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Determination of optimal conditions for electrodeposition of Tin(II) in the presence of Alizarin Red S

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Abstract

A detailed physicochemical properties of aqueous solutions of alizarin red S – tin (II) chloride, has been thoroughly investigated by extensively exploring the effect of pH, concentration and temperature on the optimal conditions for the formation of tin (II)-alizarin red S (ARS-Sn II) complex. UV-Vis spectra, electrical conductivity and pH method were also used to characterize the final product. The stoichiometry of the reaction complex formation was determined *via* different referential methods. It was observed that, the reaction complex was formed when the concentrations were smaller than a certain limit (10^{-5} M). Adjusting the pH of the reaction (typically from 3.7 to 6.0) also resulted in the formation of the complex. The formed complex was highly stable in dark conditions (absence of sunlight) and at ambient temperature. Without the use of additives and by employing the investigated optimal conditions (i.e. pH: 5.0, i: 6 mA/cm², t: 5 min, C: 0.1 M, d: 1.273×10^{-4} cm), electrodeposition of tin (II) was demonstrated to be successful.

Keywords: Physical chemistry, Organic chemistry, Materials chemistry

1. Introduction

Tin (Sn) is a soft, ductile, nontoxic, silver white metal with exceptional corrosion resistance in air [1], excellent lubricity and ability to form several industrially important alloys and several intermetallic compounds of commercial importance. Compared to normal castings, rapid solidification of metallic alloys are usually known to result in refined microstructures with reduced micro-segregation coupled with improved mechanical properties of the final products. Sn- 0.7 wt.% Cu droplets rapidly solidified under transient conditions at low cooling rates, as well as directional solidification generated by impulse atomization (IA) has been achieved and reported [2]. The high degree of solubility of several metals in liquid tin, the wettability and adhesive properties of tin extenuate why tin by itself is considered an excellent solder [3].

Up to now, the use of inorganic metals for the formation of metal complexes for industrially relevant applications has seldom been reported. Partly due to the reason that, inorganic metals results in complexes that are toxic and uncontrolled used of such inorganic complexes may result in the suppression of some biological processes [4]. On the other hand, the most commonly encountered acidic electroplating tin chemistry is based on the utilization of fluoboric acid [5], sulfuric acid [6], phenol sulfonic acid (PSA)/halogen electrolyte [7, 8], hydrochloric/hydrofluoric acid and methane sulfonic acid (MSA) [9].

The presence of a quinoid oxygen, with two hydroxyl groups at the α - and β -positions in alizarin red S (ARS; 1,2-dihydroxyl 3-anthraquinone sulphonic acid), makes it very suitable for chelation, and its derivatives are well known colorimetric reagents with several applications in the micro determination of a number of metals [10]. Furthermore, the presence of sulphonate groups in the molecule improves it

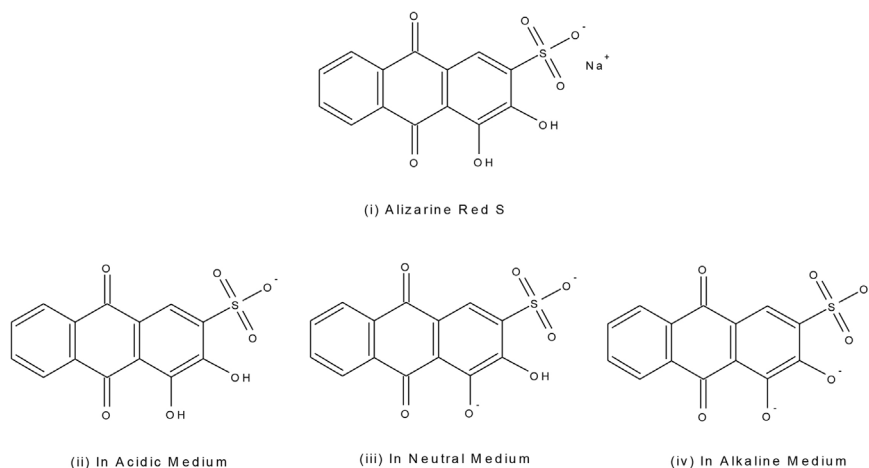


Fig. 1. Different formula of (ARS) in variable medium.

reactivity. The structure of alizarin red S dye as shown in Fig. 1 can exist in different forms depending on the type of media used (ii-iv).

The multi-structural variety of alizarin red S as shown in Fig. 1 makes it an admirable electrodeposition agent in aqueous solvents [11]. In this work, we focused on the optimal conditions to build an electrodeposition bath of tin, and finally, the successful electroplating of tin was realized and confirmed by scanning electron microscopy (SEM).

2. Experimental

2.1. Apparatus and chemicals

UV-vis spectroscopy analysis were recorded by an Optizen 2120 UV spectrophotometer. pH and electrical conductivity were performed on a GONDO PL-700PC apparatus. Dual power supply unit 30 V/AA, aux output 5 V/3A PROMAX Model FAC-622B. Resistors tray. Connecting wires. Unit digital multimeter Model M890C. SEM Photos were taken by using QUANTA 200, Coating bath consists of an anode (made of a paste of graphite and paraffin oil (from Merck)). A cylindrical cathodes which were made of industrial iron (steel) and a cylindrical stainless steel cathodes which had a commercial code (405). SnCl_2 , CH_3COONa , ARS and NaOH (Sigma-Aldrich and Merck) were used as received.

2.2. Experimental procedure

2.2.1. pH metery and electrical conductivity methods

Typically 25 mL of different percentages of $[(\text{SnCl}_2)$ and (ARS)]-mixtures with an initial concentration of 4 mM for each compound was titrated against NaOH aqueous solution (10 mM), by using the electrical conductivity and pH metery methods. Unless otherwise stated, the concentrations as mentioned above were used throughout our experimental investigations. Doubled distilled water was used throughout all the experimental procedures. The optimal conditions for the formation of the complex were also identified by electrical conductivity method. The mixtures had been studied priory without adding the buffer-solution, then we measured (pH and electrical conductivity) values for each proportion. But we didn't get any acceptable results compared with the results of the later experiments, which took acidity value into account. So in a typical procedure, 9 mL of ARS was mixed with 3 mL SnCl_2 . Subsequently, 22.5 mL [CH_3COOH and CH_3COONa (acetate buffer) aqueous solution] was added drop-wise and the pH of the resultant solution was adjusted to 5. In addition, the reaction stoichiometry was determined by taking [(3 mL) (ARS) + (750 mL) (double distilled water). pH = 5]-solution and adding (0.25 mL) drop-wise of [(6 mL) (SnCl_2)]-solution as a way to proceed (ARS)

solution titration by measuring (electrical conductivity and pH)-values, then the (SnCl_2) solution was titrated by the same way.

2.2.2. Spectrophotometric method

In a bid to optimize the reaction conditions, several experimental conditions were screened by using Sn^{2+} and ARS^- mixtures, where their initial concentrations were maintained at 5 mM for each initial solution. The optimal conditions for the formation of the complex were determined by adding the buffer solution to the mixtures and the reaction stoichiometry of the formed complex was monitored by spectrophotometric analysis.

