concentration of 900 mg/L, magnetic field intensity of 0.5 T, temperature of 303 K, time period of 54 h and flow velocity of 0.17 m/s.

From the thermodynamic equilibrium of free water and water clusters, Eq. (6) can be obtained [33].

$$H_2O(''lattice'')\underset{k_j}{\overset{k_i}{\rightleftharpoons}}H_2O(''free'') \tag{6}$$

where k_i and k_j are the forward and backward reaction rates (mol/s), respectively. The structure of water can change with the formation and destruction of hydrogen bonds. The water molecules of solution are divided into free water molecules and water clusters. Free water molecules are far away from hydrated layers, and the structure of hydrogen bonds in hydration layers can be easily affected by magnetic field [34]. Based on the two-state mode, water associa-

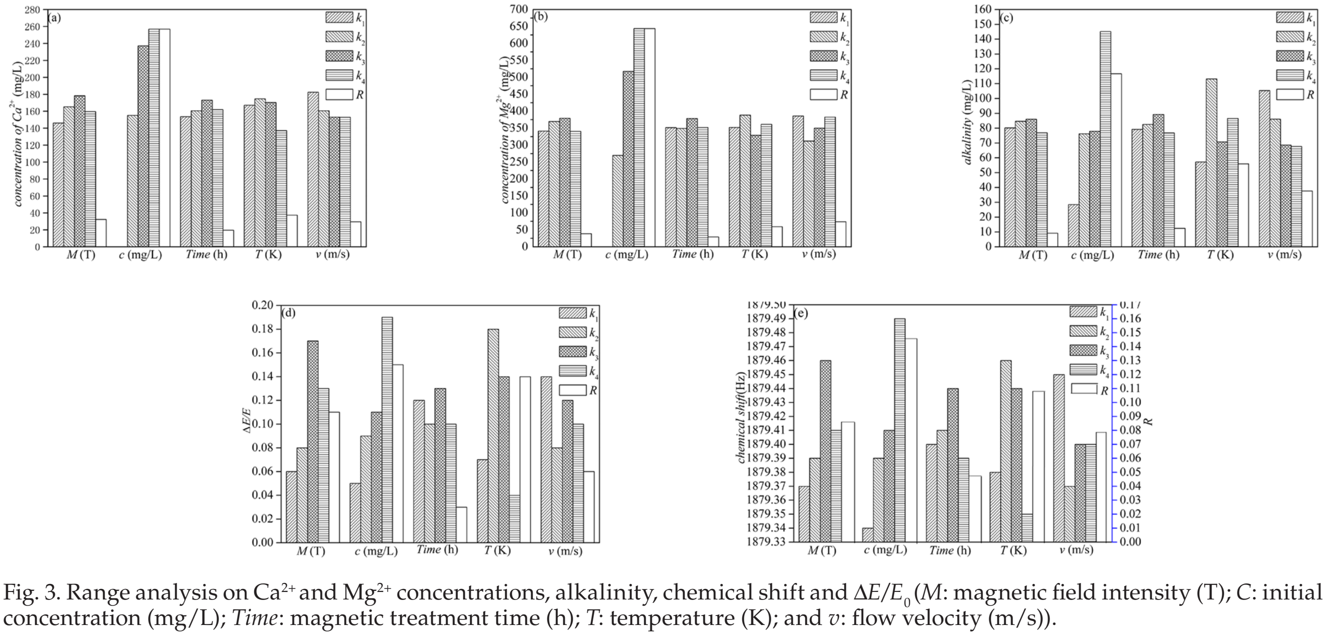

Fig. 3. Range analysis on Ca^{2+} and Mg^{2+} concentrations, alkalinity, chemical shift and $\Delta E/E_0$ (M: magnetic field intensity (T); C: initial concentration (mg/L); $Time$: magnetic treatment time (h); T: temperature (K); and v: flow velocity (m/s)).

tion is related with magnetic field. Depending on the degree of hydrogen bonds association, the internal energy of liquid water can be expressed with Eqs. (7), (8).

$$E' = x^+E'^{+}_{b} + x^-E'^{-}_{b} + (1-x^+-x^-)E'_f \tag{7}$$

$$x = \zeta C \tag{8}$$

where E' is internal energy (J); x^+ and E'^{+}_{b} are the mole fraction and internal energy of positive ion, respectively; x^- and E'^{-}_{b} are the mole fraction and internal energy of negative ion, respectively; E'_f is the internal energy of free water molecules (J); C is the concentration of ion; and ζ is constant which has nothing to do with the concentration ($0 < \zeta < 1$).

