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RESEARCH ARTICLE

STUDYING ON THE EFFECTS OF ALKYL POLYGLYCOSIDE (APG10) TO THE FORMATION OF COMPLEXES OF IONS Ni^{2+} , Co^{2+} , Sr^{2+} , Zr^{4+} WITH CITRIC ACID

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ABSTRACT

The stability constants of complexes formed by metal cations Ni^{2+} , Co^{2+} , Sr^{2+} , Zr^{4+} with citric acid ligand in water and in APG10 surfactant medium –water were determined by the pH titration method combined with using Hyss 2009 simulation software. Under the experimental conditions, metal cations Ni^{2+} , Co^{2+} , Sr^{2+} , Zr^{4+} with citric acid form some species of complexes of $[NiCit]^-$, $[NiHCit]$, $[NiCit_2]^{4-}$ and $[NiHCit_2]^{3-}$ for Ni^{2+} , $[CoCit]^-$, $[CoHCit]$ and $[CoCit_2]^{4-}$ for Co^{2+} , $[SrCit]^-$, $[SrHCit]$ and $[SrCit_2]^{4-}$ for Sr^{2+} , $[ZrCit]^{+}$, $[ZrCitH]^{2+}$ and $[ZrCit_2H]^-$ for Zr^{4+} both in water and in APG10/water solution. The $\log\beta$ values of the stability constants of the complexes are linearly dependent and decreases with increasing concentration of APG10. In 0.5% APG10 solution, the decrease in complex stability constant values were compared with the values in the aqueous environment as following: the decrease in the values from 4.367 times to 14.126 times for complexes of Ni^{2+} and citric acid; for complexes formed by Co^{2+} from 2.089 times to 5.012 times for Co^{2+} and citric acid; from 1.445 times to 3.098 times for the Sr^{2+} and citric acid and this value decreases from 2.884 times to 4.571 times for Zr^{4+} and citric acid.

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INTRODUCTION

The complexation of metal ions with chelated agents is interested in many researches and applications, which are very popular in many industries such as paper production, textiles, and water treatment to reduce the hardness of water especially in medical applications and in anticoagulant drugs or to remove toxins such as Pb, As, Hg, ... from the human body [3]. Complex reactions are also applied in analytical chemistry, production of agricultural fertilizers, cleaning products, cosmetics and radioactive detergents to remove heavy metals, including radioactive metals from the infection, isolate them in the anti-reinfection solution by chelate agents having a complex reaction with some radioactive metal ions such as Ni, Co, Sr, U ... [3,4]. In the field of past decontamination, sunfonol and the complexing agents which are sodium phosphate compounds such as sodium tripolyphosphate, sodium hexametaphosphate, and sodium pyrophosphate are used [1]. These systems have the ability to create complexes quickly, highly effective in radiation removing but harmful to the environment and easy to clump (powdered detergent), and difficult preparation. Recently, cleaning solutions often use chelated complexes instead of sodium phosphate compounds in combination with surfactants to increase cleaning activity. In particular, the system consists of a citric ring complex with APG surfactants (non-ionic surfactant are derived from sugar) is used quite popular due to its environmental friendliness and safety for users and weapons equipment.

This article introduces the research results of the influence of APG10 surfactant on the complexing of some metal ions (radioactive isotope simulator) which are stable isotopes of Ni^{2+} , Co^{2+} , Sr^{2+} , Zr^{4+} with citric acid.

EXPERIMENTAL

Chemicals: $Zr(NO_3)_4 \cdot 5H_2O$, 99% England; $Co(NO_3)_2 \cdot 6H_2O$, 99%, $Ni(NO_3)_2 \cdot 6H_2O$, 98%; $Sr(NO_3)_2$, 98%, Merck; APG10 non-ionic surfactant (Merck), citric acid, 99%, Indian; 0.1M HNO_3 standard tubes, $NaNO_3$ (p.A).

Equipment: The equipment and instruments are mainly used: Mettler Toledo S220K pH meter (Switzerland), Cole Palmer heating stirrer, Hyss 2009 simulation computer software.