2.2.3. Experimental electroplating of tin(II)

1 L electroplating bath (made of plastic material) was used for the electroplating of tin (II). The internal bath surface was pre-coated with graphite paste and used as the anode with a thickness of approximately 1 mm. In addition, a cylindrical-shape industrial iron (steel) and stainless steel, with a commercial code of 405, were used as cathode to achieve the coating process. A coating bath (made of glass material) with a capacity of 0.5 L, with an insoluble solid anodes of graphite, was used for the coating process.

For a typical deposition process, 250 mL of SnCl_2 (4 mM aqueous solution) was used for every bath coating. Similarly, 250 mL of ARS (4 mM solution) was used for every bath coating. Equal volumes of SnCl_2 and ARS (250 mL) were mixed together under vigorous stirring and 250 mL of the acetate buffer solution was subsequently added to adjust the pH of the resultant solution. The total volume of the pH-adjusted solution was 750 mL. The cathode (stainless steel or steel) was cleaned by an aqueous solution of NaOH (6 mM) for 10 min to remove any trace of fatty. Then it was washed for 2 min with doubled distilled (DI) water. After that, the cathode surface was washed for 5 min by an aqueous solution HCl (0.1 M) and then washed well with DI water. The surface of the cathode was then activated by immersing in 20 mM aqueous solution of H_2SO_4 for 1 min and further washed several times by DI water to attain an effective textured surface. The prepared cathode was weighed and immersed in the bath at a depth of 4 cm, with a typical stainless steel cathode dimensions of 10 mm (diameter) and for steel 8 mm. The electrical circuit was closed to start the coating process at a certain voltage, a certain current density and specific time without stirring the solution. The coated cathode was washed after the end of the experiment with DI water and dried with methanol. It was further weighed rapidly to prevent oxidation, and the current efficiency and coating film thickness calculated.

2.2.4. Performance determination

The current efficiency was calculated in each experiment as shown in Eq. (1) [12]:

$$BT\% = \frac{M_M}{Q \cdot I \cdot t} \times 100 \quad (1)$$

Where M_M : is deposited-metal weight on the cathode (g), where the cathode was dried and weighed carefully before and after the coating process.

$Q = (M/zF)$: is electrochemical equivalent which is equal to (2.218 g/Ah) for tin (II).

M : atomic mass of the deposited metal, $F = 26.8$ Ah, $z = 2$.

I : current intensity (A). t : electrolysis time (h).

The formed coating film thickness was also deduced from Eq. (2) [13]:

$$d = \frac{M_M}{\rho \cdot S} \quad (2)$$

Where ρ : is the density of the deposited metal on the cathode which is equal to (7.3 g/cm³) for tin, and S : is the coated surface area which is equal to (13, 35 cm²).

Deposition rate is given at (5 min) by the Eq. (3):

$$V = d/t = MM/(t \cdot \rho \cdot S) \quad (3)$$

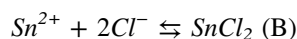
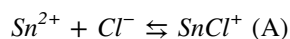
Where; d : is thickness of coating layer, t : is time of electroanalysis process (5 min), ρ : is the density of the deposited metal on the cathode which is equal to (7.3 g/cm³) for tin, and S : is the coated surface area which is equal to (13,35 cm²). (Influence of S-dodecylmercaptobenzimidazole as organic additive on electrodeposition of tin, p340)

3. Results and discussion

3.1. pH-metry method

All samples were titrated by an aqueous solution NaOH (0.01 M), and the following curves were obtained:

Fig. 2 (pH1) revealed a large acidic region of metal salt solution before the equivalence point, where the (Cl^-) ion liberates partially in the solution as shown in chemical equations A and B. The titration process shifts the equilibrium continuously toward the full displacement until the end of the titration:



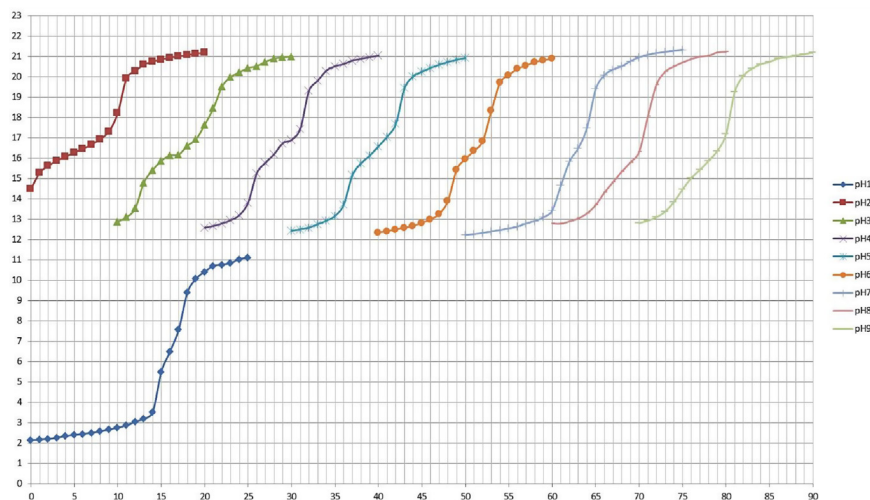


Fig. 2. pH1: titrated [(25 mL) (4×10^{-3} M) (SnCl_2)]-solution curve. pH2: titrated [(25 mL) (4×10^{-3} M) (ARS)]-solution curve. pH3: titrated [(1:4) (5 mL SnCl_2 + 20 mL ARS)]-mixture-solution curve. pH4: titrated [(1:1.5) (10 mL SnCl_2 + 15 mL ARS)]-mixture-solution curve. pH5: titrated [(1:1) (12.5 mL SnCl_2 + 12.5 mL ARS)]-mixture-solution curve. pH6: titrated [(1.5:1) (15 mL SnCl_2 + 10 mL ARS)]-mixture-solution curve. pH7: titrated [(4:1) (20 mL SnCl_2 + 5 mL ARS)]-mixture-solution curve. pH8: titrated [(1:2) (8.3333 mL SnCl_2 + 16.6666 mL ARS)]-mixture-solution curve. pH9: titrated [(1:3) (6.25 mL SnCl_2 + 18.75 mL ARS)]-mixture-solution curve.

As observed from Fig. 2 (pH2; titration-curve of reagent-solution), the addition of 1 mL NaOH solution the buffer's region is formed and this region was steady until the addition of 9 mL of NaOH which is due to the weak acidity of reagent, where the first (-OH)-group of the reagent starts to titrate in this medium. Also we refer that the reagent displaces in different mediums as shown in chemical equations C, D and E (Fig. 3) [11, 14, 15].

