

Research Article

Interference of Lithium in Measuring Magnesium by Complexometry: Discussions of the Mechanism

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There is usually a large concentration of magnesium in the brine of salt lakes and as a consequence it is difficult to measure Mg^{2+} accurately with the complexometric titration by ethylenediaminetetraacetic acid disodium salt (EDTA) because of the large levels of Li^+ also coexisting in brine samples. In this study, a relationship between the relative error related to the number of drops of the indicator and the NMR spectra of anhydrous ethanol and n-butanol, with or without LiCl, was analyzed and compared. It was then possible to suggest a mechanism to explain the interference of Li^+ when measuring Mg^{2+} and to control the interference in the alcohol mixture because Li^+ can then complex with the alcohols and mainly form a complex with n-butanol.

1. Introduction

Salt lakes are widely distributed in the western part of China, especially in the area of the Qinghai-Xizang (Tibet) Plateau and they represent rich resources in lithium and magnesium. Salt lakes of the Qaidam Basin consist of a series of lakes including Caerhan Lake, where 2 million tons of potassium fertilizer is produced per year at present, Dongtai Lake, Xitai Lake, and Yiliping Lake that are a subtype of magnesium sulfate brines famous for their abundance of inorganic salt resources of lithium, potassium, magnesium, and boron and also for the highest concentration ratio of magnesium to lithium in brines around the world from 500 to 800 [1]. It is of absolute importance to accurately measure the content of magnesium in the brine for the suitable development of resources in salt lakes. Complexometry by EDTA is usually used to measure the magnesium ions, but it was found that large amounts of lithium coexisting with magnesium would interfere with the measurement of magnesium. A method was proposed to eliminate the interference, but its applicable range of mass ratio Li/Mg was narrow [2, 3]. In the research on phase equilibrium of brine systems of lithium and magnesium, we found that the Li/Mg mass ratio can be far above 12,

which would make the available method not suitable. Using a mixture of alcohols (n-butanol and anhydrous ethanol), it was possible to extend the control of interference to a larger Li/Mg ratio [4]. In this paper, the mechanism of the interference and its elimination are discussed and precise data for measuring Mg^{2+} in brines are provided, which would be useful in the comprehensive development of resources in salt lakes.

2. Experimental

2.1. Reagents and Solutions. A standard solution of magnesium $MgSO_4$ (high purity) was heated at $680^\circ C$ for 4 h and then cooled in a desiccator. A mass of 4.9525 g was weighed and dissolved in a 1000 mL volumetric flask for a final Mg^{2+} concentration of 1.0000 mg/mL. A solution of the lithium salt $Li_2SO_4 \cdot H_2O$ (analytical reagent, A.R.) was heated at $85^\circ C$ for 4 h and then cooled down in a desiccator. A mass of 18.4591 g was weighed and dissolved in a 500 mL volumetric flask for a final Li^{2+} concentration of 4.0051 mg/mL. The two alcohols n-butanol and anhydrous ethanol (both A.R.) were mixed at a volumetric ratio of 1:10. An $NH_4Cl-NH_3 \cdot H_2O$ buffering solution was prepared with 60.00 g of NH_4Cl (A.R.) dissolved

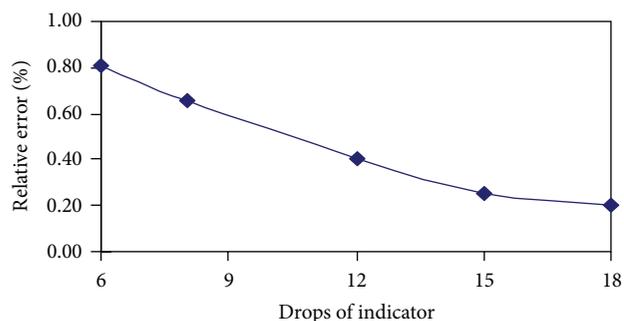


FIGURE 1: Relationship between the relative error of the titration and the number of drops of indicator.

into water and 240 mL $\text{NH}_3 \cdot \text{H}_2\text{O}$ (A. R.) added to finally be diluted to 3000 mL. The pH of the solution was approximately 10.