MATERIALS AND METHODS

The study of the complex formation of citric with metal cations in water and APG10 surfactants was conducted by titration method, combined with Hyss 2009 software [5,6]. Pipette a solution of 0.1M HNO_3 , 0.1M $NaNO_3$, 0.1M citric, 0.1M metal ions, 0.61% APG10 and water according to Table 1 ratio into a 250 mL glass beaker (total solution used in each experiment was 80mL).

Experiment 1: Used to determine the stability constant of citric acid in aqueous solution (without surfactant).

Experiment 2-6: Used to determine the stability constant of citric acid in the environment of APG10 surfactant with concentration of APG10 of 0.1%; 0.2%; 0.3%; 0.4%; 0.5%.

Experiment 7: To study the complexing of citric acid with metal cations Ni²⁺, Co²⁺, Sr²⁺, Zr⁴⁺ in aqueous environment (without surfactant).

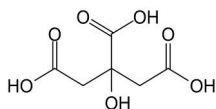
Experiment 8-12: To study the complexing of citric acid with metal cations Ni²⁺, Co²⁺, Sr²⁺, Zr⁴⁺ in the environment of APG10 surfactant with concentration of APG10 of 0.1%, 0.2%, 0.3%, 0.4%, 0.5%.

Use a 1000 μ L micropipette to drop slowly 0.1 to 0.2 mL of the 0.1M NaOH solution into a 250 mL glass beaker containing 80 mL of solution in the above experiments. Stir the solution with a magnetic stirrer with a stirring speed of 125 rpm at 30 °C. Wait for the solution to stabilize and measure the pH; record pH values and develop titration curves, in conjunction with Hyss 2009 software to determine the stability constants and the distribution of complex constituents.

RESULTS AND DISCUSSION

The influence of APG10 surfactant on the stability constant of citric acid:

Citric is a weak organic acid with molecular formula C₆H₈O₇, structural formula [2]:



In solution, citric dissociates in 3 steps (denoted by citric acid as H₃Cit) to form H₂Cit⁻, HCit²⁻ and Cit³⁻ ions. The stability constants of H₃Cit, H₂Cit⁻, HCit²⁻ components are β_{H_3Cit} , $\beta_{H_2Cit^-}$, $\beta_{HCit^{2-}}$, respectively submission (1); (2); (3).



$$\beta_{H_3Cit} = \frac{[H_3Cit]}{[Cit^{3-}] \times [H^+]^3}$$

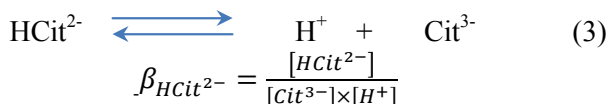
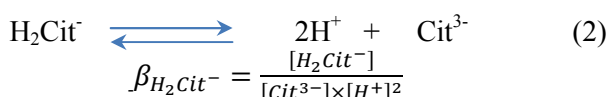


Figure 1 leads to a complex titration curve and distribution of concentrations of citric acid components in water as follows:

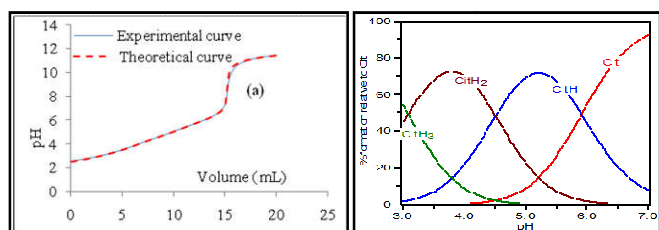


Figure 1. Complexation titration curve (1a) and the distribution concentration of citric acid constituents in water (1b)

In experimental solution, citric acid exists in 4 forms: H₃Cit, H₂Cit⁻, HCit²⁻ and Cit³⁻. The ratio of the above components depends on the pH of the environment. When pH increases, the

content of H₃Cit decreases, Cit³⁻ increases; the content of H₂Cit⁻ reaches its maximum at pH = 4 while HCit²⁻ maximizes at pH = 5.5. When pH > 7, there is a primary concentration of Cit³⁻ in solution (Figure 1b). From the software, we can determine the stability constant value of citric acid under experimental conditions as shown in Table 2

Table 2. Stability constants of citric acid in water

| Constituent | log β |
|---------------------------------|------------------|
| HCit ²⁻ | 5.91 \pm 0.05 |
| H ₂ Cit ⁻ | 10.42 \pm 0.07 |
| H ₃ Cit | 13.50 \pm 0.08 |

From the software, we can determine the stability constant value of citric acid under experimental conditions as shown in Table 2.