On the other hand, the interaction between water and ions can be obtained from the Jones-Dole empirical equation as Eq. (9) [35–36].

$$\frac{\eta_1}{\eta_2} = 1 + A\sqrt{C} + BC + DC^2 \tag{9}$$

where η_1 is the viscosity of solution, η_2 is the viscosity of solvent, and C is the concentration. The coefficient A is the Falkenhagen coefficient which represents solute-solute or electrostatic interactions. The coefficient B represents solute-solvent interactions. The coefficient D reflects solute-solute and solute-solvent interactions. However, the value of A is usually small and therefore omitted [37,38]. As shown in Eq. (9), the viscosity of a solution increases with increasing the concentration of solvent. According to the equation of $\Delta E' = -\Delta E$, where $\Delta E'$ denotes the change of internal energy and ΔE represents the change of activation energy, the combination of Eqs. (7) and (9) leads to that the viscosity and activation energy will also increase with an increase of ion concentration [39]. Then the internal energy decreases and the value of $(1 - x^+ - x^-)$ will also decrease according to Eq. (7). In other words, the ratio of E'_f will decrease. Therefore, higher concentration will enhance water association. In addition, the magnetic field promotes the electron delocalization of hydrogen bonds among water molecules. The electron delocalization can lead to the formation of water clusters, promote the formation of hydrogen bonds and combine several hydration ions [40]. However such improvements are affected when Lorentz force exerting on moving ions increases beyond a critical value [41]. Particles with charge move through a uniform magnetic field with a velocity of v and are deflected by the Lorentz force within a helix. According to the equation ($f_c = eB/2\pi m_e$) of cyclotron frequency, the higher magnetic field intensity is, the higher is cyclotron frequency. The continuing increase of cyclotron frequency will promote the combination of negative and positive ions, leading to more scale formation [42]. So magnetic field intensity has an optimum value. According to Fig. 3a,b, the Ca^{2+} and Mg^{2+} concentrations decreased at magnetic field intensity of 0.8 T. Based on the concentrations of Ca^{2+} and Mg^{2+} without magnetic field, the variation of positive ion concentration reaches the peak at 0.5 T. This increase of concentration decreases the activation energy of free water. That is, appropriate magnetic field intensity can strengthen water association. However, if magnetic field intensity is beyond the optimum value, it will promote scale formation.

3.2. Effect of ion concentration on water association

To investigate the effect of ion concentration on water association, the chemical shift was analyzed. The relationship between chemical shift and concentration is shown as the following Eq. (10) [43]:

$$\delta = x^+\delta_b^+ + x^-\delta_b^- + (1-x^+-x^-)\delta_f \tag{10}$$

where δ is chemical shift (Hz); x^+ and δ_b^+ are the mole fraction and chemical shift of positive ions, respectively; x^- and δ_b^- are the mole fraction and chemical shift of negative ions, respectively; δ_f is the chemical shift of free water. The concentration variations of positive ions can be obtained in Eqs. (11)–(13).

$$\Delta C_1^+ = \frac{C_{Ca}^1 - C_{Ca}^0}{M_{Ca}} + \frac{C_{Mg}^1 - C_{Mg}^0}{M_{Mg}} = \frac{242.82-184.64}{40} + \frac{692.25-546.22}{24} = 7.56\times10^{-3}\left(mol/L\right) \tag{11}$$

$$\Delta C_2^+ = \frac{C_{Ca}^2 - C_{Ca}^0}{M_{Ca}} + \frac{C_{Mg}^2 - C_{Mg}^0}{M_{Mg}} = \frac{294.26-184.64}{40} + \frac{801.58-546.22}{24} = 14.25\times10^{-3}\left(mol/L\right) \tag{12}$$

$$\Delta C_3^+ = \frac{C_{Ca}^3 - C_{Ca}^0}{M_{Ca}} + \frac{C_{Mg}^3 - C_{Mg}^0}{M_{Mg}} = \frac{279.05-184.64}{40} + \frac{722.17-546.22}{24} = 9.59\times10^{-3}\left(mol/L\right) \tag{13}$$

where ΔC_1^+, ΔC_2^+, and ΔC_3^+ are the concentration variation of positive ions (mol/L) at magnetic field intensity of 0.2, 0.5, and 0.8 T, respectively; C_{Ca}^0, C_{Ca}^1, and C_{Ca}^3 are the concentration of Ca^{2+} (mol/L) at magnetic field intensity of 0, 0.2 , 0.5, and 0.8 T, respectively; C_{Mg}^0, C_{Mg}^1 , C_{Mg}^2, C_{Mg}^3 are concentration of Mg^{2+} (mol/L) at 0, 0.2, 0.5, and 0.8 T, respectively; and M_{Ca} and M_{Mg} denote the molar weights of calcium and magnesium, respectively. The concentration variation of negative ions can be calculated with the following Eqs. (14)–(16).