Fig. 2 (pH3) shows low (pH)-value of the solution of approximately (2.89), which is probably due to the fact that, both the reagent and metal ions solutions have two

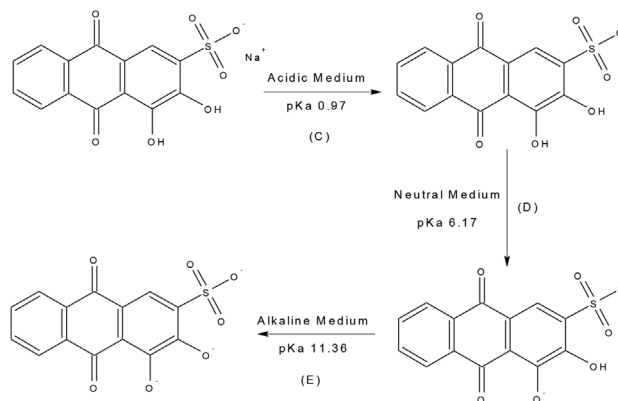


Fig. 3. Alizarine Red S displaces in different mediums.

initial (pH)-values, the first one (reagent solution) is close to the neutral medium where the reagent's molecules is partly displaced, and the second one (metal-ions solution) is close to acidic medium. Therefore reagent's molecules bond with (SnCl^+)-ions and (H^+ and Cl^-) forms as a byproduct in the solution, since the alkali-solution additions before reaching the second equivalence point are consumed for the first(-OH)-group titration of the remaining non-linked reagent, and also they are consumed to titrate hydrochloric acid, which is as a result of the interaction depicted in the chemical equation F (Fig. 4).

The evidence of the complex formation, which was described as a product of the previous reaction, is the forming of a new colored product (orange) in the solution at (pH)-value of the first equivalence point. The amount of product can be seen clearly by the naked eye, so it can be noted that the products' color before first equivalence point is close to reagent-solution's color (yellow), because of mixing with low-percentage salt's color (orange) (ARS-SnCl without donating bonds). It was noted that 5 mL of each of the reagent's solution or metal-ions' solution, which has the least volume in the mixture, leads to the formation of ($\text{H}^+ + \text{Cl}^-$) in the whole solution (or when the two volumes are equal). That formation delays reaching the end of the first equivalence point, where that delaying is equal to 2.5 mL of alkali's solution, and that observation is noted for all studied mixtures.

Also, it is noted that there is a long transition region between the equivalence points, this may be as a result of the presence of non-linked reagent's ions with metal's ions. In addition, reagent's molecules ionize partially (that means only first hydroxyl-group ionizes) and a larger volume of the alkali-solution is consumed to get to the second equivalence point, leading to less consumption of alkali-solution to get the first equivalence point when (pH3)-curve is compared with (pH1)-curve. This phenomenon is due to the steady formation of buffer after the addition of NaOH aqueous solution.

Fig. 2 (pH4) shows clearly reveal that, by increasing the volume of the metal-ions solution and decreasing in the surplus of the reagent's volume, there is a steady approach to the equivalence points. By comparing Fig. 2 (pH4) with Fig. 2 (pH5), it is observed that the volumes of mixture components are the appropriate volumes to give the first sign as the best reaction stoichiometry (1:1). Also, it should be noted that the resultant formula remains as a salt formula until reaching the

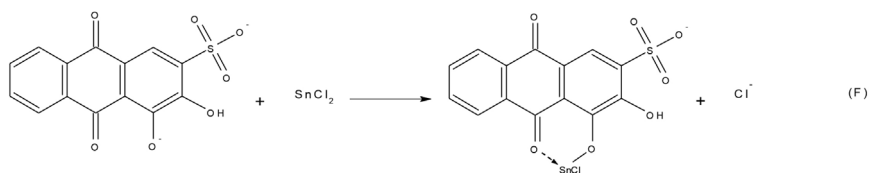


Fig. 4. The interaction between Alizarine Red S and tin(II) chloride.

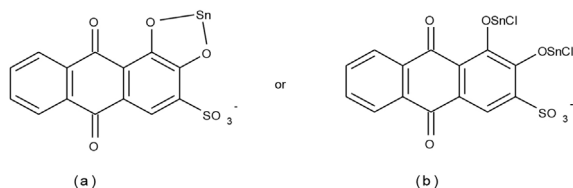


Fig. 5. Two possibilities for product formula.

appropriate acidity for forming a complex at the first equivalence point. There is a decrease in length (Fig. 2 (pH6)) of the transition region between the two equivalence points as compared to that observed in Fig. 2 (pH5). This suggests the presence of excess metal-ions in the solution, strongly suggesting that the reaction stoichiometry is (1:1). In Fig. 2 (pH7), the length of the transition region between the two equivalence points is observed to increase, indicating the presence of excess metal-ions in the solution. Noteworthy, the reaction between the metal ions and the reagent's ions at the equivalence point for the second (-OH)-group, where that reaction refers to the reagent displacement completely and that gives two product formula possibilities. So it is either the formed pentagonal ring Figure, or it is two linked (SnCl^+)-ions with a reagent ion as they are shown in Fig. 5

Fig. 5a shows that the first expected formula is the likely impact of the reaction's product depending on the displacement reaction as described in chemical equation (B) above; that means the (SnCl^+)-ions do not exist in this case. It also shows the titration of the second (-OH)-group and the surplus molecules of (SnCl_2) together, because of reaching the alkali medium. Hence, the expected reaction in alkaline medium is shown in chemical equation G (Fig. 6).

3.1.1. Denoting of (Mixtures (pH)-values and the consumed volume of the alkali solution) at the end of the first titration point

We focused on the first equivalence point for all the mixtures described in this investigations, because the best fitting medium for the formation of the complex were obtained at the first equivalence points as described earlier. By considering the titration curves for the remaining percentages which are evident in Fig. 2 (pH8 and pH9) and drawing the curve of the consumed alkali-solution's volume at the first equivalence point for all ratios, the following figure has been obtained:

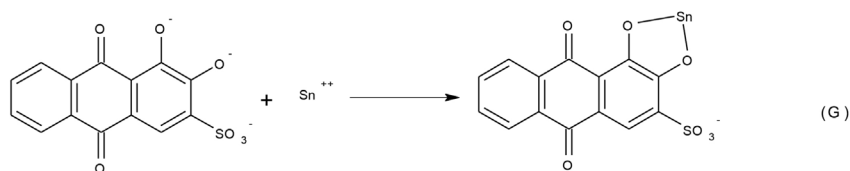


Fig. 6. The interaction between Alizarine Red S ions and tin(II) ions in alkaline medium.

In Fig. 7, the results reveal that the first equivalence point, which belongs to the (SnCl₂ 1:1 ARS)-mixture titration process, consumes the largest volume of alkali-solution when compared with the other mixtures analyzed in this investigations. Which is due to the ionizing of most increasable protons, which required excess amount (volume) of alkali-solution for the naturalization process, and this also provides a direct evidence for attaining the appropriate percentage of reaction stoichiometry. As well as the fact that this curve determines the optimal (pH)-value to form the complex. After (SnCl₂ 1:1 ARS)-mixture, a significant increase in the consumption of NaOH is observed as a result of the difference between initial (pH)-values of each of (reagent and metal-ions)-solutions. So the curve without surplus of metal-ions solution is observed as normal peak, but for these studied solutions, when the volume of metal-ions solution is larger than the volume of the reagent solution, the mixture-titration axiomatically consumes larger volume of alkali-solution to reach the first equivalence point than the other mixtures because of the reason which was mentioned previously.