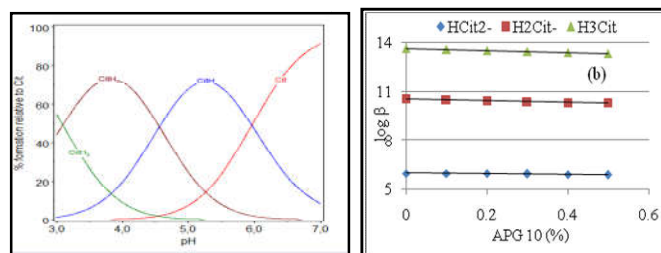


Figure 2. Graph of content distribution of citric acid components in APG10 medium (2a) and dependence of log β according to APG10 concentration (2b)

From Figure 2b, as the concentration of APG10 in solution increases, the stability constant of components decreases. At APG10 concentration of 0.5%, the stability constant of H₃Cit, H₂Cit⁻, HCit²⁻, respectively is 4.169.10¹³; 3.311.10¹⁰; 9.120.10⁵ decreased corresponding to 2.188; 1.778; 1.318 times higher than that values in water. Thus, the presence of APG10 has affected the dissociation of citric acid in solution. The formation of micelles can reduce the interaction of complexing constituents thereby reducing the stability constants and the degree of interaction attenuation increases as the number and size of micelles increase, which means that the concentration of APG10 increases.

Complexization of metal ions with citric acid in water: Based on Hyss software, it is shown that under experimental conditions, citric acid complexes with Ni²⁺ form the NiCit⁻, NiHCit, NiCit₂⁴⁻ and NiHCit₃³⁻ complexes; for Sr²⁺ form SrCit⁻, SrHCit and SrCit₂⁴⁻; for Co²⁺ create CoCit⁻, CoHCit and CoCit₂⁴⁻ complexes, while Zr⁴⁺ create complexes of ZrCit⁺, ZrCitH²⁺ and ZrCit₂H. The ratio of complexes depends on the pH of the solution.

For complexes of Ni²⁺ (Figure 3a), there exist mainly NiCitH and NiCit₂H³⁻ (pH = 3-4), NiCit⁻ and NiCit₂⁴⁻ complexes when pH reaches 6, when pH > 7, in the main solution complex in the form of NiCit₂⁴⁻.

For Co²⁺ complex, from the results of Figure 3b, it is found that the complex is in the form of CoCitH, CoCit⁻ and free Co²⁺ ions when the pH is 3-4, in the existing solution and the content of the CoCitH complex, Co²⁺ ion decreases, CoCit⁻ content is directly proportional to the value of pH. When pH > 5, the solution mainly exists in the form of CoCit₂⁴⁻ with increasing content according to raising pH value.