To prepare the indicator, 0.20 g of Eriochrome Black T (NaInd) was dissolved in 10 mL of the $\text{NH}_4\text{Cl} \cdot \text{NH}_3 \cdot \text{H}_2\text{O}$ buffer solution and then diluted to 100 mL with ethanol (A.R., 95%). For the standard solution of EDTA, 73.81 g of the disodium salt was dissolved into 4000 mL water, and it was standardized by the standard solution of MgSO_4 . Double-distilled water was treated by electro dialysis desalination and ion exchange and had conductivity at less than 1.2×10^{-4} S/m.

2.2. Methodology. Solutions that contain 25.00 mg Mg^{2+} and 6.02 mg Li^+ were added into an Erlenmeyer Flask; six to 18 drops of NaInd indicator were added followed by 10 mL of the $\text{NH}_4\text{Cl} \cdot \text{NH}_3 \cdot \text{H}_2\text{O}$ buffer solution. Each solution was titrated with the standard solution of EDTA from the tartaric red to azure. LiCl was dissolved into ethanol and n-butanol, respectively, and then the solutions were analyzed with a Bruker-AM300 NMR (Germany).

3. Results and Discussion

3.1. Interference of Li^+ to the Measurement of Mg^{2+} . The relationship between the amount of indicator added and the relative error (RE) of the titration was plotted in Figure 1. It was found that when the Li/Mg mass ratio was less than 1, the titration relative error was declined with increasing the number of drops of the indicator. From the experimental data, it was found that 13 to 16 drops of NaInd indicator were optimum when Li/Mg was less than 1. From the NMR spectra of n-butanol presented in Figures 2 and 3, it can be seen that, at δ 3.6 to 3.7 ppm, the coupling of vicinal $-\text{CH}_2$ and $-\text{OH}$ made it appear as a quartet. When LiCl was added, there was no splitting, and it became a broadband. From δ 1.3 to 1.7 ppm, the spectra of $-\text{CH}_2$ and $-\text{OH}$ were layered together to form a multiplet. When LiCl was added, it also became a broadband. At δ 0.9 to 1.0 ppm, the triplet also became a broadband when LiCl was added to the solution. The same phenomena were observed with ethanol in Figures 4 and 5. Since there were various ligands to complex with the metal

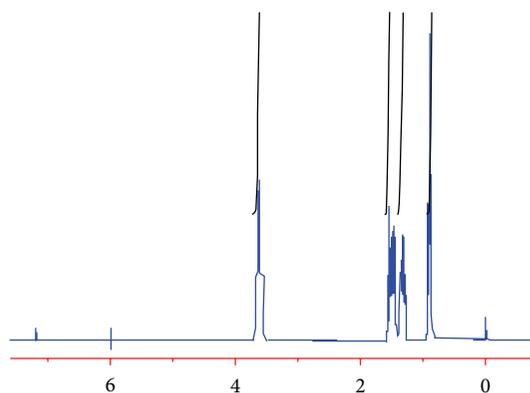


FIGURE 2: NMR spectrum of n-butanol.

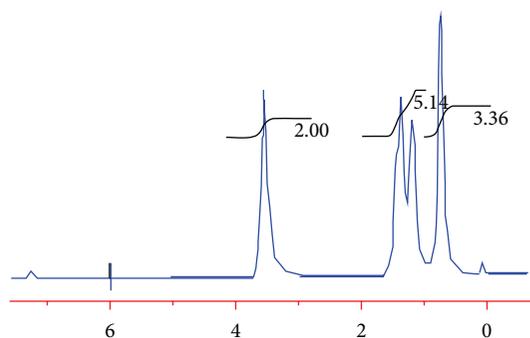


FIGURE 3: NMR spectrum of n-butanol with LiCl.

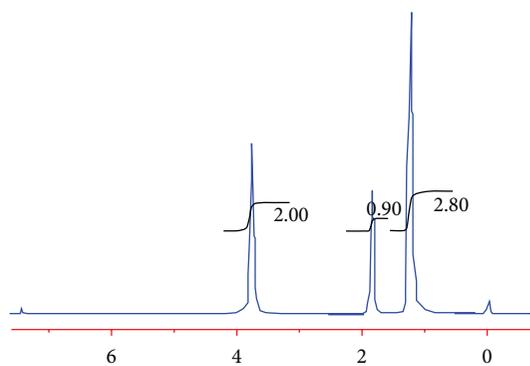


FIGURE 4: NMR spectrum of ethanol.

ion, it would make the splitting effect caused by the vicinal protons disappear. The disappearance of the multiple spectrum (Figures 2 and 4) and the formation of broad spectrum (Figures 3 and 5) indicate various structures of the alcohols in the mixture. These resulted from the complexation between the alcohols and the lithium complex.

