

# Study of the Nickel Complex Formation with Citric Acid in A Mixture Alkyl Polyglycoside10 (APG10) Surfactant/Water System

Do Xuan Truong<sup>1</sup>, Nguyen Van Hoang<sup>2</sup>, To Van Thiep<sup>3</sup>

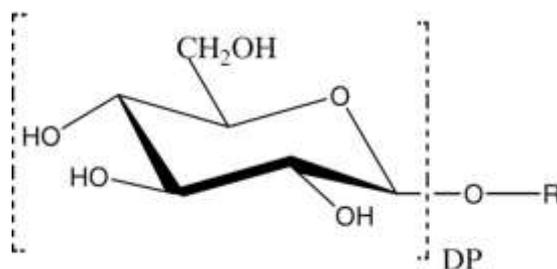
New Technology Institute and Environmental Protection, Academy of Military Science and Technology

**Abstract**— The stability constants of complexes formed by metal cations Ni(II) and citric acid in water and in APG10 surfactant/water medium are determined by the pH titration method combined with using Hyss 2009 simulation software. Under experimental conditions, the Ni(II) complexes with citric acid ligand were determined consisting of  $[NiCit]^-$ ,  $[NiHCit]$ ,  $[NiCit_2]^{4-}$  and  $[NiHCit_2]^{3-}$ . The  $\log\beta$  values of the stability constants of the complex species are linearly dependent and decreases with increasing concentration of APG10. The influence of APG10 surfactant on the decrease of stability constants maybe explained by the interaction of the surfactant micelles with the complex species. In 0.5% APG10/water solution, the decrease in stability constant value of Ni(II) - Citric complexes compared to these values in the aqueous environment are from 4.367 to 14.126 times.

**Keywords**— Stability constant, Complex, Citric acid, APG10 non-ionic surfactant.

## I. INTRODUCTION

The Complexes of metal ions with chelated agents exhibits great concern in many approaches of researches and applications, such as paper production, textiles, medicine, biology and water treatment [1-3]. The complexes of heavy metal ions as such Ni, Co, Sr, U ... with chelating organic ligands in aqueous media were studied [4-7]. The formation of metal ions – chelating organic ligands in mixed surfactant compounds/water is received a great interest due to their advantage of micelles present in media to the possibility varying the complex stability constants [8-10]. In this paper, the nickel Ni(II) complex formation with citric acid in a mixed alkyl polyglycoside (APG10) was studied in detail. Alkyl polyglycoside is a biodegradable ingredient that is growing in popularity due to its favorable environmental profile, is non-ionic surfactant widely used in a variety of cosmetic, household, and industrial applications [11-12]. The raw materials to produce alkyl polyglycoside are typically starch and fat. The final products of this process are typically complex mixtures of compounds with different sugars comprising the hydrophilic end and alkyl groups of hydrophobic. The molecular structure of an alkyl polyglycoside may be presented as following:



Here DP is degree of polymerization (DP)

Ni(II) – Citric acid complex is formed in aqueous media, but the complex stability constant might be influenced by adding APG10. This influence will be studied in detail in this paper. The formation of Ni(II) -Citric acid in the mixed alkyl polyglycoside surfactant/water system can let's applying in practice to clearing the nickel contaminated media like liquid or solid surface. From here, an application of metal – Citric acid complexes to removal of metal ions in any media with the presence of alkyl polyglycosides.

## II. EXPERIMENTAL

### 2.1 Chemicals

Chemicals used in this study involve as follows:

Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Merck; APG10 non-ionic surfactant (Merck), citric acid, 99%, Indian; 0.1M HNO<sub>3</sub> standard tubes, NaNO<sub>3</sub> (p.A).

