

Synthesis of polymer-surfactants by gamma irradiation for removal nickel ions from aqueous solution

Mai M. Mamdouh^{a*}, Fatma H. abdel-salam^b, Nabila A. Maziad^c and Omyma A. M. Ali^a

^aChemistry Department, Faculty of Women for Arts, Science and Education, Ain Shams University, Cairo, Egypt.

^bChemistry Department, Faculty of Science (Girl's), Al-Azhar University, Cairo, Egypt.

^cPolymer Chemistry Department, National Center for Radiation Research and Technology Atomic Energy Authority, Cairo, Egypt.

Abstract

Two amphoteric surfactants 2-((3-carboxyacryloxy)oxy)-3-(hexadecyloxy)-N,N,N-trimethylpropane-1-ammonium chloride and N-(2-(carboxylatomethoxy)-3-(hexadecyloxypropyl)dimethyl glycinate were synthesized and characterized by different techniques. Then, two polymer surfactants were prepared from the reaction of acrylic acid and acrylamide with two amphoteric surfactants by gamma irradiation. The functional and bond structure of these polymer surfactant compounds were established by FT-IR. The critical micelle concentration (cmc) and surface tensions were measured and the values lie in the range 0.0005 - 0.00141 mol L⁻¹. The swelling of the two polymer surfactants was studied. The swelling percentages of the two surfactants are 1790 and 1492 %, respectively. The copolymers hydrogel were used in removal of heavy metal from waste water. The factors affecting the removal of heavy metal as contact time, initial concentration of metal ion, and temperature were investigated. It was found that the percentage of removal of nickel ion increases with increasing the time and temperature.

Keywords: Gamma irradiation; surfactants; polymers; swelling

1. Introduction

Water pollution with heavy metal ions is a serious problem due to their serious toxicity to human beings and other living organisms, heavy metals cause serious health effects, including cancer, organ damage, nervous system damage, and in extreme cases death [1-3]. Numerous research

***Corresponding author:** Mai M. Mamdouh, Chemistry Department, Faculty of Women for Arts, Science and Education, Ain Shams University.

E-mail: Mai.mamdoh23@yahoo.com

efforts are being done to develop methods to remove heavy metal ions. These techniques include filtration, chemical precipitation, neutralization, chelating ion- exchange and adsorption [4-9]. Among these techniques, adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness [10-11]. In this paper we use adsorption method by using polymer surfactant interaction due to great interest in many applications such as drug delivery, inks, cosmetics, detergents, and other industrial purposes as waste water treatment [12-15]. Zwitterion surfactants which contain both positively and negatively charged are increasingly attracting the interest of researchers both an industrial application and within academic fields. This is due to their unique properties [16-19] such as excellent water solubility, broad isoelectric ranges, mildness to the skin and eyes, high foam stability in sensitivity to the presence of salts and to temperature, synergistic effect with a wide variety of ionic and nonionic surfactants and resistance to hard water and to degradation by oxidizing and reducing agents [20]. Betaines important zwitterion surfactants are widely used in cosmetic, pesticides, leather and have been proposed for enhanced oil recovery. In order to demonstrate our recovery, two betaines are synthesized. The surface activity of the two prepared surfactants at 25°C is evaluated. Hydrogels are three dimensionally dense cross-linked polymer network structures composed of functional hydrophilic groups which have the ability to absorb significant amount of water and solute molecules. The ability to absorption of hydrogel is dependent on the presence of hydrophilic functional groups such as OH, COOH which make hydrogel hydrophilic [21-22]. The presence of functional groups and the nature of cross-linking agents are important parameters that control the swelling ability of the hydrogel [23-24]. Hydrogel has a porous structure and many hydrophilic groups, which can be used for heavy-metal ion removal [25]. Many researchers concentrated on the metal ion recovery using polymers because they are usable, easy handing and have higher adsorption capacities, efficiencies as well as high selectivity to some metal ions. Thus, the present aim of the work is to studied the application of the prepared polymer-surfactant compounds to remove heavy metals especially Ni⁺² from waste water.

2. Experimental

2.1. Materials and methods

Acrylic acid (AAc) and acrylamide (AAM) were purchased from Merck Germany Company with purity 99%. All used chemicals were used without further purification. The FTIR measurements (KBr pellets) were recorded using a Perkin-Elmer spectrophotometer model 1430, in the range of 400-4000 cm^{-1} . ^1H NMR spectra were performed on Bruker 500 MHz spectrometer using CDCl_3 with TMS as internal standard. Elemental analysis was carried out using Perkin-Elmer elemental analyzer.

2.2. Synthesis of 1-chloro-3-(hexadecyloxy)propane-2OL (1)

This compound was prepared according to the method described elsewhere in detail [24].

2.3. Synthesis of 2-((3-carboxyacryloxy)oxy)3-(hexadecyloxy)-1-propyl chloride (2)

1-chloro-3-(hexadecyloxy)propane-2OL (1) (0.11 mol) was loaded into a two neck flask and heated to 60-70°C. The temperature was kept to be constant at this level and maleic anhydride (0.12 mol) was continuously added by stirring and temperature was kept on a constant level. The heat of the reaction caused the anhydride to melt. The temperature was raised to 120-130 °C in presence of P-toulene sulfonic acid and benzene as solvent. The water removed from the mixture was collected using Dean-Starr apparatus and the completion of the reaction was achieved by measuring the volume of the collected water which equal to the theoretical volume of the reaction. The crude product was purified by crystallization with petroleum ether/ethanol (30:50 v/v) several times and the purified ester was dried [24].