Fig. 8 has been obtained when the (pH)-values were drawn versus the changing of the mixture composition at the first equivalence point of the mixtures-titration:

Fig. 8 shows that the (pH)-values at first equivalence point decreases up to ~ 33% of metal-ions-solution volume, then the (pH)-values increase at first equivalence point. That is evidence of changing in product structures; that means there is changing in structures of products to form the complex at (40%) of metal-ions solution volume. The curve also shows that the (pH)-value is as high as possible at the reaction stoichiometry (1:1), and it shows the highest (pH)-value where the complex can be formed at that value, which is equal to (4.55), although the conductivity measurement method “as we will note” refers to the higher (pH)-value than the pH-metry method. And (3.7) value can be considered as the lowest (pH)-

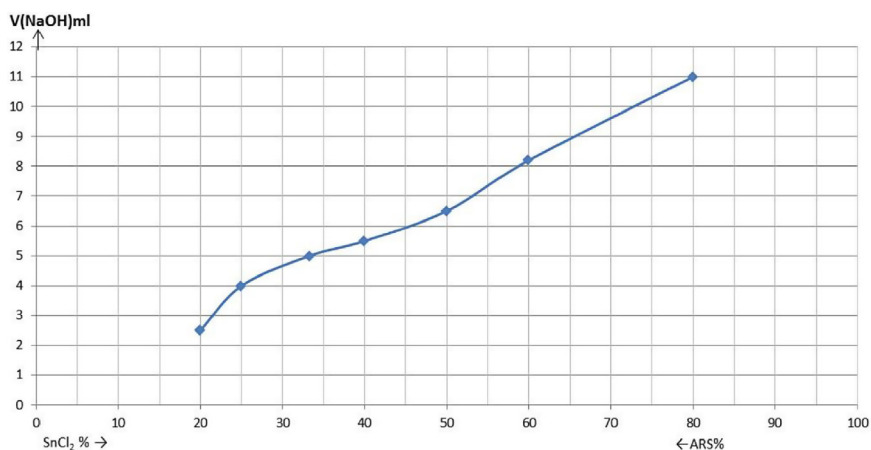


Fig. 7. The consumed volumes of (0.01 M NaOH) to reach the first titration points for all various mixtures.

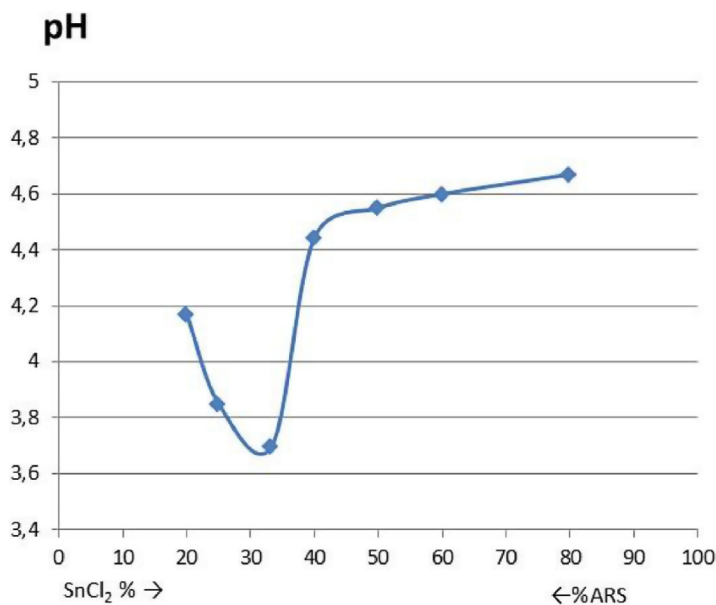


Fig. 8. (pH)-values at the first titration points for all various mixtures, where (0.01 M NaOH)-solution was used.

value which the complex structure can be fixed at. With looking at the percentages that are larger than (50%) of metal-ions-solution volume, the surplus of metal ions solution effect widely in mixture acidity because of the considered difference between initial (pH)-values as it was mentioned earlier. As a result, the range of (pH)-values were determined toward larger values where the complex structure can be fixed at it without change. It is also noted that the highest (pH)-value, which the complex structure remains fixed at it, is very useful in the coating process. Where it is known that the lower the acidity of the medium close to the neutral medium, the better coating process [16]. The use of that value is evidence of a small number of protons, which provides the reaction stoichiometry (1:1) resulting in less impact on the activity of the buffer solution, which is used to adjust the (pH)-value (if mixture solution was titrated to reach the first equivalence point of the titration, then the buffer solution was added as a next step). To keep the complex structure stable, it is preferred to work at (pH)-value which is equal to (4.5) as this method refers to. In conclude, the range of appropriate (pH)-values was determined by pH-metry method to form the complex, which is (3.7 – 4.55).

3.1.2. Study of the concentrations effect on (pH)-value and the form of the compound

(pH)-values of the various mixtures were measured without adding the buffer solution. The reaction stoichiometry which was indicated in Fig. 9 to form a salt and not to form a complex, that reaction stoichiometry is (2:1) because there is the

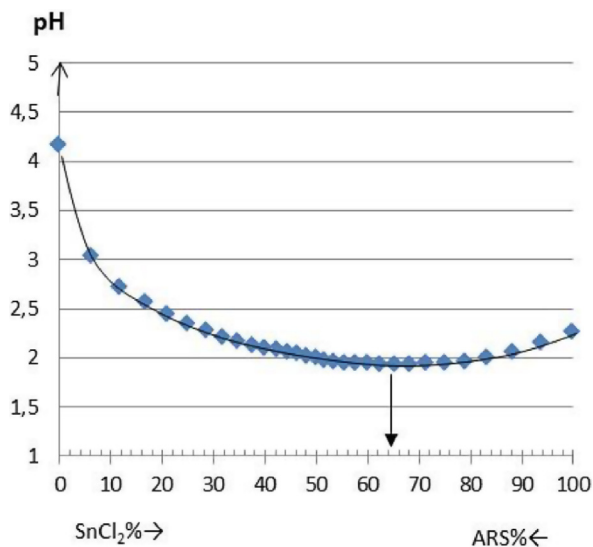


Fig. 9. Curve of (pH)-values versus mixture compositions without adding the buffer solution.

highest proportion of salt at it, where each of (ARS + SnCl₂) compounds shares giving the acidic character of the entire solution.

Based on the above, when we did not use any buffer solution which has suitable range of (pH)-values to form the complex, the mixing of (reagent and metal-ions)-solutions by (2:1) gives the lowest (pH)-value and it is (pH = 1.94) which is evident in Fig. 9. As a result, reaching the lowest (pH)-value is not the evidence of the complex forming. But if concentrations were decreased for each of the two solutions to be within the range. (1.3×10^{-6} – 1.6×10^{-5} M), the (pH)-value remains within the range (4.48–5.73) without adding the buffer solution for all studied various mixtures in this research. So (reagent and metal-ions)-solutions have been prepared, with initial concentration (4×10^{-3} M) for each, by taking the (3 mL ARS + 750 mL double distilled water, pH = 5)-solution and adding the (6 mL SnCl₂)-solution to have the same optimal concentration, where in each batch has been added (0.25 mL) as a way for (ARS)-solution titration process by measuring the (pH)-values. Then the (SnCl₂)-solution was titrated by the same way. Fig. 10 shows the result of (pH)-curve against mixture compositions.