## 2.2 Equipment

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

## 2.3 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].

TABLE 1

THE RATIO OF COMPONENTS OF THE EXPERIMENTAL SOLUTION TO DETERMINE THE STABILITY CONSTANTS OF THE COMPLEXES WHICH ARE CREATED BY Ni<sup>2+</sup>, WITH CITRIC ACID IN WATER AND APG10 SURFACTANT

Numerical order	V <sub>HNO<sub>3</sub></sub> (mL)	V <sub>H<sub>2</sub>O</sub> (mL)	V <sub>NaNO<sub>3</sub></sub> (mL)	V <sub>citric</sub> (mL)	V <sub>APG10</sub> (mL)	V(Ni(II)) (mL)
1	1.6	66.4	8	4	0	0
2	1.6	53.3	8	4	13.1	0
3	1.6	40.2	8	4	26.2	0
4	1.6	27.0	8	4	39.4	0
5	1.6	13.9	8	4	52.5	0
6	1.6	0.8	8	4	65.6	0
7	1.6	65.6	8	4	0	0.8
8	1.6	52.5	8	4	13.1	0.8
9	1.6	39.4	8	4	26.2	0.8
10	1.6	26.2	8	4	39.4	0.8
11	1.6	13.1	8	4	52.5	0.8
12	1.6	0	8	4	65.6	0.8

Pipette a solution of 0.1M HNO<sub>3</sub>, 1M NaNO<sub>3</sub>, 0.1M citric, 0.1M Ni(II) ions, 0.61% APG10 and water according to Table 1 ratio into a 250 mL glass beaker (total solution used in each experiment was 80 mL).

**Experiment N0.1:** Used to determine the stability constant of citric acid in aqueous solution (without surfactant).

**Experiment N0. 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 N0. 7:** To study the complexing of citric acid with metal cations Ni(II), in aqueous environment (without surfactant).

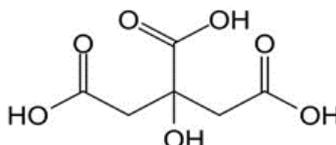
**Experiment N0. 8-12:** To study the complexing of citric acid with metal cations Ni<sup>2+</sup>, Co<sup>2+</sup>, Sr<sup>2+</sup>, Zr<sup>4+</sup> in the environment of APG10 surfactant with concentration of APG10 of 0.1%, 0.2%, 0.3%, 0.4%, 0.5%.

Use a 1000 μL micropipette to drop slowly about 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 [13] to determine the stability constants and the distribution of complex constituents.

## III. RESULTS AND DISCUSSION

### 3.1 The influence of APG10 surfactant on the stability constant of citric acid

Citric is a weak organic acid with molecular formula C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>, structural formula [2]



In solution, citric acid dissociates in 3 steps (denoted by citric acid as  $H_3Cit$ ) to form  $H_2Cit^-$ ,  $HCit^{2-}$  and  $Cit^{3-}$  ions. The stability constants of  $H_3Cit$ ,  $H_2Cit^-$ ,  $HCit^{2-}$  species are denoted  $\beta_{H_3Cit}$ ,  $\beta_{H_2Cit^-}$ ,  $\beta_{HCit^{2-}}$  respectively. The alkalimetric titration curve for citric acid in aqueous medium is given in Figure 1. This titration curve exhibits the acid-base equilibrium is active in the pH range from 2.5 to 11. In experimental solution, citric acid exists in 4 forms:  $H_3Cit$ ,  $H_2Cit^-$ ,  $HCit^{2-}$  and  $Cit^{3-}$ . The ratio of the above species depends on the pH of the environment. When pH increases, the content of  $H_3Cit$  decreases,  $Cit^{3-}$  increases; the content of  $H_2Cit^-$  reaches its maximum at pH = 4 while  $HCit^{2-}$  maximizes at pH = 5.5. When pH > 7, there is only species of  $Cit^{3-}$  in solution (Figure 1b).