2.4. Synthesis of 2-((3-carboxyacryloxy)oxy)-3-(hexadecyloxy)-N,N,N-trimethylpropane-1-ammonium chloride (3)

2-((3-carboxyacryloxy)oxy)3-(hexadecyloxy)-1-propyl chloride (2) (0.01 mol) was added to 0.01 mol of sodium bicarbonate and the reaction mixture was stirred for 30 min. Using acetone as solvent. The reaction was carried out below 20 °C. To this solution 0.01 mol of trimethylamine was added and the whole contents were refluxed with stirring for 8 hrs. It was advised to take

trimethylamine little excess. The obtained crude material was filtered on hot to remove the inorganic salt. The product was recrystallized from a mixture of acetone and methanol twice and was dried in vacuum and stored in cool, dry desiccator. The overall yield was 95%.

2.5. Synthesis of sodium salt of N-(2-(carboxylatomethoxy)-3-(hexadecyloxypropyl)dimethyl glycinate (4)

2-((3-carboxyacryloxy)oxy)3-(hexadecyloxy)-1-propyl chloride (2) (0.01 mol) was added to 0.01 mol of dimethylamine 33 %, 1 g of NaOH and 5 ml of distilled water using anhydrous ethanol as solvent. The reaction mixture was stirred for 4 hrs at 75 °C in the water bath. Then 0.12 mol of sodium chloroacetate were added drop wise to the reaction mixture and was stirred for 6-8 hrs at 75 °C in water bath. The crude product was recrystallized with mixed ethanol and ethyl acetate then it was dried. The yield percent of the product was 97 %.

2.6. Synthesis of poly (AAc/AAm/surfactant (3))

Different weights of surfactants (3) (0.01, 0.02, 0.03, 0.04, 0.05, 0.0005 g) were added to mixture of 60 ml of acrylamide (AAm) which equal 42.6 g, 60 ml of acrylic acid (AAc) and 80 ml of distilled water, each mixture was stirred for two hrs, then the resulted mixtures were polymerized by using Gamma irradiation at 25 KGy [27-29].

2.7. Synthesis of poly (AAc/AAm/surfactant (4))

Repeat the previous procedure at different weights of surfactant (4) (0.01, 0.02, 0.03, 0.04, 0.05, 0.00141 g) [27-29].

2.8. Metal uptake studies

The adsorption of nickel ion in presence of polymer was performed by introducing constant weight (0.1 g) of polymer-surfactant in a flask containing 10 mL of a 900 ppm solution of nickel ions. The mixture was stirred by a magnetic stirrer at room temperature and filtered. The residual nickel concentration was determined by complexometric titration with EDTA. The amount of metal ion uptake was calculated from the difference between a blank experiment without polymer and the reading in the actual experiment [30].

The removal percentage % was calculated using the following equation:

$$\text{Removal \%} = \frac{C_0 - C}{C_0} \times 100$$

Where C_0 is the initial concentrations of metal ion (mg L^{-1}), C is the concentration of metal ion at equilibrium (mg L^{-1}).

2.8.1. Effect of time

Contact time adsorption experiments were studied at room temperature at various time intervals (30–120 min) at constant concentration of nickel ion solution (900 ppm) and constant weight of polymer surfactant (0.1 g). The mixture was stirred at the different time intervals. Then, the concentration of residual nickel ion was determined by EDTA at the end of each time [27-29].

2.8.2. Effect of nickel ion concentration

The effect of nickel ion concentration (1150, 900, 600 and 300 ppm) on the percentage of metal uptake was studied. For each concentration, 0.1 g of polymer-surfactant was added and mixed at the optimum time. Then, the removal percentage of metal ion was calculated [27-29].

2.8.3. Effect of temperature

Adsorption test was carried out in a series of flasks in a thermostatic cell at three different temperatures 40, 50 and 60 °C. Each flask was filled with 10 mL of nickel ion solution (900 ppm) and 0.1 g of polymer-surfactant following the above mentioned procedure [27-29].

3. Results and Discussion

The structures of purified surfactants (3) and (4) were confirmed by elemental analysis. The results of elemental analyses (carbon, hydrogen and nitrogen contents) with the molecular formula and melting points are presented in **Table (1)**. The experimental results were in a good agreement with those calculated for the suggested formula. Also all prepared surfactants were showed as waxy materials.

Table 1. Analytical and physical data of the prepared surfactants

| Compound | M.Wt. | Color | Elemental analysis found (Calc.) | | |
|--|-------|-------------|-------------------------------------|------------------|----------------|
| | | | C % | H % | N % |
| Surfactant (3) C ₂ H ₅₀ NO ₅ | 498 | Yellow waxy | 68.42 (68.41) | 10.96 (10.94) | 3.07 (3.06) |
| Surfactant (4) C ₂ H ₄₈ NO ₆ Na ₂ | 532 | Brown waxy | 59.52 (59.51) | 9.52 (9.51) | 2.77 (2.75) |