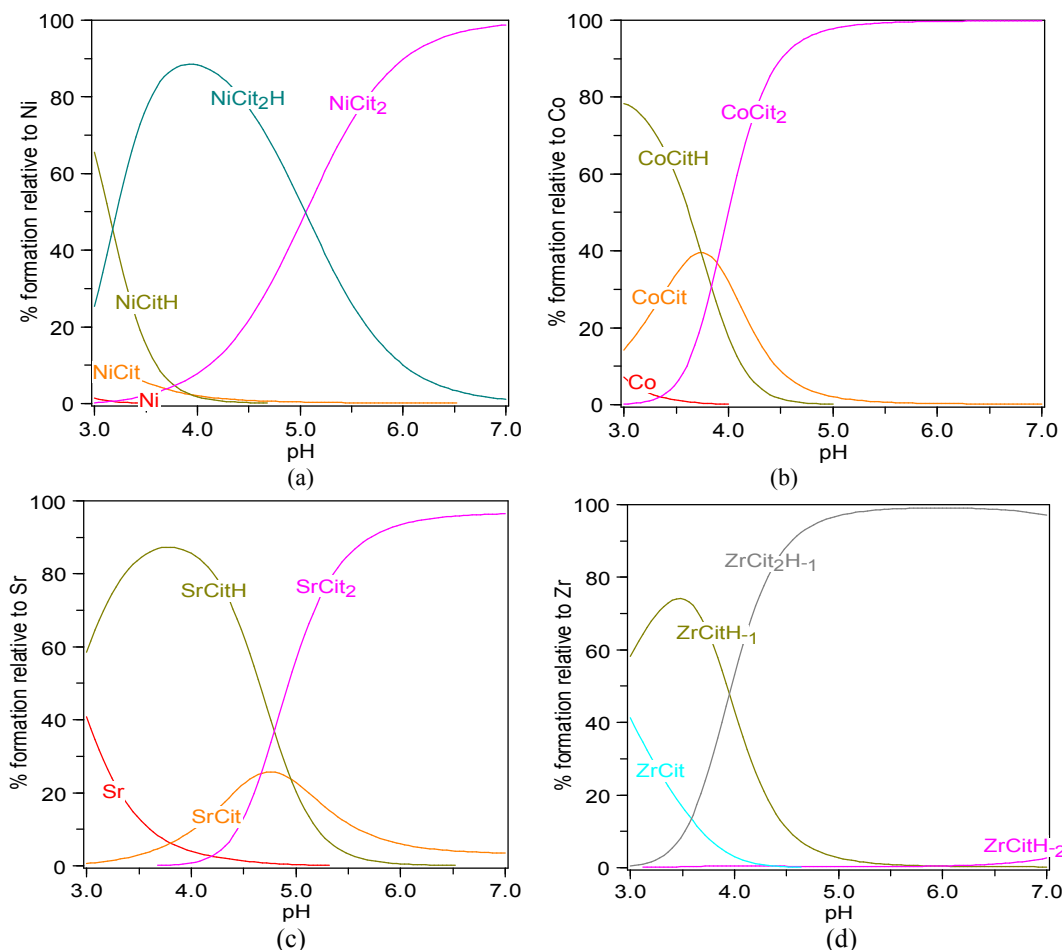


Figure 3. Graph of distribution of complexes of Ni^{2+} (3a), Co^{2+} (3b), Sr^{2+} (3c), Zr^{4+} (3d) with citric acid in solution under environmental pH

For the Sr^{2+} complex (Figure 3c), when the pH is 3-4, the solution exists mainly in the form of SrCitH and free Sr^{2+} ions, at pH reaching 6-7, the complex mainly exists in the form of SrCit^- and SrCit_2^{4-} .

For complexes of Zr^{4+} with citric acid, the results of Figure 3d show: When the pH value is low from 3-4, the solution exists mainly in the form of ZrCit^+ , ZrCitH^{2+} . When $\text{pH} > 4.5$, the complex is mainly in the form of ZrCit_2H^- . When the pH changes in solution, there is almost no Zr^{4+} ion, indicating that Zr^{4+} makes a very good complex with citric acid.

Based on the complexing reaction, the experimental results and using of Hyss 2009 program have determined the existence of complexes in solution and the corresponding stability constant in Table 3.

Table 3. The stability constants of complexes which are made up of citric acid and some metal cations in water

| Constituent | β | Constituent | β |
|-------------------------------|----------------------|----------------------------|----------------------|
| NiCit^- | $4.79 \cdot 10^5$ | CoCit^- | $4.07 \cdot 10^5$ |
| NiCitH | $6.61 \cdot 10^9$ | CoCitH | $1.78 \cdot 10^9$ |
| NiCit_2^{4-} | $5.01 \cdot 10^9$ | CoCit_2^{4-} | $9.33 \cdot 10^8$ |
| $\text{NiCit}_2\text{H}^{3-}$ | $3.55 \cdot 10^{14}$ | | |
| SrCit^- | $3.09 \cdot 10^3$ | ZrCit^+ | $7.24 \cdot 10^9$ |
| SrCitH | $1.74 \cdot 10^8$ | ZrCitH^{2+} | $1.51 \cdot 10^7$ |
| SrCit_2^{4-} | $3.31 \cdot 10^5$ | ZrCit_2H^- | $1.51 \cdot 10^{10}$ |