Fig. 10 indicates that the correct reaction stoichiometry is (1:1), because the lowest (pH)-value refers to the maximum number of protons which result from the linking of the largest possible amount of (SnCl⁺) with the maximum possible amount of reagent ions.

3.2. Conductivity method

Various samples have been titrated versus (0.01 M NaOH)-solution, and the curves as shown in Fig. 11 have been obtained:

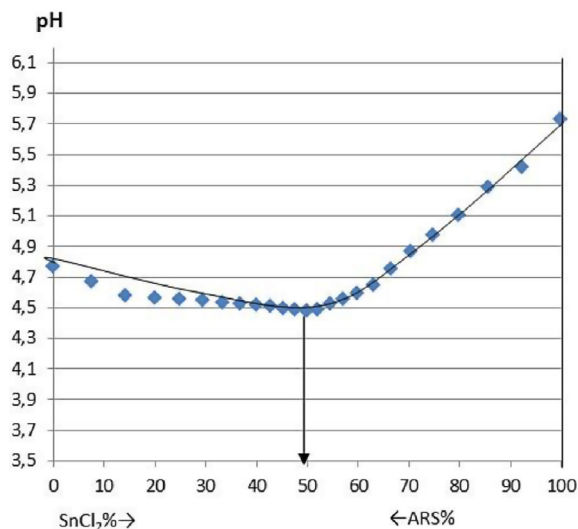


Fig. 10. Curve of (pH)-values versus mixture compositions, where the suitable concentrations were used to remain the (pH)-values within a suitable domain, which is required for forming the complex and to calculate the reaction stoichiometry.

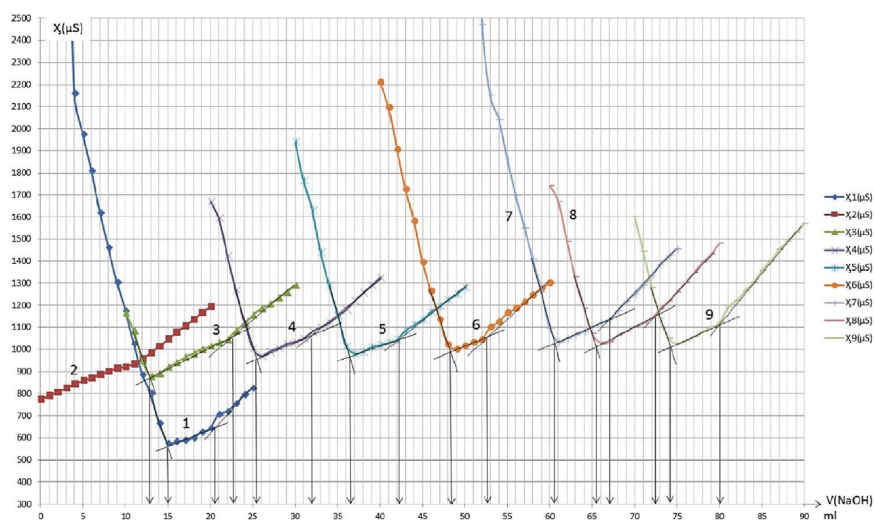


Fig. 11. 1: titrated [(25 mL) (4×10^{-3} M) (SnCl_2)]-solution curve. 2: titrated [(25 mL) (4×10^{-3} M) (ARS)]-solution curve. 3: titrated [(1:4) (5 mL SnCl_2 + 20 mL ARS)]-mixture-solution curve. 4: titrated [(1:1.5) (10 mL SnCl_2 + 15 mL ARS)]-mixture-solution curve. 5: titrated [(1:1) (12.5 mL SnCl_2 + 12.5 mL ARS)]-mixture-solution curve. 6: titrated [(1.5:1) (15 mL SnCl_2 + 10 mL ARS)]-mixture-solution curve. 7: titrated [(4:1) (20 mL SnCl_2 + 5 mL ARS)]-mixture-solution curve. 8: titrated [(1:2) (8.3333 mL SnCl_2 + 16.6666 mL ARS)]-mixture-solution curve. 9: titrated [(1:3) (6.25 mL SnCl_2 + 18.75 mL ARS)]-mixture-solution curve.

Titration curves in Fig. 11 was obtained by measuring the conductivity of solutions. It was found that the curves of the titrated various solutions by measuring the conductivity were identical to the curves of the pH-metry method, with consideration that the titration method of conductivity is more accurate than the pH-metry method especially at first equivalence point and that difference does not exceed (1 mL), and Fig. 7 remains true also for the method of conductivity measurement. In Fig. 12 the curves obtained by measuring the conductivity of different mixtures composition at the first equivalence point are shown:

Fig. 12 shows the best studied mixtures, because (1:4), (1:3), (1:2) and (4:1) mixtures have very high or very low conductivity values indicating to a non-linked surplus quantity of one of reagent or metal ions in mixture solutions, while the best mixtures are (1:1.5), (1:1) and (1.5:1). So only those mixtures can be studied, but to explain all reactions in all mediums the study of whole mixtures is preferred.

3.2.1. Study of the concentration effect on the conductivity values of the mixtures solutions

The increase in the tin (II) ions concentration (Fig. 13) causes the increase in the conductivity of the overall solution and reaches a maximum of 70%. A sudden decrease in conductivity is observed thereafter, it may be due to the precipitation of salt when the used concentrations are (4×10^{-3} M), which leads to obstruction the electrolyte movement in the solution, The comparison between Fig. 9 and Fig. 13 emphasizes that the complex does not exist, where the complex forming process results the biggest amount of protons to get the highest value of conductivity and the lowest value of the (pH) at that reaction stoichiometry which is the largest

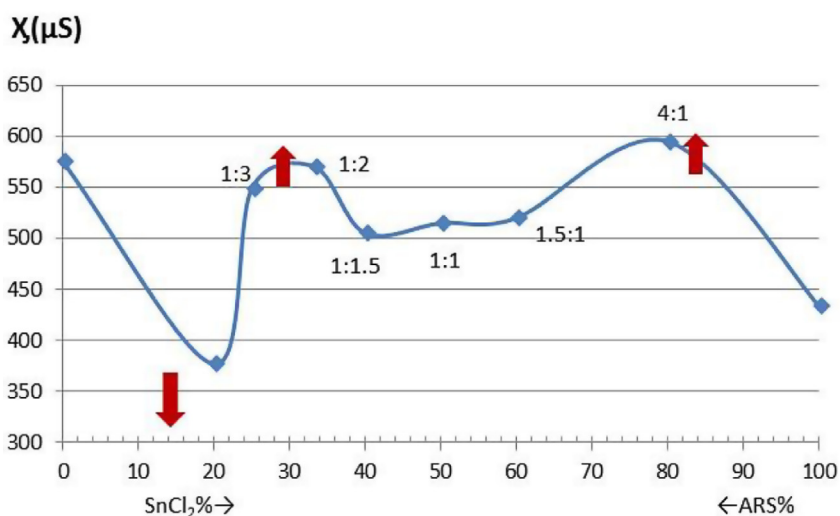


Fig. 12. Conductivity values of the different mixtures compositions at the first equivalence point of the titration.