3.1. FT-IR spectra

The FT-IR spectrum (**Fig. 1**) of 1-chloro-3-(hexadecyloxy)propane-2-OL (1) showed band at 3364 cm⁻¹ indicating the presence of hydroxyl group (OH). The absorption band at 2917 cm⁻¹, 2831 cm⁻¹ indicated the presence of C-H stretching of methyl group for cetyl moiety while bands at 1392 cm⁻¹ and 1463 cm⁻¹ for CH of CH₃ group as bending. The band at 730 cm⁻¹ was referred to C-Cl. The FT-IR spectrum of 2-((3-carboxyacryloxy)oxy)3-(hexadecyloxy)-1-propyl chloride (2) showed the characteristic absorption bands at 3395 and 1729 cm⁻¹ indicating the presence of hydroxyl group of acid for maleyl moiety and carbonyl group of acid moiety, respectively. CH stretching of CH₂ and CH₃ groups of cetyl moiety appeared at 2283 and 2922 cm⁻¹. Also, the bands at 1204 cm⁻¹ and 717 cm⁻¹ confirmed the presence of C-O ester and C-Cl, respectively. The band at 1644 cm⁻¹ depicted the presence of C=O group of ester. The FT-IR spectrum of purified compound (3) (**Fig. 2**) observed the absorption band at 3427 cm⁻¹ for acid and quaternary ammonium salt and the band of C-Cl at 717 cm⁻¹ disappeared due to quaternarization. FT-IR spectrum of surfactant (4) showed absorption bands at 3427, 2925, 2739, 1729, 1641, 1259 and 1120 cm⁻¹ for tertiaryamine, CH symmetric of CH₃, CH asymmetric, CH stretching of CH₃, carboxyl group, C=C, C-N and C-O group, respectively. FT-IR spectrum of poly (AAc/AAm/Surfactant (3)) (**Fig.3**) showed absorption bands at 3432 and 1633 cm⁻¹ indicating the presence of hydroxyl group of acid and amide group, respectively. FT-IR spectrum of poly (AAc/AAm/Surfactant (4)) (**Fig.4**) showed absorption bands at 3430, 1645, 1453 and 1166 cm⁻¹

indicating the presence of hydroxyl group of acid, carbonyl of amide group, C-O of ether and C-N, respectively.

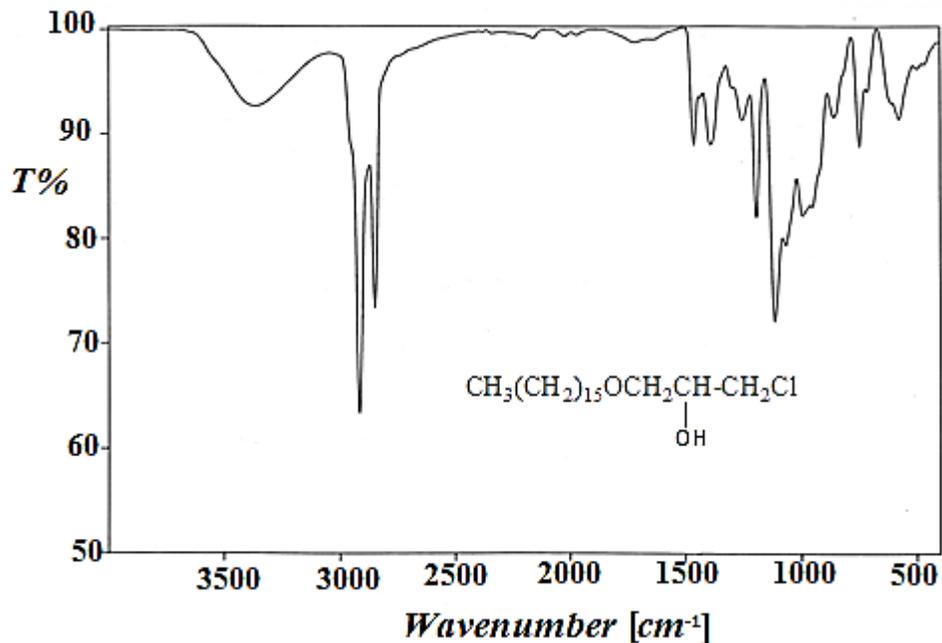


Fig.1. FT-IR spectrum of 1-chloro-3-(hexadecyloxy)propane-2-OL (1)

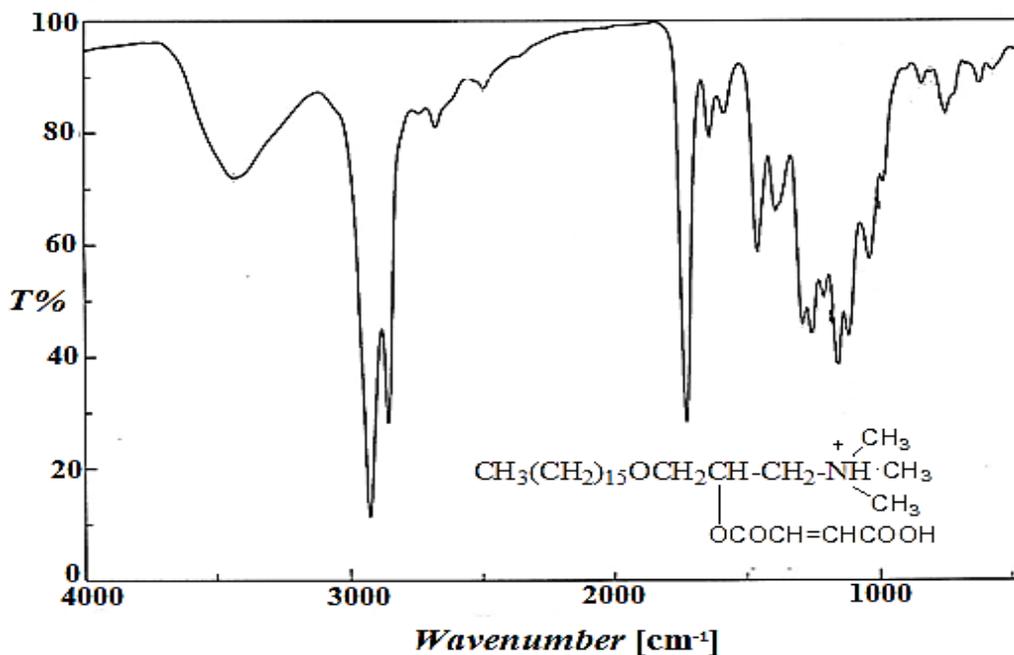


Fig.2. FT-IR spectrum of 2-((3-carboxyacryloxy)oxy)-3-(hexadecyloxy)-N,N,N-trimethylpropane-1-ammonium chloride (3)