Complexization of metal ions with citric acid in APG10 medium: From the results of titration determination of the stability constants of complexes in aqueous environment, determination of the stability constants in APG10 surfactant solution:

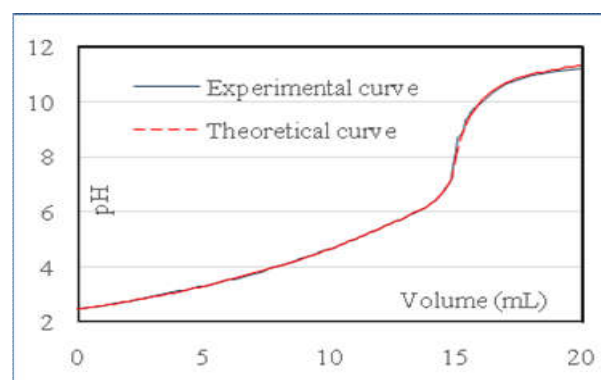


Figure 4. Complexing curve of citric acid and Ni^{2+} in 0.4% APG10 solution

From the results of Figure 4, it is found that the theoretical and experimental curves have a great overlap, so the method using Hyss 2009 simulation software can be used to calculate the stability constants in APG10 solutions. The results of determining the stability constants of complexes formed by Ni^{2+} and citric acid in APG10 surfactants are shown in Table 4. Results of Table 4 shows, when APG10 concentration increases, the stability constant decreases; the stability constant values of NiCit^- , NiCitH , NiCit_2^{4-} , $\text{NiCit}_2\text{H}^{3-}$ at 0.5%, respectively, down to 4.367; 5.623; 14.126; 9.550 times compared to that values in the absence of surfactants. Studying on the complexing of metal ions (Co^{2+} , Sr^{2+} , Zr^{4+}) in APG10 solution also gave similar results to the case of Ni^{2+} ions, when concentration of surfactant in solution increases, the stability constant of the complexes tend to decrease.

Table 4. Dependence of the stability constants of complexes formed by Ni²⁺ and citric acid according to APG10 concentration

| APG10(%) | β | | | |
|----------|----------------------|----------------------|----------------------------------|------------------------------------|
| | NiCit ⁻ | NiCitH | NiCit ₂ ⁴⁺ | NiCit ₂ H ³⁻ |
| 0 | 4.79.10 ⁵ | 6.61.10 ⁹ | 5.01.10 ⁹ | 3.55.10 ¹⁴ |
| 01 | 2.19.10 ⁵ | 2.51.10 ⁹ | 1.86.10 ⁹ | 1.23.10 ¹⁴ |
| 02 | 1.58.10 ⁵ | 1.90.10 ⁹ | 1.10.10 ⁹ | 6.61.10 ¹³ |
| 03 | 1.38.10 ⁵ | 1.58.10 ⁹ | 7.08.10 ⁸ | 4.90.10 ¹³ |
| 04 | 1.20.10 ⁵ | 1.32.10 ⁹ | 4.79.10 ⁸ | 4.07.10 ¹³ |
| 05 | 1.10.10 ⁵ | 1.17.10 ⁹ | 3.55.10 ⁸ | 3.71.10 ¹³ |