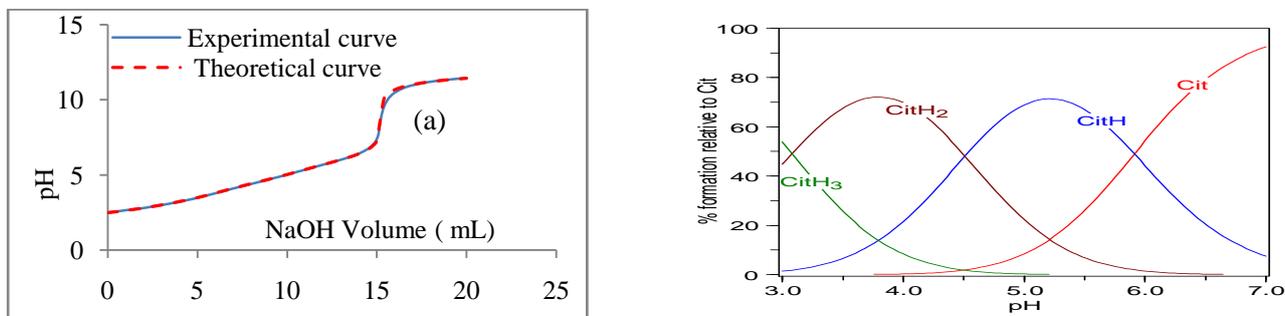


FIGURE 1. Alkalimetric titration curve (1a) and the distribution concentration of citric acid constituents in water (1b).

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

TABLE 2  
STABILITY CONSTANTS OF CITRIC ACID IN WATER

Values of	$\log \beta$
$HCit^{2-}$	$5,91 \pm 0,05$
$H_2Cit^-$	$10,42 \pm 0,07$
$H_3Cit$	$13,50 \pm 0,08$

By the same method, the stability constants ( $\beta$ ) of these species in mixed AVG 10/water system were determined. The dependence of  $\log \beta$  on the APG10 concentration varying from 0 to 0.5% (in water) is represented in Figure 2. Thus, the presence of APG 10 has affected the dissociation of citric acid in water solution. The formation of micelles APG10 might reduce the interaction of citric acid species leading to reduce the stability constants in water. This phenomenon is almost the same as the case that was published in the literature [6].

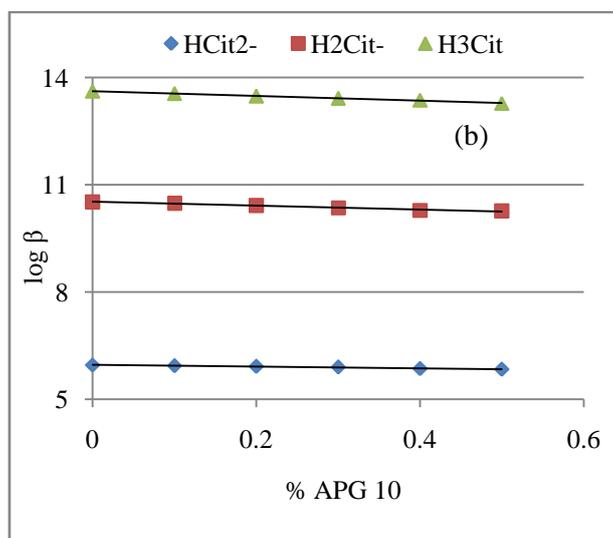


FIGURE 2. The dependence of  $\log \beta$  on varying APG 10 concentration

### 3.2 Complexization of Ni(II) ions with citric acid in water

Based on Hyss software, under experimental conditions, the species of complexes of Ni(II) with Citric acid were determined, consisting of  $[\text{NiCit}]^-$ ,  $[\text{NiHCit}]$ ,  $[\text{NiCit}_2]^{4-}$  and  $[\text{NiHCit}_2]^{3-}$ . The species of complexes depend on the pH of the solution.