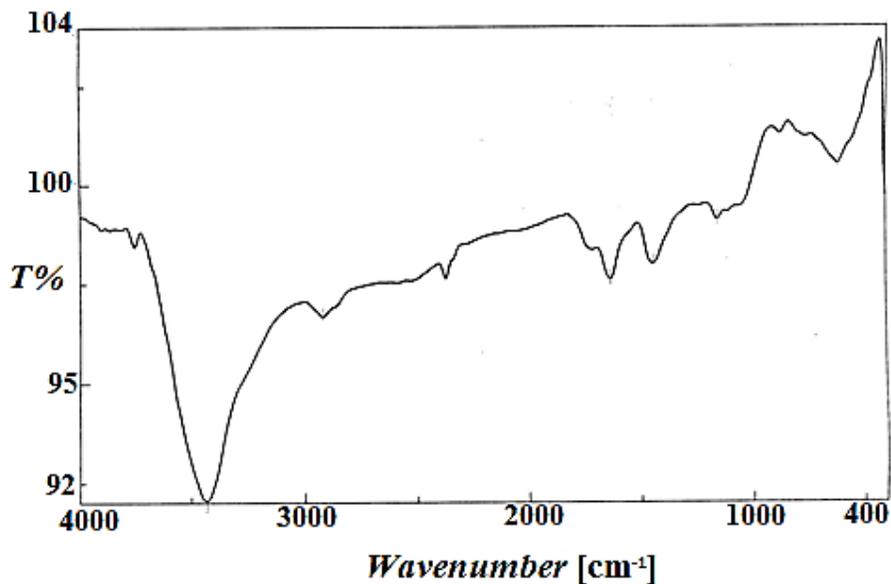


Fig.3. FT-IR spectrum of poly (AAc/AAm/surfactant (3))

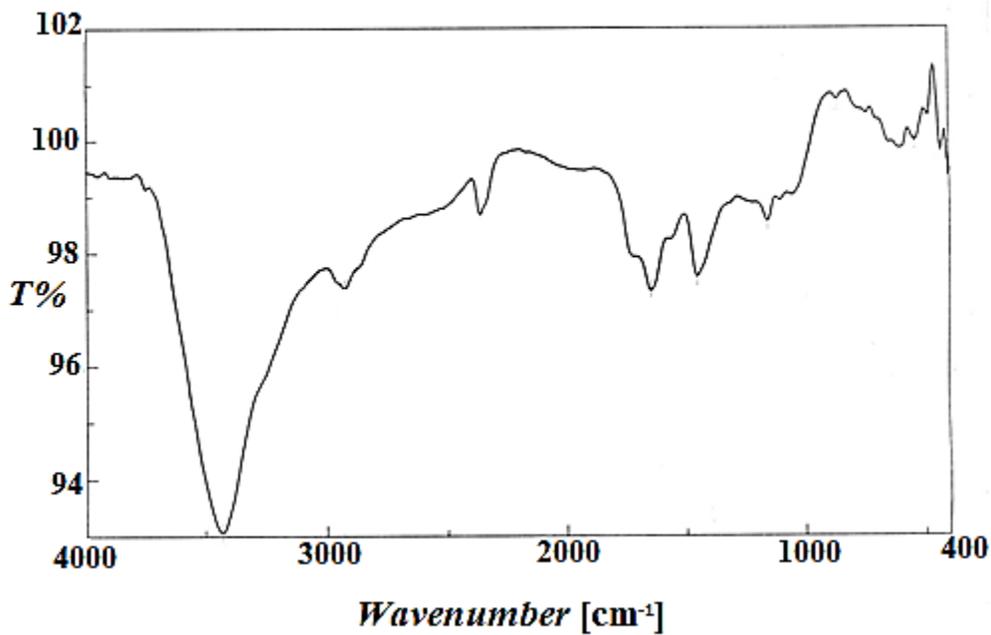


Fig.4. FT-IR spectrum of poly (AAc/AAm/surfactant (4))

3.2. ^1H NMR spectra

^1H NMR spectrum of compound (1) showed the chemical shift of δ 0.85-0.89 (t, 3H, CH_3); δ 1.25 (m, 22H, $(\text{CH}_2)_{11}$); δ 1.53 (m, 2H, $(\text{CH}_2)_{11}\text{CH}_2$); δ 1.54 (m, 2H, $(\text{CH}_2)_2\text{CH}_2$); δ 1.56 (m, 2H, $(\text{CH}_2)_{13}\text{CH}_2$); δ 1.58 (m, $(\text{CH}_2)_{14}\text{CH}_2$); δ 3.40-3.48 (m, 2H, OCH_2); δ 3.51-3.80 (m, 2H, CH_2O); δ 3.93-3.97 (m, 1H, $\text{CH}-\text{CH}_2$); δ 4.64 (m, 2H, CHCH_2Cl) and δ 7.26 (s, 1H, OH).