3.2. The Reactions. The complexation titration by EDTA is commonly used to measure Mg^{2+} in the salt lake brine with

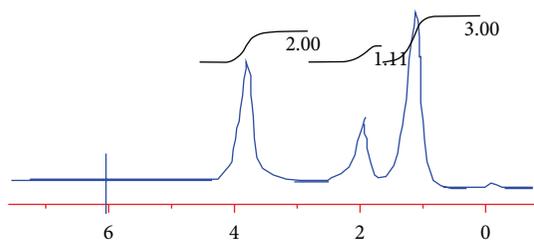
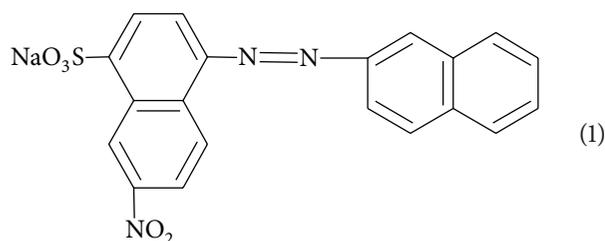
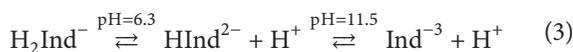


FIGURE 5: NMR spectrum of ethanol with LiCl.

NaInd as the indicator. The molecular structure of NaInd is given below [5]:

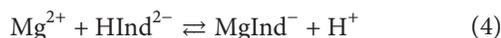


The dissociation equation of indicator NaInd in the solution is [6]



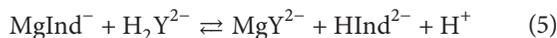
(H_2Ind^- , HInd^{2-} , and Ind^{3-} are tartaric red, azure, and orange, respectively, and change points are in the previously mentioned different pHs).

When there is Mg^{2+} , it would react with NaInd as follows:



(HInd^{2-} is azure, and MgInd^- is tartaric red.)

When titrated with EDTA ($\text{Na}_2\text{H}_2\text{Y}$), it would react as follows:



At the end of the titration, MgInd^- turns into HInd^{2-} completely, and the solution becomes azure. However, when there is a large amount of Li^+ in solution, the end point would lag and sometimes the solution cannot turn azure.

3.3. The Interference Mechanism. The cation Li^+ can also complex with EDTA as Mg^{2+} , the log of their complexation constants being 2.8 for K_{LiY} and 8.7 for K_{MgY} , respectively. The log of the complexation constant of Mg^{2+} with the indicator K_{MgIn} is 7.0 or 5.75 (when $\text{pH} = 10$, 25°C) [5, 7].

From the data given above, it can be easily seen that the stability of the complex formed with Li^+ is much lower than that formed with Mg^{2+} . At the proximity of the end point, some Li^+ will substitute Mg^{2+} from MgY^{2-} and some Mg^{2+}

will complex with the indicator to form the tartaric red MgInd^- , which makes the titration completion lag and change the stability constant. It is suggested that Li^+ would also complex with the indicator (Ind^{2-}), the color of the formed complex LiInd^- being similar to that of MgInd^- . As the stability constant of LiY^{2-} is small, it becomes difficult for EDTA to substitute Li^+ from LiInd^- . With increasing concentrations of Li^+ , the $m_{\text{LiInd}^-}/m_{\text{Ind}^{2-}}$ ratio will increase, the color of the solution will be a mixture of azure and tartaric red, and it will become hard to determine the end point. When EDTA is in excess, the equilibrium of the EDTA titration will shift to the right, and the color of the solution becomes azure gradually until it reaches the end point. However, when a large amount of Li^+ is present in the solution, the $m_{\text{LiInd}^-}/m_{\text{Ind}^{2-}}$ ratio will increase rapidly. It became indispensable to add a large amount of EDTA to make the solution reach the end azure color, which made the measurement of Mg^{2+} incorrect as follows:

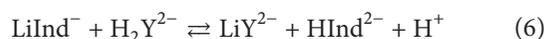


Figure 1 indicates that when there was a small amount of Li^+ in the solution, the RE of titration decreased as more indicator was added. It shows that it was hard for EDTA to substitute Li^+ in LiInd^- ; as the amount of indicator was increased, the $m_{\text{LiInd}^-}/m_{\text{Ind}^{2-}}$ ratio decreased and the equation (6) shifted to the left and the titration end point was easier to be reached.