From Figure 3, there are  $[\text{NiCitH}]$  and  $[\text{NiCit}_2\text{H}]^{3-}$  at pH of 3-4,  $[\text{NiCit}]^-$  and  $[\text{NiCit}_2]^{4-}$  complexes at pH of 6. At pH > 7 there is only form of  $[\text{NiCit}_2]^{4-}$ .

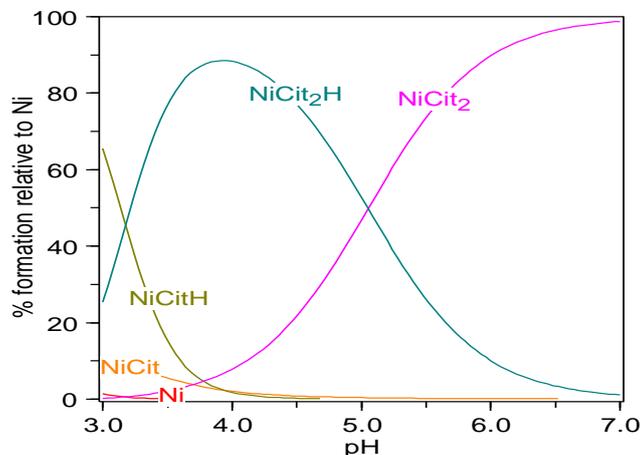


FIGURE 3. The species of Ni(II)-Cit complex compounds in aqueous medium

### 3.3 Complexization of Ni(II) ions with citric acid in APG10/Water medium

From the alkalimetric titration curve (Figure 4) the stability constants of Ni(II)-Cit species in APG10 surfactant /water solution were determined and presented in Table 3.

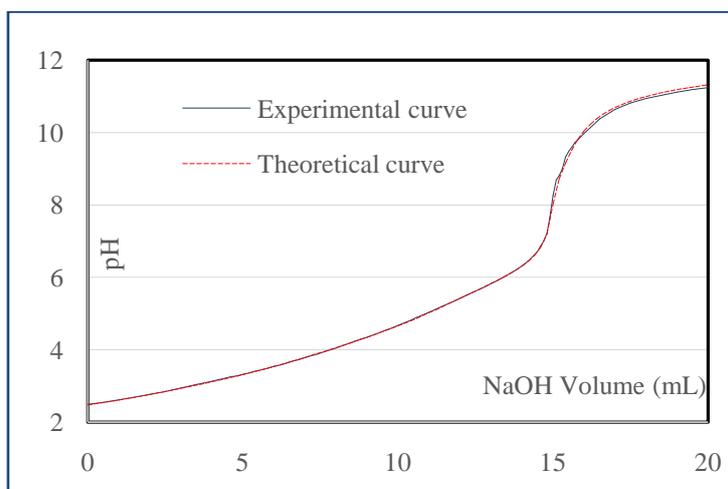
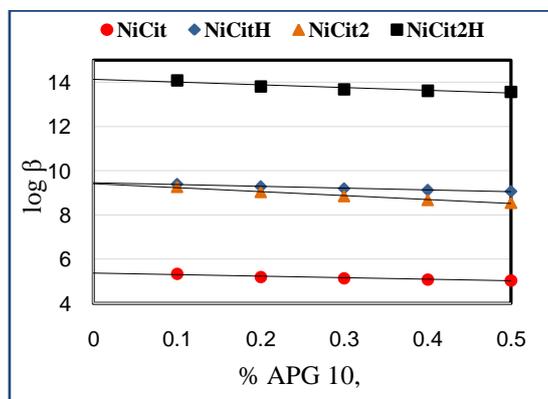


FIGURE 4. Alkalimetric titration curve of Ni(II)-Cit in APG10 surfactant /water system.