^1H NMR spectrum of 2-((3-carboxyacryloxy)oxy)3-(hexadecyloxy)-1-propyl chloride (2) showed δ 0.85-0.88 (t, 3H, CH_3); δ 1.25 (m, 22H, $(\text{CH}_2)_{11}$); δ 1.54 (m, 24 H, $(\text{CH}_2)_{11}\text{CH}_2$); δ 1.56 (m, 26H, $(\text{CH}_2)_{12}\text{CH}_2$); δ 1.58 (m, 28H, $(\text{CH}_2)_{13}\text{CH}_2$); δ 3.45 (m, 2H, OCH_2); δ 3.75-3.62 (m, 2H, CH_2O); δ 3.64-3.76 (m, 1H, CH); δ 3.95-3.98 (m, 2H, CH_2Cl); δ 6.83 (s, 1H, $\text{CH}=\text{CH}$) and δ 7.26 (s, 1H, OH of acid).

^1H NMR spectrum of compound (3) in CDCl_3 (**Fig. 5(a, b)**) showed a chemical signals at δ 0.78 (t, 3H, CH_3); δ 1.18 (m, 26H, $(\text{CH}_2)_{13}$); δ 1.41 (m, 2H, $(\text{CH}_2)_{13}-\text{CH}_2$); δ 1.52 (m, 2H, $(\text{CH}_2)_{14}\text{CH}_2$); δ 3.4 (s, 2H, CH_2OCH_2); δ 3.73 (t, 2H, $\text{CH}-\text{OCH}_2$); δ 3.29 (s, 9H, $\text{N}(\text{CH}_3)_3$); δ 3.52 (d, 2H, $\text{CH}-\text{CH}_2$); δ 5.4 (s, H, CH); δ 6.37 (d, 1H, $\text{CH}=\text{CH}$) and δ 6.50 (d, 1H, $\text{CH}=\text{CH}$).

^1H NMR spectrum of surfactant(4) (**Fig.7**) showed chemical signals at δ 0.75-0.79 (t, 3H, CH_3); δ 1.08 (m, 24H, $(\text{CH}_2)_{12}$); δ 1.12 (m, 2H, $(\text{CH}_2)_{12}\text{CH}_2$); δ 1.14 (m, 2H, $(\text{CH}_2)_{13}-\text{CH}_2$); δ 1.16 (m, 2H, $(\text{CH}_2)_{14}\text{CH}_2$); δ 3.40 (s, 2H, CH_2O); δ 3.84 (s, 2H, OCH_2); δ 3.45 (d, 1H, OCH_2-CH); δ 2.60 (s, 2H, CH_2N); δ 2.85 (s, 6H, $\text{N}(\text{CH}_3)_2$); δ 3.39 (s, 2H, NCH_2COO); δ 4.07 (s, 1H, CH); δ 4.08 (d, 1H, $\text{CH}=\text{CH}$) and δ 5.9 (s, 1H, $\text{CH}=\text{CH}$).

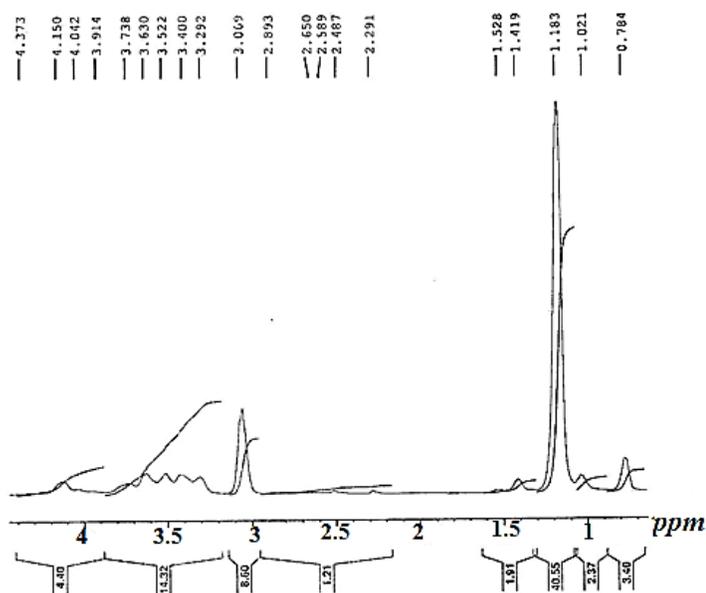


Fig.5.a ^1H NMR spectrum of 2-((3-carboxyacryloxy)oxy)-3-(hexadecyloxy)-N,N,N-trimethyl propane-1-ammonium chloride (3)

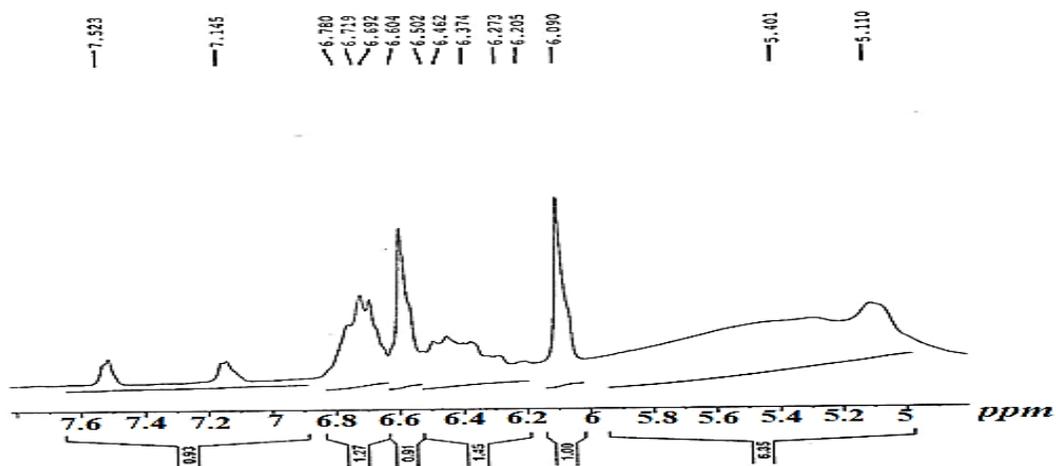


Fig.5.b ^1H NMR spectrum of 2-((3-carboxyacryloxy)oxy)-3-(hexadecyloxy)-N,N,N-trimethyl propane-1-ammonium chloride (3)