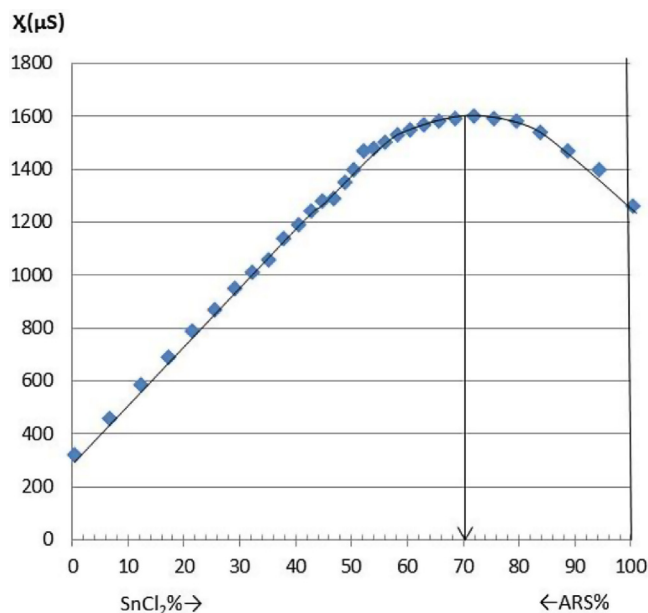


Fig. 13. Curve of the conductivity values versus the various mixtures compositions.

between (reagent and metal)-ions, so the complex privation is because the (pH)-range doesn't help to form the complex and that range is (pH = 1.94–4.2). Where the reaction stoichiometry that has been reached in Fig. 13 is (2:1), and the reaction stoichiometry in the pH-metry method (Fig. 9 was also (2:1)).

3.2.2. Study of the (pH)-values effect on the conductivity of the mixtures

The appropriate conditions have been determined to form the complex. Where the conductivity method and buffer solution were used to measure conductivity values and to control the (pH)-value. Table 1 shows the used mixture composition versus both of the (pH)-values and conductivity values of the mixture solutions.

The relationship between the (pH)-values and the conductivity values are shown in Fig. 14.

It was found that appropriate (pH)-value to get the highest value of the conductivity of the solution is equal to (pH = 5), where this value refers to the conductivity value to form the complex in specified optimal conditions, which means the existence of the highest amount of protons in these conditions. The pH value which is equal to 6 and can be considered as the highest value of (pH) which the complex structure can be fixed at in this method depending on the considered conductivity difference change between each (pH)-value and another subsequent (pH)-value, so the conductivity method determined rang of (pH)-values, which is (3.7–6), that is bigger than the range of pH-metry method.

Table 1. Statement of used mixture composition and conductivity values at the different (pH)-values.

	pH	X (mixture) (μS)
(ARS)(9 mL) + (SnCl ₂)(3 mL)	2.33	815
	3	714
	4	1890
	5	2750
	6	2920
	7	2970
	9	2980
	11	2980
	(CH ₃ COOH + NaOH) (22.5 mL)	

3.2.3. Use of the conductivity method to determine the reaction stoichiometry of complex formation

The reaction stoichiometry has been studied by taking [(3 mL) (4×10^{-3} M)] of metal-ion solutions and adding (750 mL) of the double distilled water to adjust the (pH)-value which was (pH = 5), then adding [(6 mL) (4×10^{-3} M)] of the reagent solution in batches, where each batch was (0.25 mL) and measuring the conductivity. Conductivity values have been corrected by the Eq. (4) [17]:

$$\left\{ \frac{V_{\text{mL}}(\text{ARS}) + V_{\text{mL}}(\text{SnCl}_2)}{V_{\text{mL}}(\text{SnCl}_2)} \right\} \times \text{observed conductivity (ms)} = \text{corrected conductivity (ms)} \quad (4)$$

The results are shown in Table 2.

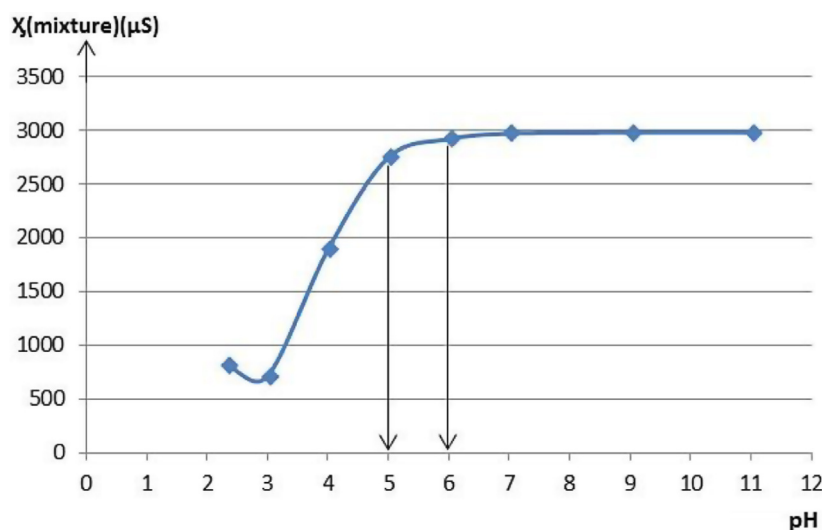
**Fig. 14.** The curve of the conductivity values versus the various (pH)-values to determine the suitable (pH)-value.

Table 2. Statement of used mixture composition and conductivity values at the different (pH)-values.

VmL (SnCl ₂)	vmL (ARS)	observed conductivity (mS)	corrected conductivity (mS)
3	0	0	0
3	0.25	0.0226	0.022608
3	0.5	0.0239	0.023916
3	0.75	0.0246	0.02463
3	1	0.0256	0.025634
3	1.25	0.0268	0.0268445
3	1.5	0.0277	0.0277552
3	1.75	0.0285	0.028566
3	2	0.0296	0.029679
3	2.25	0.0307	0.030792
3	2.5	0.0318	0.0319056
3	2.75	0.0326	0.0327191
3	3	0.0335	0.0336335
3	3.25	0.0347	0.0348498
3	3.5	0.0398	0.03998
3	3.75	0.0402	0.0404002
3	4	0.0424	0.0426252
3	4.25	0.0445	0.0447512
3	4.5	0.0464	0.0466773
3	4.75	0.0487	0.04900721
3	5	0.0506	0.05094
3	5.25	0.0528	0.05317
3	5.5	0.0549	0.0553
3	5.75	0.0567	0.05713
3	6	0.0586	0.05907

The relationship between the corrected conductivity values and the additive volumes of the reagent solution are shown in Fig. 15. Fig. 15 confirms the link proportion between the metal-ions (Sn²⁺) and reagent-ions (ARS⁻) which is equal to (1:1).