$$\Delta C_1^- = \frac{C_A^1 - C_A^0}{M_{CaCO_3}} = \frac{209.89-186.8}{100} = 2.3\times10^{-4}\left(mol/L\right) \tag{14}$$

$$\Delta C_2^- = \frac{C_A^2 - C_A^0}{M_{CaCO_3}} = \frac{212.09-186.8}{100} = 2.5\times10^{-4}\left(mol/L\right) \tag{15}$$

$$\Delta C_3^- = \frac{C_A^3 - C_A^0}{M_{CaCO_3}} = \frac{207.62-186.8}{100} = 2\times10^{-4}\left(mol/L\right) \tag{16}$$

where ΔC_1^-, ΔC_2^-, and ΔC_3^- denote the concentration variation of negative ions (mol/L) at 0.2, 0.5, and 0.8 T, respectively; and C_A^0, C_A^1, C_A^2, C_A^3 denote the concentration of alkali (mol/L) at 0, 0.2, 0.5, and 0.8 T, respectively; M_{CaCO3} is molar weight of $CaCO_3$. The variation of chemical shift can be calculated with Eqs. (17)–(20).

$$\Delta\delta_0 = \delta_0 - \delta_0 = 1879.4 - 1879.4 = 0\ (Hz) \tag{17}$$

$$\Delta\delta_1 = \delta_{0.2} - \delta_0 = 1879.6 - 1879.4 = 0.2\ (Hz) \tag{18}$$

$$\Delta\delta_2 = \delta_{0.5} - \delta_0 = 1879.96–1879.4 = 0.54 \text{ (Hz)} \quad (19)$$

$$\Delta\delta_3 = \delta_{0.8} - \delta_0 = 1879.82–1879.4 = 0.42 \text{ (Hz)} \quad (20)$$

where $\Delta\delta_0$, $\Delta\delta_1$, $\Delta\delta_2$, and $\Delta\delta_3$ denote the variations in chemical shift between the value without magnetic field and that with different magnetic field intensities, respectively; δ_0, $\delta_{0.2}$, $\delta_{0.5}$, and $\delta_{0.8}$ are the chemical shift at magnetic field intensity of 0, 0.2, 0.5, and 0.8 T, respectively. According to Eq. (11), the results can be calculated as the following Eqs. (21)–(23).

$$\Delta\delta_1 = \zeta^+\Delta C_1^+\delta_b^+ + \zeta^-\Delta C_1^-\delta_b^- + (1–\zeta^+\Delta C_1^+ + \zeta^-\Delta C_1^-)\delta_f$$
$$0.2 = (7.56\zeta^+\delta_b^+ + 0.23\zeta^-\delta_b^-) + (1–7.56\zeta^+–0.23\zeta^-)\delta_f) \times 10^{-3} \quad (21)$$

$$\Delta\delta_2 = \zeta^+\Delta C_2^+\delta_b^+ + \zeta^-\Delta C_2^-\delta_b^- + (1–\zeta^+\Delta C_2^+ + \zeta^-\Delta C_2^-)\delta_f$$
$$0.54 = (14.25\zeta^+\delta_b^+ + 0.25\zeta^-\delta_b^- + (1–14.25\zeta^+–0.25\zeta^-)\delta_f) \times 10^{-3} \quad (22)$$

$$\Delta\delta_3 = \zeta^+\Delta C_3^+\delta_b^+ + \zeta^-\Delta C_3^-\delta_b^- + (1–\zeta^+\Delta C_3^+ + \zeta^-\Delta C_3^-)\delta_f$$
$$0.42 = (9.59\zeta^+\delta_b^+ + 0.2\zeta^-\delta_b^- + (1–9.59\zeta^+ + 0.2\zeta^-)\delta_f) \times 10^{-3} \quad (23)$$