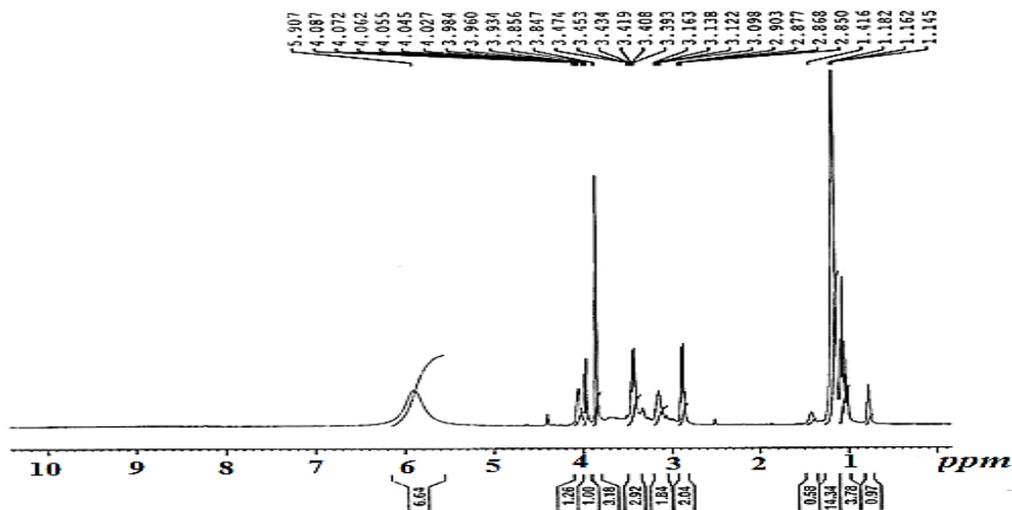


Fig.6. ^1H NMR spectrum of N-(2-(carboxylatomethoxy)-3-(hexadecyloxypropyl)dimethyl glycinate (4)

3.3. Surface tension measurements

Surface tension (ST) measurements were performed with freshly prepared solutions of surfactants in a concentration range from 10^{-1} to 10^{-6} mol L $^{-1}$ at 25 °C using a Du-Nouy tensiometer. These values, which were remained to be constant for a period over 30 minutes are taken as the surface tension of the solution. The results were accurate within ± 0.1 mN m $^{-1}$. The relation between surface tension (σ) versus logarithm of concentration ($-\log C$) for the prepared surfactants aqueous solution was obtained at 25 °C as shown in **Fig. (7)**. The critical micelle concentration (cmc) and surface tensions were determined as the values of the break point of surface tension versus logarithm concentration plots. From figure (7), the cmc of both surfactants (3) and (4) were found to be 0.0005 and 0.00141 mN m $^{-1}$, respectively [31].

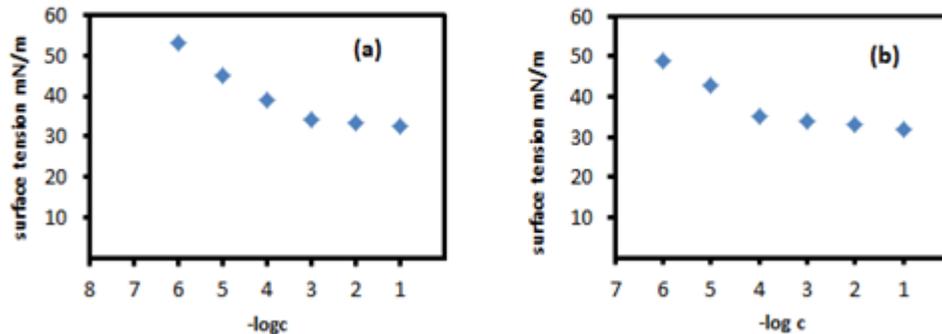


Fig.7. Surface tension of surfactant (3) (a) and surfactant (4) (b)

3.4. Effect of contact time on swelling percentage of poly (AAc/AAm/surfactant (3))

The effect of the time on the swelling ratio for poly (AAc/AAm/surfactant (3)) at different weight of surfactant (3) (0.01, 0.02, 0.03, 0.04, 0.05, 0.005 g) in distilled water was shown in **Fig. (8)**. The figure showed that the swelling percent of the hydrogels increased with increasing the contact time up to 24 hrs and then leaves off. The highest swelling percent was 1790 % at surfactant weight =0.04 g compared with 300% for swelling percentage of poly acrylic acid/poly vinyl alcohol and 150 % for swelling percentage of poly acrylic acid [29].