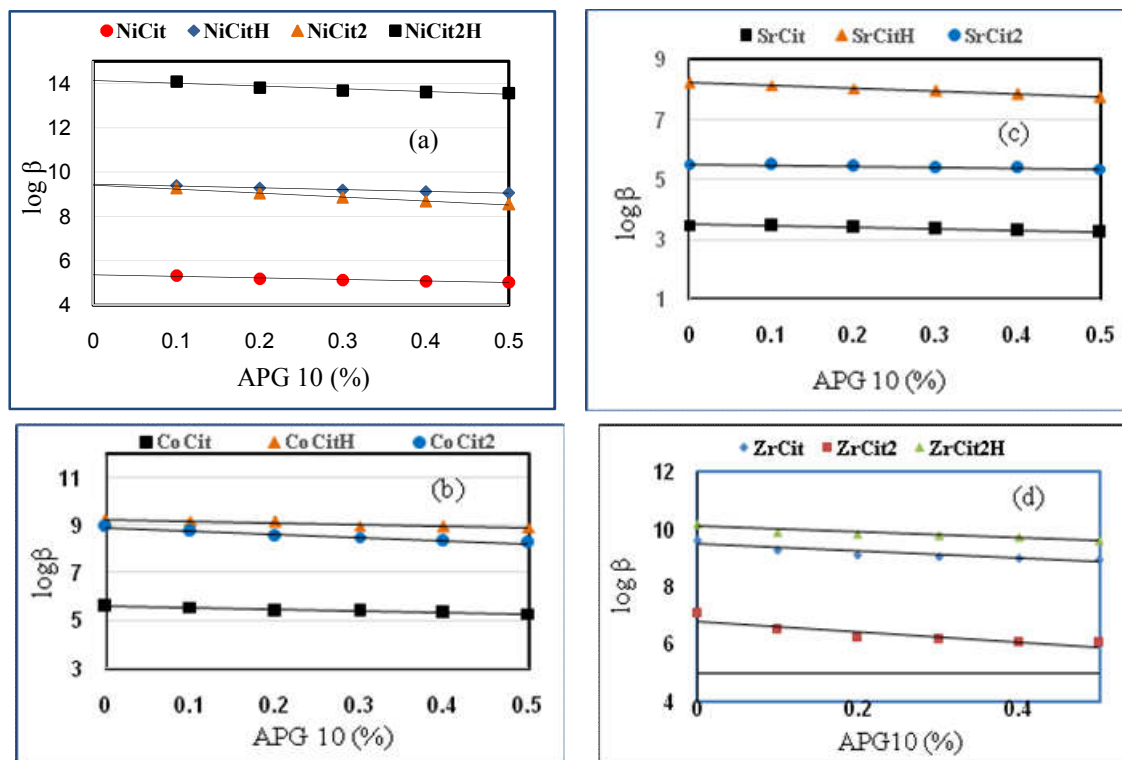
**Figure 5. Dependence of log β of complexes Ni²⁺, Co²⁺, Sr²⁺, Zr⁴⁺ with citric acid according to APG10 concentration (%)**

Figure 5 shows a graph depicting the stability constant change of complexes formed between metal ions (Ni²⁺, Co²⁺, Sr²⁺, Zr⁴⁺) and citric acid in APG10 solution. From the graph Figure 5 shows, log β is linearly dependent on APG10 concentration in inverse relation. This can be explained by the formation of micelles leading to the distribution of complex components into different micelle phases, hindering the combination of complex components so the stability constant decreases. An increase in the concentration of APG10 leads to a change in shape and an increase in micelle size, which leads to a decrease in the stability constant.

Conclusions

In the environment of APG10 surfactants, the metal cations Ni²⁺, Co²⁺, Sr²⁺, Zr⁴⁺ form complexes with citric acid in the same complex form as in the water environment. However, the constituent content of citric acid and complexes and the stability constant values have been changed. For citric acid, when the concentration of APG10 increased to 0.5% of the values β_{H_3Cit} , $\beta_{H_2Cit^-}$, $\beta_{HCit^{2-}}$ have decreased by 2.188; 1.778; 1.318 times compared with the stability constant values in water environment. For Ni²⁺ complexes, these values decrease gradually for NiCit⁻, NiCitH, NiCit₂⁴⁺, NiCit₂H³⁻ complexes, which are 4.367 times; 5.623 times; 14.126 times; 9.550 times at APG10 0.5%. Similarly, for the CoCit⁻, CoCitH, CoCit₂⁴⁺ complex these values decrease by 2.138 times, 2.089 times,

5.012 times; besides, SrCit⁻, SrCitH, SrCit₂⁴⁺ decrease by 1,698 times; 3,090 times; 1,445 times. For ZrCit⁻, ZrCitH²⁺ and ZrCit₂H complexes, these values decreased by 2.884 times; 3.890 times; 4.571 times. In general, the complexes of Ni²⁺ have the largest attenuation while the complexes of Sr²⁺ have the smallest attenuation.

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