TABLE 3  
DEPENDENCE OF THE STABILITY CONSTANTS OF COMPLEX SPECIES FORMED BY Ni(II) AND CITRIC ACID IN VARYING APG10 CONCENTRATIONS

APG 10(%)	$\beta$			
	$\text{NiCit}^-$	$\text{NiCitH}$	$\text{NiCit}_2^{4-}$	$\text{NiCit}_2\text{H}^{3-}$
0	$4.79 \cdot 10^5$	$6.61 \cdot 10^9$	$5.01 \cdot 10^9$	$3.55 \cdot 10^{14}$
0.1	$2.19 \cdot 10^5$	$2.51 \cdot 10^9$	$1.86 \cdot 10^9$	$1.23 \cdot 10^{14}$
0.2	$1.58 \cdot 10^5$	$1.90 \cdot 10^9$	$1.10 \cdot 10^9$	$6.61 \cdot 10^{13}$
0.3	$1.38 \cdot 10^5$	$1.58 \cdot 10^9$	$7.08 \cdot 10^8$	$4.90 \cdot 10^{13}$
0.4	$1.20 \cdot 10^5$	$1.32 \cdot 10^9$	$4.79 \cdot 10^8$	$4.07 \cdot 10^{13}$
0.5	$1.10 \cdot 10^5$	$1.17 \cdot 10^9$	$3.55 \cdot 10^8$	$3.71 \cdot 10^{13}$

The results of Table 3 shows, with APG10 concentration increasing, the stability constant of complex species decrease. The stability constant values of  $[\text{NiCit}]^-$ ,  $[\text{NiCitH}]$ ,  $[\text{NiCit}_2]^{4-}$ ,  $[\text{NiCit}_2\text{H}]^{3-}$  at 0.5% APG, respectively decrease to 4.367; 5.623; 14.126; 9.550 times compared to the values in the absence of surfactants, respectively. The dependence of  $\log \beta$  on APG10 concentration varying is presented in Figure 5.



**FIGURE 5. The dependence of  $\log \beta$  of complexes formed between metal ions Ni(II) and citric acid in APG10/water solution.**

The Figure 5 shows,  $\log \beta$  is linearly decreasing on APG10 concentration increasing. This can be explained by the formation of APG 10 micelles leading to the distribution of complex species 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, similarly published in [6, 14, 15].

#### IV. CONCLUSION

In the environment of APG10 surfactants/water system, the metal ions Ni(II) form complexes with citric acid in the same complex form as in the aqueous medium. However, the constituent content of citric acid, complexes and the stability constant values have changed. For citric acid, when the concentration of APG10 increased to 0.5% of the values  $\beta(\text{H}_3\text{Cit})$ ,  $\beta(\text{H}_2\text{Cit})$ ,  $\beta(\text{HCit}^{2-})$  decreased by 2.188; 1.778; 1.318 times compared with the stability constant value in water environment. For  $\text{Ni}^{2+}$  complexes, this value decreases gradually for  $[\text{NiCit}]^-$ ,  $[\text{NiCitH}]$ ,  $[\text{NiCit}_2]^{4-}$ ,  $[\text{NiCit}_2\text{H}]^{3-}$  complexes, being 4.367; 5.623 ; 14.126 ; 9.550 times respectively at APG10 0.5%.