Combining Eqs. (21)–(23), the results can be obtained as follows (Eqs. (24)–(26)):

$$\delta_b^+ = \frac{28.79 + 247.89\zeta^+}{\zeta^+} > 0 \quad (24)$$

$$\delta_b^- = -\frac{1154.58 - 247.92\zeta^-}{\zeta^-} < 0 \quad (25)$$

$$\delta_f = 247.89 \text{(Hz)} \quad (26)$$

In the presence of salts, the chemical shift of liquid water generally reflects the effects of ions on water structure. When the chemical shifts are positive, they can strengthen water structure, otherwise they will damage water structure [44]. Therefore, Ca^{2+} and Mg^{2+} can promote water structure, but HCO_3^- and CO_3^{2-} will damage water structure. Thus an increase of Ca^{2+} and Mg^{2+} concentration can promote hydrogen bonds formation and enhance water association. However, an increase of HCO_3^- and CO_3^{2-} concentration will decrease water association. The formation of hydrogen bonds makes anions more stable which promotes the dissolution of $CaCO_3$ and $MgCO_3$ [45]. Due to the HCO_3^- and CO_3^{2-} become more stable, the number of Ca^{2+} and Mg^{2+} are greater and more water clusters are formed. Therefore the higher the concentration of positive ion is, the greater is the water association. The decrease of negative ion concentration will contribute to water association formation.

3.3. Relationship between $\Delta E/E_0$ and $\Delta\delta$

To study the changes of water association, it is necessary to investigate the relationship between $\Delta E/E_0$ and $\Delta\delta$ which can be obtained by the linear fitting. The results are shown in Fig. 4.

Fig. 4 shows that the chemical shift variation of positive ions is proportional to $\Delta E/E_0$. And the higher $\Delta E/E_0$ is, the stronger is the water association. According to the fitting equation ($\Delta E/E_0 = 1.52\Delta\delta - 0.12$), the relationship between $\Delta E/E_0$ and ion concentration can be obtained as follows [Eq. (27)]:

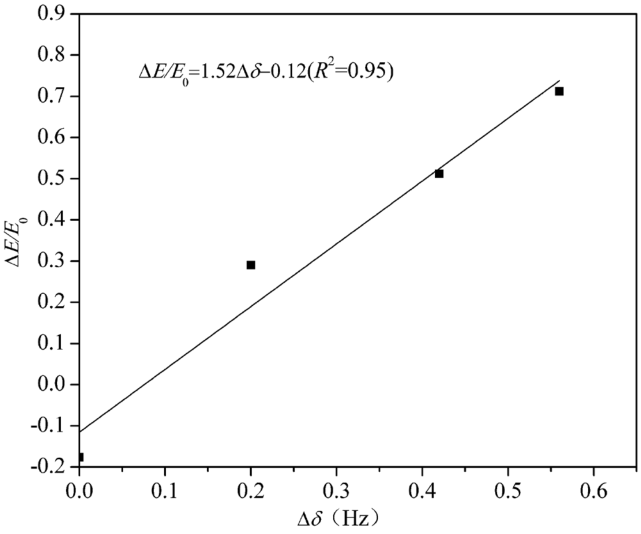

Fig. 4. Relationship between $\Delta E/E_0$ and $\Delta\delta$.

$$\Delta E/E_0 = 1.52\cdot(\zeta^+\Delta C^+\delta_b^+ + \zeta^-\Delta C^-\delta_b^- + (1–\zeta^+\Delta C^+–\zeta^-\delta_b^-)\delta_f)–0.12 \quad (27)$$

Combining with Eqs. (24)–(27), the relationship between $\Delta E/E_0$ and concentration variation can be obtained as Eq. (28).

$$\Delta E/E_0 = 43.76\Delta C^+ - (1754.96 - 0.05\zeta^-)\Delta C^- + 376.67 \quad (28)$$

As the internal energy variation is equal to the negative of activation energy variation, strengthening of water association can decrease internal energy. Eq. (28) indicates that an increase of positive ion concentration can raise activation energy and promote water association. However, the contribution of negative ions for activation energy is negative. Therefore, $\Delta E/E_0$ can determine the degree of water association based on ion concentration.

3.4. Effect of magnetic field intensity on water association

Fig. 5 shows the changes of Ca^{2+} and Mg^{2+} concentration, alkalinity and $\Delta E/E_0$ with time at different magnetic field intensities. One can see from Fig. 5a and 5b that, the Ca^{2+} and Mg^{2+} concentrations decrease quickly with increase of time without magnetic field, which implies that most calcium and magnesium carbonate precipitation is formed. Combining with the above results, one can say that the degree of water association will decrease. Fig. 5c shows that the results for alkalinity are the same, which restrained water association. Therefore, the decrease of Ca^{2+} and Mg^{2+} concentration will reduce $\Delta E/E_0$ and break water association. However, these objectives first decreased and then gradually stabilized with time at the presence of a magnetic field. The Ca^{2+} and Mg^{2+} concentration increased because magnetic field promoted the formation of hydrogen bonds. Fig. 5d shows that, with an increase in magnetic field intensity, $\Delta E/E_0$ first increases and then decreases. $\Delta E/E_0$ reaches