3.3. Spectrophotometric method

Several investigations were conducted in order to obtain the characteristic spectrum of the complex and without use any buffer solution or change in (pH)-value. Fig. 16 shows that there is no formed-complex spectrum, which should be distinct from the reagent spectrum, and there is no shift of reagent spectrum toward longer wave lengths when its solution mixes with metal-ion solution with a variable concentration. That state happens when there is no any suitable adjustment of the (pH)-value, which is required to form the complex.

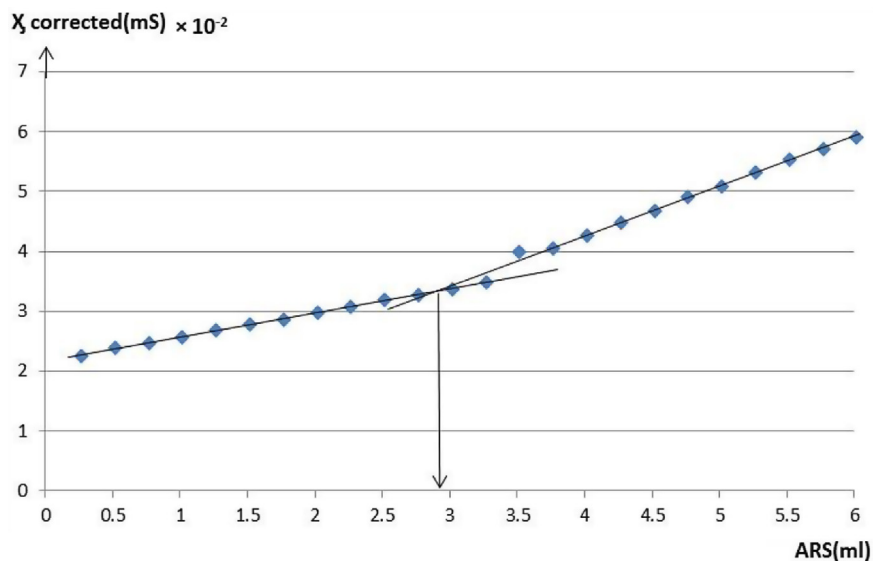


Fig. 15. Statement of the reaction stoichiometry by using the conductivity measurement method, [(3 mL) (4×10^{-3} M)] of metal-ions solution with (750 mL) of double-distilled water and adding [(6 mL) (4×10^{-3} M)] of reagent solution gradually.

3.3.1. The effect of (pH)-values on the absorption spectrum of the studied solution

The appropriate (pH)-value has been determined by carrying out the experiments within the activity range of the buffer solution, Fig. 17 shows a characteristic

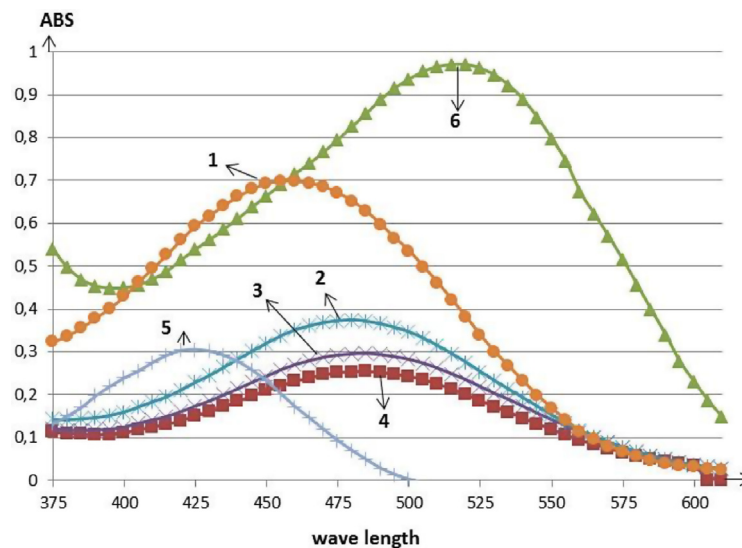


Fig. 16. Absorption spectrum change with change of ratio which is between the volume of the reagent solution and the volume of the metal-ions solution with initial concentration (5×10^{-4} M) for each: 1- spectrum of (12 mL ARS + 8 mL SnCl₂)-mixture solution, 2- spectrum of (10 mL ARS + 10 mL SnCl₂)-mixture solution, 3- spectrum of (8 mL ARS + 12 mL SnCl₂)-mixture solution, 4- spectrum of (6 mL ARS + 12 mL SnCl₂)-mixture solution, 5- spectrum of (12 mL ARS) solution.

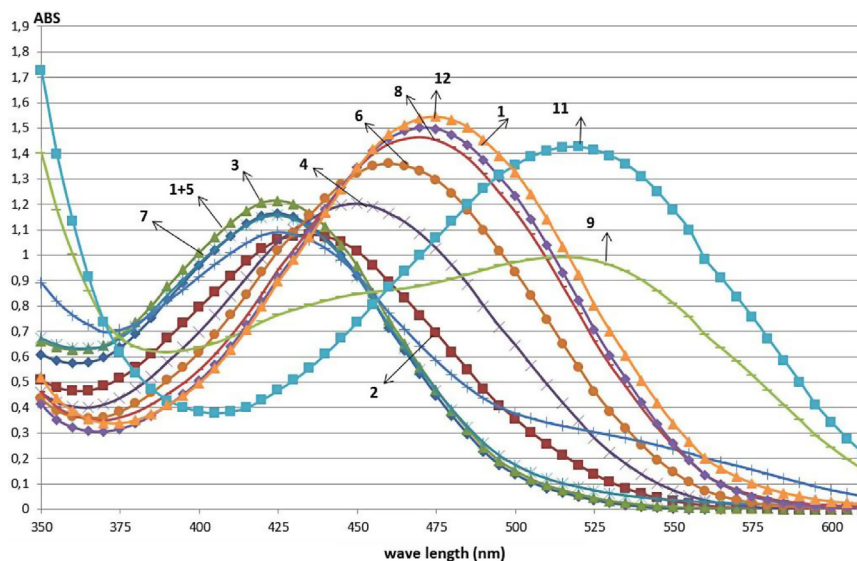


Fig. 17. Change of absorption spectra of the reagent solution by adding the metal-ion solution, where the concentration is (4×10^{-3} M) for both of them at selected (pH)-values: 1-spectrum of (ARS, pH = 2) solution, 2- spectrum of (ARS + SnCl₂, pH = 2)-mixture solution, 3- spectrum of (ARS, pH = 3) solution, 4- spectrum of (ARS + SnCl₂, pH = 3)-mixture solution, 5-spectrum of (ARS, pH = 4) solution, 6-spectrum of (ARS + SnCl₂, pH = 4)-mixture solution, 7- spectrum of (ARS, pH = 5) solution, 8- spectrum of (ARS + SnCl₂, pH = 5)-mixture solution, 9- spectrum of (ARS, pH = 6) solution, 10- spectrum of (ARS + SnCl₂, pH = 6)-mixture solution, 11- spectrum of (ARS, pH = 7) solution, 12- spectrum of (ARS + SnCl₂, pH = 7)-mixture solution.

spectrum of the complex and suggest that the best value of the (pH)-values is (pH = 5).