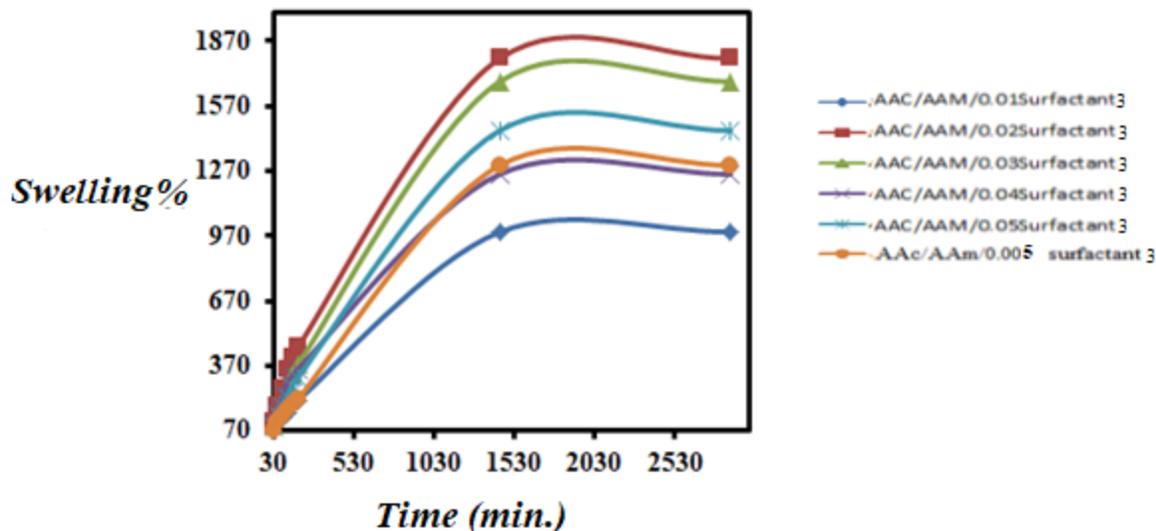


Fig.8. Effect of time on the swelling % of poly (AAc/AAM/surfactant (3)) at 25 KGy

3.5. Effect of contact time on swelling percentage of poly (AAc/AAM/surfactant (4))

The effect of the time on the swelling ratio for poly (AAc/AAM/surfactant (4)) at different weight of surfactant (4) (0.01, 0.02, 0.03, 0.04, 0.05, 0.00141 g) in distilled water is shown in **Fig.9**. The figure showed that the swelling percent of the hydrogels increased with increasing the contact time up to 24 hrs and then leaves off. The highest swelling percent was 1492 % at surfactant weight =0.02 g compared with 300% for swelling percentage of poly acrylic acid/poly vinyl alcohol and 150 % for swelling percentage of poly acrylic acid [29].

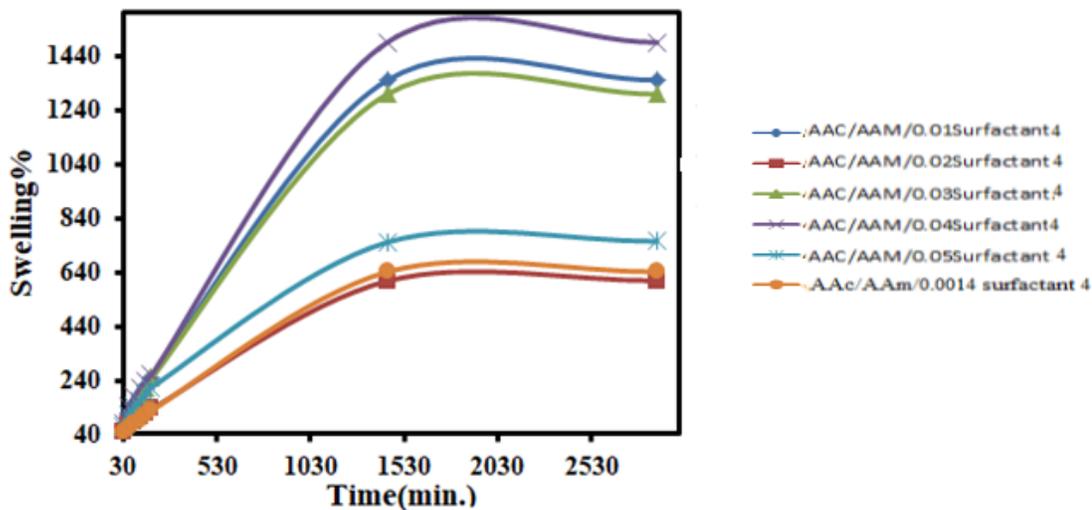


Fig.9. Effect of contact time on swelling % of poly (AAc/AAM/surfactant (4)) at 25KGy

3.6. Application

3.6.1. Metal uptake study

The effect of the contact time on removal percentage of nickel ion by poly (AAc/AAM/surfactant (3)) and poly (AAc/AAM/surfactant (4)) shown in **Fig.10 (a, b)**. The results showed that the removal percentage increased with the contact time till reach to optimum removal 40 % after 3 hrs by poly (AAc/AAM/surfactant (3)) and 35 % after 2 hrs by poly (AAc/AAM/surfactant (4)) [27-29].