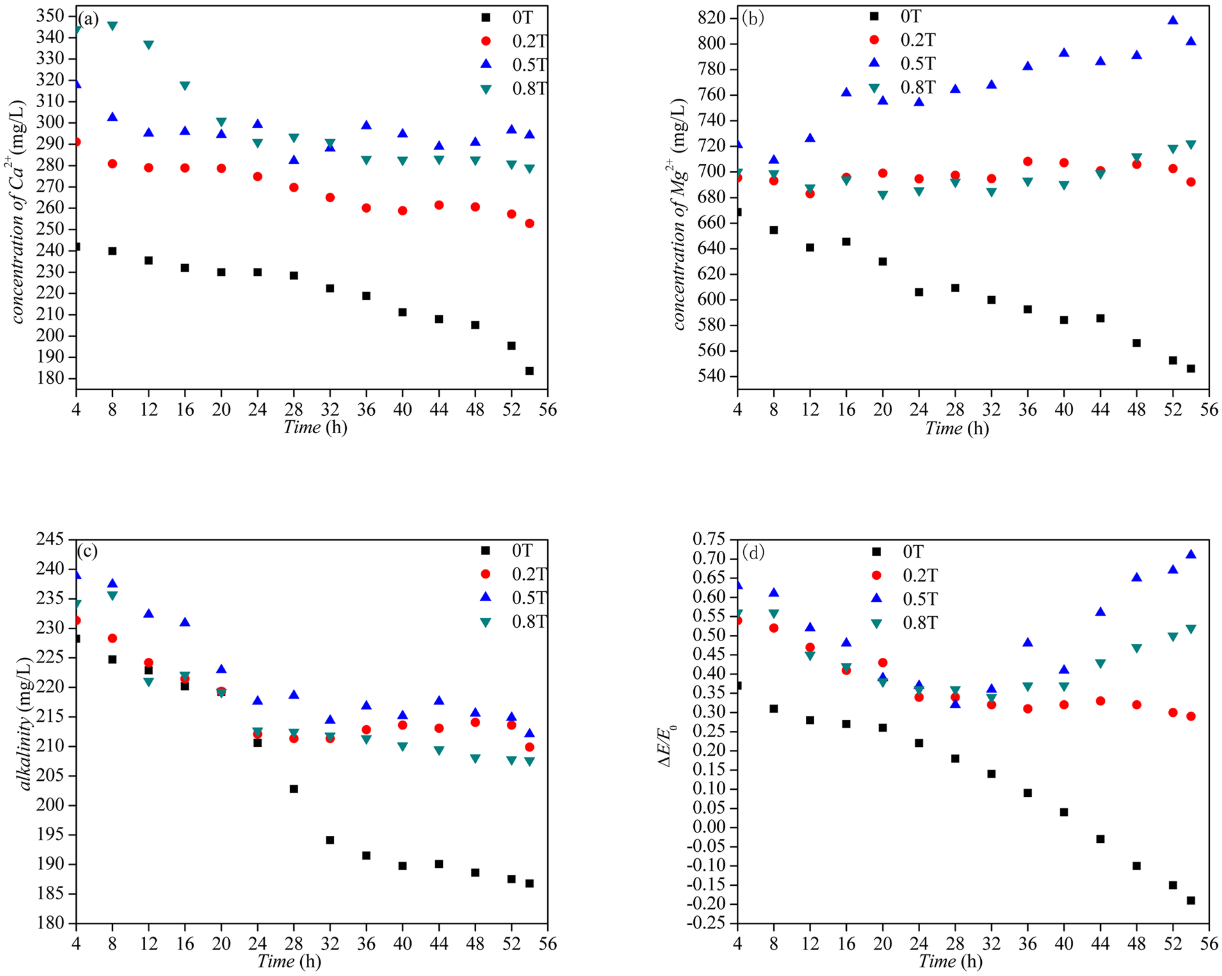

Fig. 5. Effect of magnetic field intensity on ion concentration, alkalinity and $\Delta E/E_0$.

its maximum at the magnetic field intensity of 0.5 T and then decreases when the magnetic field intensity is beyond 0.5 T. This shows that the magnetic field has an optimum intensity. If the Lorentz force is beyond the optimum value, the magnetic field can promote the combination of positive and negative ions, and break water association. Fig. 5a also shows that the concentration of Ca^{2+} increases from 32 to 56 h with a magnetic field intensity of 0.5 T, while the Mg^{2+} concentration increases from 4 to 54 h at the same magnetic field intensity, which may indicate that the force between Mg^{2+} and water clusters is stronger than that of Ca^{2+}. Therefore, the effect of Mg^{2+} on water association is more significant than that of Ca^{2+}, which may be attributed to that the radius of Mg^{2+} is smaller than that of Ca^{2+}. The smaller the radius of cationic ion is, the greater is the degree of water association [46].