3.4. Mechanism of Interference Elimination

3.4.1. Analysis of the NMR Spectrum. Figures 2 to 5 reveal that adding the mixture of alcohols can eliminate the interference of Li^+ to the measurement of Mg^{2+} because Li^+ would form complexes with ethanol and n-butanol and the stability constant of Li^+ with alcohols is far larger than that of LiInd^- . Consequently, most of Li^+ would exist in the complex, so the interference to the end point color decreases or even disappears. It could also explain what was discussed in our paper [4] about the elimination of the Li^+ interference to the measurement of Mg^{2+} with the addition of the alcohol mixture.

3.4.2. Analysis of the Experimental Values. When the alcohol mixture was added to solutions without Li^+ or with a small amount of Li^+ , it would make a negative error on the titration [4]. The reason could be that Mg^{2+} could also form a complex with the alcohols, though the stability constant of the Mg^{2+} complex was much lower than that of MgInd^- . Nevertheless, a small amount of Mg^{2+} would form a complex with the remaining alcohol mixture, which resulted in a negative error on the titration.

From this previous work [4], it was found that a volume ratio of n-butanol and anhydrous ethanol between 1:7 and 1:10 could have an optimum effect. It was observed that the alcohol mixture could not dissolve completely in water. Since n-butanol is immiscible with water, it could not effectively form a complex with Li^+ and it gave a large positive error.

When the ratio was greater than 1:8, the relative error increased as the amount of n-butanol decreased. It indicated that Li^+ would react mainly with n-butanol to form a complex.

3.4.3. *Analysis of Fuoss Theory.* According to the Fuoss theory on electrolytic conductance [8, 9],

$$K_A = \left(\frac{4\pi N a^3}{3000} \right) \exp \left(\frac{e^2}{a D k T} \right), \quad (7)$$

where K_A is the complex stability constant, D is the dielectric constant, N is the Avogadro number, a is the distance between particles, k is the Boltzmann constant (J/K), and T is temperature (K). The permittivity constants D at 20°C of the three used solvents are 25.30, 17.84, and 80.20, for ethanol, n-butanol, and water, respectively [10].

It can be presumed that, in the solutions of this study, all the factors remain the same except for D . From the simple additive rule, D of the solution becomes smaller when the alcohol mixture is added, which then makes the complexation constant in solution increase. It agrees well with the suggestion mentioned above that Li^+ and Mg^{2+} form complexes in the solution. The lithium and magnesium both have the ability of complexing but because of their different atomic structures, their respective abilities of complexing are different. The similarity in complexation causes interference to the measurement of Mg^{2+} when Li^+ is present in the system. With this investigation on the mechanism of the interference, we propose to explain it by the fact that Li^+ can complex with the indicator and K_{LiInd^-} is larger than K_{MgInd^-} . It is possible to explain the elimination of the interference in the alcohol mixture because Li^+ can then complex with the alcohols and mainly form a complex with n-butanol, whose stability is greater than K_{LiInd^-} whereas the stability constant of the Mg^{2+} complex with the alcohol mixture is much lower than that of K_{MgInd^-} .

4. Conclusion

The presence of high concentrations of the lithium ion Li^+ can interfere with the determination of Mg^{2+} by EDTA complexometric titration. It is possible to control this interference by using a mixture of anhydrous ethanol and n-butanol. It is proposed that a complex is formed between Li^+ and n-butanol, thus preventing the formation of a complex of Li^+ with the indicator NaInd at the proximity of the end point, which is causing a delay in the color change in the complexation of Mg^{2+} by EDTA. This is an important aspect of the titration to consider in water containing high Li^+ levels such as salt brines.

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