#### REFERENCES

- [1] Nethala Vijaya Kumar, Bathula Srekanth and Gollapalli Nageswara Rao, Speciation of L-Aspartic acid complexes of Co(II), Ni(II), Cu(II) and Zn(II) in acetonitrile and ethylene glycol – water. 2012, Bull. Chem. Soc. Ethiop. 26(2), 239-247.
- [2] Bathula Srikanth, Pedada Srinivasa Rao, Vasa Samba Siva Rao, Charla Kamala Sastry and Gollapalli Nageswara Rao. Effect of micelles on the chemical speciation of binary complexes of Co(II), Ni(II), Cu(II) and Zn(II) with succinic acid, 2009, J. Serb. Chem. Soc. 74 (7) 745–754 (2009), JSCS–3872.
- [3] M. Padma Latha, V. Maheswara Rao, T. Siva Rao and G. Nageswara Rao Chemical speciation of Pb(II), Cd(I), Hg(II), Co(II), Ni(II), Cu(II) and Zn(II) binary complexes of L-methionine in 1,2 propanediol-water mixture. 2007, Bull. Chem. Soc. Ethiop., 21(3), 363-372.
- [4] D. Wyrzykowski • L . Chmurzynski Thermodynamics of citrate complexation with  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ions, J. Therm Anal Calorim (2010) 102:61–64, DOI 10.1007/s10973-009-0523-4.
- [5] Malla Ramanaiiah S. Goutham Sri and B.B.V. Sailaja Stability of binary complexes of Pb(II), Cd(II) AND Hg(II) with maleic acid in TX 100- water mixtures. Bull. Chem. Soc. Ethiop. 2014, 28(3), 383-391. ISSN 1011-3924.
- [6] Srinivasa Rao Pedada, Srikanth Bathula, Samba Siva Rao Vasa, Kamala Sastry Charla and Nageswara Rao Gollapalli\* Micellar effect on metal –ligand complexes of Co(II), Ni(II), Cu(II) AND Zn(II) with acid citric. Bull. Chem. Soc. Ethiop. 2009, 23(3), 347-358.
- [7] W von Rybinski; K Hill (1998). "Alkyl Polyglycosides—Properties and Applications of a new Class of Surfactants". Angewandte Chemie International Edition. 37 (10): 1328–1345,
- [8] Gang Li, Lifeng Chen, Yang Ruan, Qiao Guo, Xingao Liao & Bowen Zhang Alkyl polyglycoside: a green and efficient surfactant for enhancing heavy oil recovery at high-temperature and high-salinity condition, *Journal of Petroleum Exploration and Production Technology* volume 9, pages2671–2680(2019).
- [9] Dorota Kolodyńska, *Chelating Agents of a New Generation as an Alternative to Conventional Chelators for Heavy Metal Ions Removal from Different Waste Waters*, Maria Curie-Skłodowska University, Poland (2011).

- [10] John Drake, *Evaluation of nine chemical-based technologies for removal of radiological contamination from concrete surfaces*, U.S. Environmental Protection Agency (EPA), pp. 3 (2011).
- [11] Rakesh M. Tada\*, Pankaj B. Nariya, Naimish K. Chavda and Manish K. Shah, *Evaluation of stability constants of 1-(3-bromo-4-hydroxy-5-methoxy benzylidene) thiosemicarbazide(TRM-1) with copper (II), cobalt (II) and nickel (II) complexes by pH metric method*, Der Pharma Chemica, **5(4)**, 244-251 (2013).
- [12] Surya Sunitha P1, Nageswara Rao Ch2\*, Sujatha P3, and Sailaja BBV, *Formation and Confirmation of Binary Complexes of Co (II), Ni (II) and Cu (II) with L-Cysteine in SLS-water media*, Research Journal of Pharmaceutical, Biological and Chemical Science (2017).
- [13] Lucia Alderighi a , Peter Gans b,\*, Andrea Ienco a , Daniel Peters, Antonio Sabatini a , Alberto Vacca. Hyperquad simulation and speciation (HySS): a utility program for the investigation of equilibria involving soluble and partially soluble species. *Coordination Chemistry Reviews* 184 (1999) 311–318.
- [14] Greisser, R. and Sigel, H. 1970. Ternary complexes in solutionVIII: complex formation between the copper(II) -2, 20 -bipyridyl 1 : 1 complex and ligands containing oxygen and(or) nitrogen donor atoms. *Inorg. Chem.*, 9, 1238 – 1243. Greisser, R. and Sigel, H. 1971. Ternary complexes in solution.
- [15] Greisser, R. and Sigel, H. 1974. Ternary complexes in solutionXVI: Influence of the size of the chelate rings on the stability of mixed ligand copper(II) complexes containing aliphatic ligands. *Inorg. Chem.*, 13, 462 – 465.