4. Conclusions

The effect of permanent magnetic field on water association in circulating water was experimentally studied. $L_{16}(4^5)$ orthogonal experiments were designed and implemented to focus on the factors of initial concentration, magnetic field intensity, temperature, time and flow velocity. The results show that the chemical shift, alkalinity, relative variations of activation energy and Ca^{2+} and Mg^{2+} concentrations varied considerably under orthogonal experimental design conditions. The results of range analysis show that the magnetic field intensity is the key factor affecting water clusters formation. The optimum conditions for the present facility are 900 mg/L of initial concentration, 0.5 T of magnetic field intensity, 303 K of temperature, 54 h of time and 0.17 m/s of water flow velocity. High initial concentrations of Ca^{2+} and Mg^{2+} have considerable influence on hydrogen bond formation. The effect of Mg^{2+} concentration on water association is greater than that of Ca^{2+}. However, the increase of CO_3^- and CO_3^{2-} concentrations will break water clusters and water association. The presence of magnetic field promoted water association. The effect of preventing scale will be decreased as the magnetic field intensity exceeds the optimum value, which reduces water association.

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Symbols

$C_{\text{EDTA-Na2}}$ — Concentration of EDTA-Na_2 (mol/L)
M — Quantity of $MgCl_2 \cdot 6H_2O$ (g)
M — Molecular weight of $MgCl_2 \cdot 6H_2O$ (g/mol)
$V_{\text{EDTA-Na}_2}$ — Volume of EDTA-Na_2 (L)
M_{CaO} — Molecular weights of CaO (g/mol)
M_{Ca} — Molecular weights of Ca (g/mol)
M_{Mg} — Molecular weights of Mg (g/mol)
V_{water} — Volume of water (L)
C_{Ca} — Concentration of Ca^{2+} (mol/L)
C_{Mg} — Concentration of Mg^{2+} (mol/L)
p — Volume of HCl when phenolphthalein is fading (L)
C_{HCl} — Concentration of hydrochloric acid standard solution (mol/L)
M_{CaCO_3} — Molecular weight of $CaCO_3$ (g/mol)
V_{water} — Volume of water (L)
$\Delta E/E_0$ — Relative variation of activation energy
E — Activation energy of experimental water (kJ/mol)
E_0 — Activation energy of ultra-pure water (kJ/mol)
h — Planck constant ($h = 6.626 \times 10^{-34}$ J·s)
N_A — Avogadro′s number ($N_A = 6.02 \times 10^{23}$/mol)
V_m — Molar volume of liquid (L/mol)
η — Viscosity of experimental water (mPa·s)
η_0 — Viscosity of ultra-pure water (mPa·s)
η_1 — Viscosity of solution(mPa·s)
η_2 — Viscosity of solvent (mPa·s)
K_i — Average value of the objective variable
R_j — Range calculated from the difference between maximum and minimum of k_i for a certain factor
E' — Internal energy level (J)
x^+ — Mole fraction of positive ions
E'^{+}_{b} — Molar internal energy of positive ions (J)
x^- — Mole fraction of negative ions
E'^{-}_{b} — Internal energy of negative ions (J)
E'_f — Internal energy of free water molecules (J)
C — Concentration of ions (mol/L)
ζ — Constant which has nothing to do with the concentration
A — Falkenhagen coefficient
B — Solute-solvent interactions
D — Solute-solute and solute-solvent interactions
f_c — Cyclotron frequency (Hz)
B — Magnetic field intensity (T)
δ — Chemical shift (Hz)
$\Delta\delta_0$ — Variation of chemical shift at 0 T (Hz)
$\Delta\delta_1$ — Variation of chemical shift at 0.2 T (Hz)
$\Delta\delta_2$ — Variation of chemical shift at 0.5T (Hz)
$\Delta\delta_3$ — Variation of chemical shift at 0.8 T (Hz)
δ_0 — Chemical shift at 0 T (Hz)
$\delta_{0.2}$ — Chemical shift at 0.2 T (Hz)
$\delta_{0.5}$ — Chemical shift at 0.5 T (Hz)
$\delta_{0.8}$ — Chemical shift at 0.8 T (Hz)

References

[1] T.Y. Chen, S.H. Chan, Novel biological inhibitors of fouling and scale formation on heat transfer surfaces through genetic engineering, Microscale Thermophys. Eng., 4 (2000) 103–108.