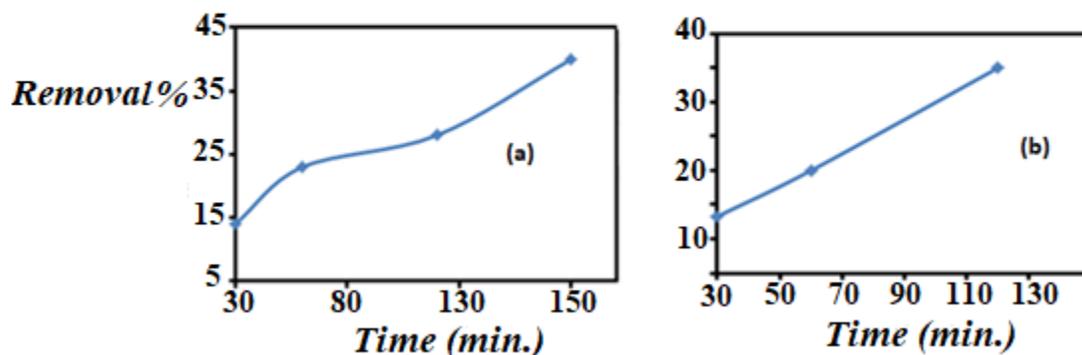


Fig.10. Effect of time on removal percentage of nickel ion of poly (AAc/AAm/Surfactant (3)) (a) and poly (AAc/AAm/surfactant (4)) (b).

The relation between the initial nickel ion concentration and removal percentage was determined by poly (AAc/AAm/Surfactant (3)) and poly (AAc/AAm/Surfactant (4)) (**Fig.11 (a, b)**) at the optimum time 2 and 3 hrs, respectively. The results showed that the removal percentage increased as concentration of nickel ion solution decrease till reach to optimum removal 78 % at 300 ppm of nickel ion by poly (AAc/AAm/Surfactant (3)) and 67 % at 300 ppm of nickel ion by poly (AAc/AAm/Surfactant (4)) [27-29].

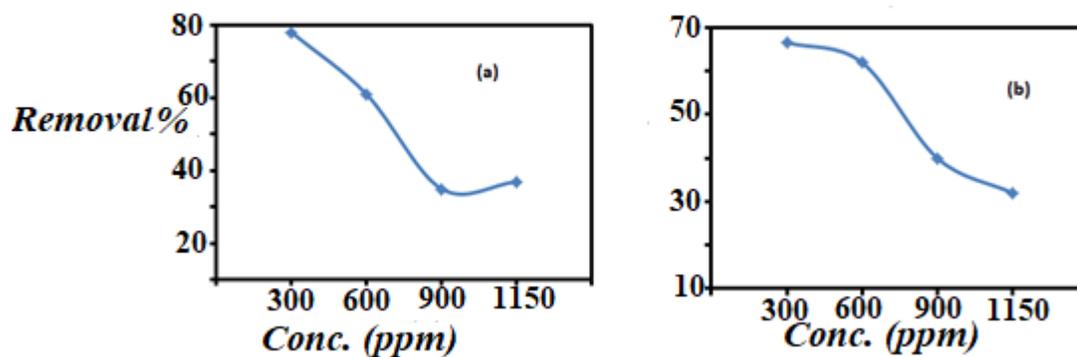


Fig.11. Effect of initial concentration of nickel ion solution on removal percentage by poly (AAc/AAm/Surfactant (3)) (a) and poly (AAc/AAm/Surfactant (4)) (b)

The effect of temperature on removal percentage was studied by poly (AAc/AAm/Surfactant (3)) at the optimum time 2 hrs and poly (AAc/AAm/Surfactant (4)) at the optimum time 3 hrs (**Fig.12** (a, b)). The results showed that the removal percentage increased with temperature. The optimum removal percentage at 60°C was reached at 67 % by poly (AAc/AAm/Surfactant (3)) and 73 % by poly (AAc/AAm/Surfactant (4)) [27-29].

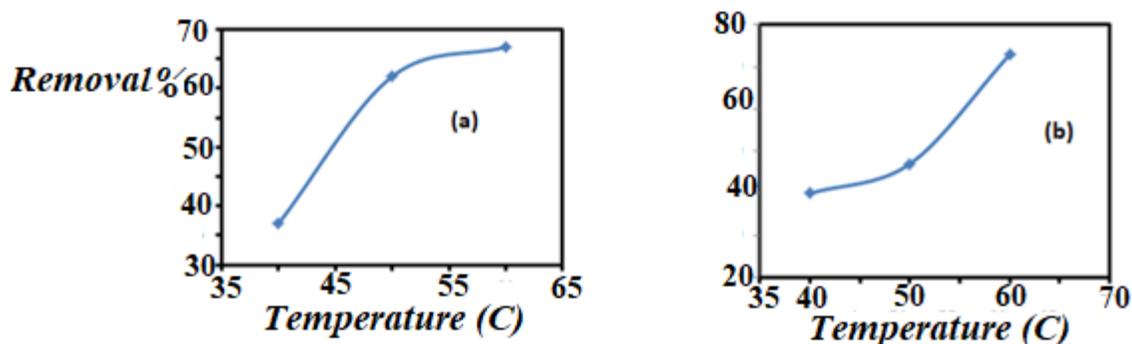


Fig.15. Effect of temperature on removal percentage of nickel ion by poly (AAc/AAm/Surfactant (3)) (a) and poly (AAc/AAm/Surfactant (4)) (b)

4. Conclusion

In this study gamma irradiation was used for the synthesis of poly acrylic acid /acrylamide with two amphoteric surfactants for the purpose of removal of heavy metal from waste water. The functional groups and crosslinking chemical structure of the amphoteric surfactants and polymer surfactant are confirmed by Fourier transform infrared spectrometry (FTIR) and ^1H NMR spectra. The kinetic swelling behavior was determined. The prepared hydrogels were examined for Ni^{+2} removals from aqueous solution. The factors affecting the removal percentage such as contact time, initial metal ion concentration and temperature were studied.

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