[2] X. Wang, B.I. Lee, L. Mann, Dispersion of barium titanate with polyaspartic acidin aqueous media, Colloid Surf. A, 202 (2002) 71–80.

[3] D. Lisitsin, Q. Yang, D. Hasson, R. Semiat, Inhibition of $CaCO_3$ scaling on RO membranes by trace amounts of zinc ions, Desalination, 183 (2005) 289–300.

[4] R. Ketrane, B. Saidani, O. Gil, L. Leleyter, F. Baraud, Efficiency of five scale inhibitors on calcium carbonate precipitation from hard water: effect of temperature and concentration, Desalination, 249 (2009) 1397–1404.

[5] N.N. Al-Mutairi, F.A. Aleem, M.I. Al-Ahmad, Effect of antiscalants for inhibition of calcium sulfate deposition in thermal desalination systems, Desal. Water Treat., 10 (2009) 39–46.

[6] D.J. Kukulka, M. Devgun, Fluid temperature and velocity effect on fouling, Appl. Therm. Eng., 27 (2007) 2732–2744.

[7] J. Macadam, S.A. Parsons, Calcium carbonate scale control, effect of material and inhibitors, Water Sci. Technol., 49 (2004) 153–159.

[8] S.S. Al-Jaroudi, A. Ul-Hamid, J.A. Al-Matar, Prevention of failure in a distillation unit exhibiting extensive scale formation, Desalination, 260 (2010) 119–128.

[9] V. Kozic, A. Hamler, I. Ban, L.C. Lipus, Magnetic water treatment for scale control in heating and alkaline conditions, Desal. Water Treat., 22 (2010) 65–71.

[10] R.A. Barrett, S.A. Parsons, The influence of magnetic fields on calcium carbonate precipitation, Water Res., 32 (1998) 609–612.

[11] T. Vermeiren, Magnetic treatment of liquids for scale and corrosion prevention, Cor. Technol., 5 (1958) 215–219.

[12] F. Alimi, M. Tlili, M.B. Amor, C. Gabrielli, G. Maurin, Influence of magnetic field on calcium carbonate precipitation, Desalination, 206 (2007) 163–168.

[13] J.M.D. Coey, S. Cass, Magnetic water treatment, J. Magn. Magn. Mater., 209 (2000) 71–74.

[14] I.M. Glushchenko, S.P. Grishaenko, Y.V. Myagkov, Magnetic apparatus for the coke and chemical industry, Coke Chem. (USSR) (Engl. Transl.), 11 (1983) 61–65.

[15] L.L. Jiang, J.L. Zhang, D.K. Li, Effects of permanent magnetic field on calcium carbonate scaling of circulating water, Desal. Water Treat., 53 (2015) 1275–1285.

[16] E.J.L. Toledo, T.C. Ramalho, Z.M. Magriotis, Influence of magnetic field on physical-chemical properties of the liquid water: insights from experimental and theoretical models, J. Mol. Struct., 888 (2008) 409–425.

[17] K. Kronenberg, Experimental evidence for effects of magnetic fields on moving water, IEEE Trans. Magnet., 21 (1985) 2059–2061.

[18] K.T. Chang, C.I. Weng, The effect of an external magnetic field on the structure of liquid water using molecular dynamics simulation, J. Appl. Phys., 100 (2006) 043917–043923.

[19] K. Higashitani, J. Oshitani, Measurements of magnetic effects on electrolyte solutions by atomic force microscope, Process Saf. Environ. Prot., 75 (1997) 115–119.

[20] K. Higashitani, A. Kage, S. Katamura, K. Imai, S. Hatade, Effects of magnetic field on formation of $CaCO_3$ particles, J. Colloid Interf. Sci., 156 (1993) 90–95.

[21] V. Arulmozhi, A.S. Rao, Proton magnetic resonance relaxation studies in aqueous solutions of alkali halides and sugars, Phys. Chem. Liq., 26 (1993) 201–207.

[22] R.A. Horne, D.S. Johnson, The viscosity of water under pressure, J. Phys. Chem., 70 (1966) 2182–2190.

[23] R.H. Li, Z.P. Jiang, S. Shi, H. Yang, Raman spectra and ^{17}O NMR study effects of $CaCl_2$ and $MgCl_2$ on water structure, J. Mol. Struct., 645 (2003) 69–75.

[24] R.E. Waskylishen, S. Moobroek, J.B. Macdonald, A more reliable oxygen^{-17} absolute chemical shielding scale, J. Chem. Phys., 81 (1984) 1057–1059.

[25] H. Jin, X. Li, M. Maroncelli, Heterogeneous solute dynamics in room temperature ionic liquids, J. Phys. Chem., 111 (2007) 13473–13478.

[26] A. Paul, P.K. Mandal, A. Samanta, On the optical properties of the imidazolium ionic liquids, J. Chem. Phys. B, 109 (2005) 9148–9153.

[27] Z. Hu, C.J. Margulis, Heterogeneity in a room-temperature ionic liquid: persistent local environments and the red-edge effect, Proc. Natl. Acad. Sci. USA, 103 (2006) 831–836.

[28] S. Saha, H. Hamaguchi, Effect of water on the molecular structure and arrangement of nitrile-Functionalized Ionic Liquids, J. Phys. Chem. B, 110 (2006) 2777–2781.

[29] L. Cammarata, S.G. Kazarian, P.A. Salter, T. Welton, Molecular states of water in room temperature ionic liquids, Phys. Chem. Chem. Phys., 3 (2001) 5192–5200.

[30] C.D. Tran, S.H.P. Lacerda, D. Oliveira, Absorption of water by room-temperature ionic liquids: effect of anions on concentration and state of water, Appl. Spectrosc., 57 (2003) 152–157.

[31] T.S. Jang, J.J. Lee, D.H. Lee, Y.S. Yoon, Systematic methodology for the design of a flexible keel for energy-storing prosthetic feet, Med & Bio Eng & Comp., 39 (2001) 56–64.

[32] R. Cai, H.W. Yang, J.S. He, W.P. Zhu, The effect of magnetic fields on water molecular hydrogen bonds, J. Mol. Struct., 938 (2009) 15–19.

[33] J.C. Hindman, A.J. Zielen, A. Svirmickas, M. Wood, Relaxation processes in water the spin-lattice relaxation of the deuteron in D_2O and oxygen^{-17} in $H_2{}^{17}O$, J. Phys. Chem., 54 (1971) 621–634.

[34] J.S. He, H.W. Yang, X.L. Gan, Energy characterization of effect for ions on the structure of water, Acta Phys. Chim. Sin., 27 (2011) 2499–2505.

[35] G. Jones, M. Dole, The viscosity of aqueous solutions of strong electrolytes with special reference to barium chloride, J. Amer. Chem. Soc., 51 (1929) 2950–2964.

[36] N. Martinus, D. Crawford, D. Sinclair, C.A. Vincent, The extended jones-dole equation, Electrochim. Acta, 22 (1977) 1183–1187.

[37] L.A. Gribov, Yu.A. Pentin, Conference on the theory of the structure and spectra of complex molecules, J. Struct. Chem., 36 (1995) 179–179.

[38] H. Donald, B. Jenkins, Y. Marcus, Viscosity B-coefficients of ions in solution, Chem. Rev., 95 (1995) 2695–2724.

[39] M. Biskup, L. Chayes, R. Kotecký, A proof of the Gibbs-Thomson formula in the droplet formation regime, J. Stat. Phy., 116 (2004) 175–203.

[40] H. Hosoda, H. Mori, N. Sogoshi, S. Nakabayashi, Refractive indices of water and aqueous electrolyte solutions under high magnetic fields, J. Phys. Chem. A, 108 (2004) 1461–1464.

[41] K. Higashitani, A. Kage, S. Katamura, K. Imai, S. Hatade, Effects of magnetic field on the formation $CaCO_3$ particles, J. Colloid Interface Sci., 156 (1993) 90–95.

[42] H.E. Madsen, Influence of magnetic field on the precipitation of some inorganic salts, J. Cryst., 152 (1995) 94–100.

[43] J.S. He, H.W. Yang, X.L. Gan, Energy characterization of effect for ions on the structure of water, Acta Phys.- Chim. Sin., 27 (2011) 2499–2504.

[44] R.H. Li, Z.R. Jiang, S. Shi, H. Yang, Raman spectra and ^{17}O-NMR study effect of $CaCl_2$ and $MgCl_2$ on water structure, J. Mol. Struct., 645 (2003) 69–75.

[45] G.R. Pan, Extensive influence of hydrogen bond on the nature of matter and chemical reaction, Guangdong chemical industry, 40 (2013) 120–121.

[46] R.H. Li, Z.P. Jiang, S.Q. Shi, H.W. Yang, S.Y. Yuan, Effect of common ions in water on water association by ^{17}O-NMR, A. environ. Sci., 23 (2002) 45–48.