3.3.2. Determining the required reaction stoichiometry to form the complex

To determine the reaction stoichiometry and changing the concentrations of reagent solutions and metal-ion solution, a standard series of solutions was prepared. Where the volume of the solution in each sample was equal to (12 mL), and stock solutions of both (metal-ion solution and reagent solution) was equal to (1.6×10^{-5} M). Then an absorbance change was measured and scanned at variable wavelength versus double distilled water. Depending on the *Job's method*, which is continuous variety [18], the reaction stoichiometry has been calculated when the wavelength was (475 nm) as shown in Fig. 18.

Fig. 18 determines the reaction stoichiometry, which is (1:1), by proceeding the following accounts:

$$\{V(M) / [V(M) + V(L)]\} = 0.492, \{V(L) / [V(M) + V(L)]\} = 0.508$$

$$\Rightarrow [V(L) / V(M)] = 1.033 \approx 1 \Rightarrow V(L) = V(M)$$

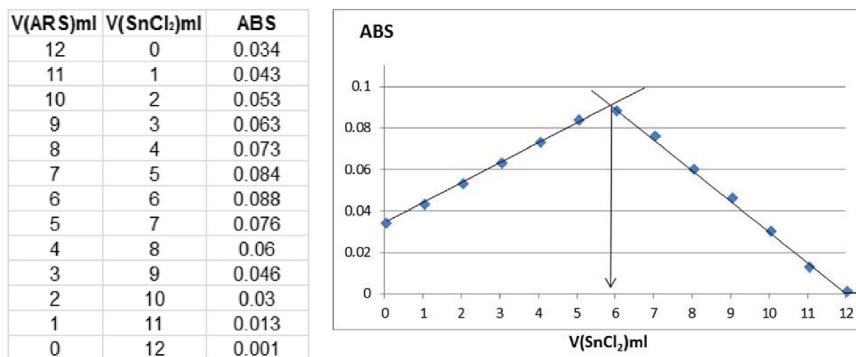


Fig. 18. Using of continuous-variety method to calculate the reaction stoichiometry (the change of the absorbance values versus the change of the concentrations with the constancy of total volume).

3.3.3. Study of the effect of time change on the absorbency of the formed complex (study of the stability of the complex during the time)

The change of complex absorbance has been studied versus the time, where the wavelength was (475 nm). We have found that the complex structure is stable away from a high temperature and light as shown in Fig. 19:

As a result; the expected reaction under those conditions, which have been reached in several ways, is as in the reaction F.

3.4. Experimental electroplating of tin (II)

The use of the anodic graphite paste bath, as shown in Fig. 20a, caused a heavy sludge in the solution, in addition to causing a change in the composition of the

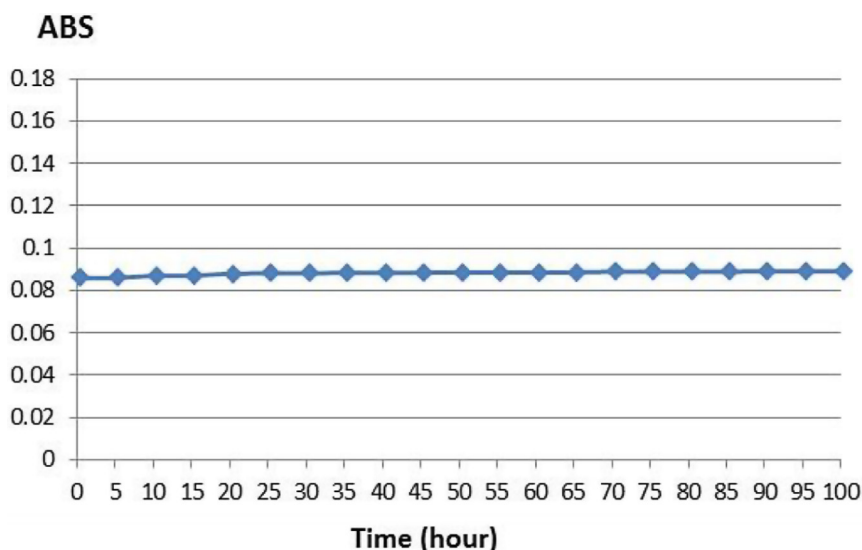


Fig. 19. Absorbance change with time, where the concentration was equal to (1.6×10^{-5} M) for each of metal-ions and reagent-ions in the same solution to form the complex.



Fig. 20. Coating bath, (A): coating bath with anodic graphite paste, (B): coating bath with insoluble anodic graphite.

Table 3. Current efficiency values of tin coating versus (pH)-values.

pH	Cathode weight (g) before coating	Cathode weight (g) after coating	Tin weight (g)	Current efficiency (BT%)
2	46.7564	46.7593	0.0029	43.65%
3	46.5415	46.5457	0.0042	63.21%
4	46.8436	46.8487	0.0051	76.76%
5	46.4226	46.4285	0.0059	88.8%
6	46.6547	46.6594	0.0047	70.74%
7	46.9631	46.9673	0.0042	63.21%

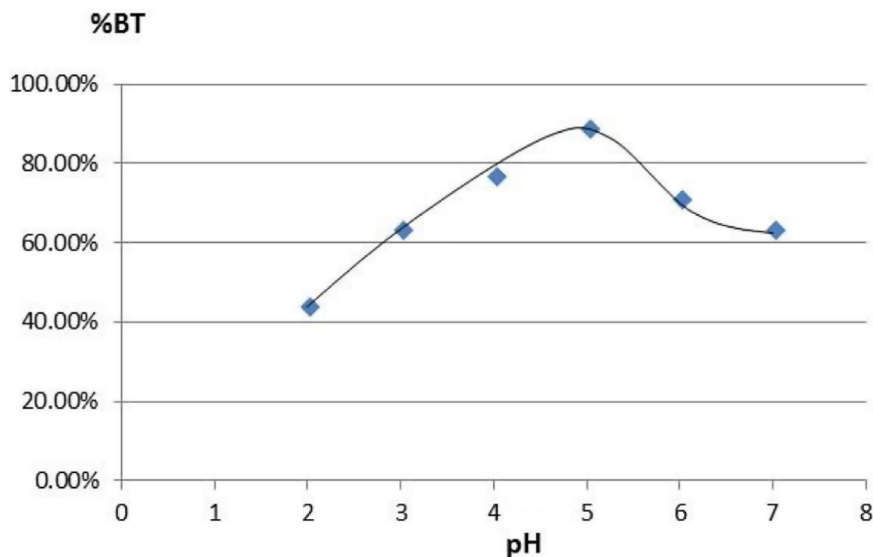


Fig. 21. Curve of current efficiency values of tin coating versus (pH)-values.

solution resulting from mixing graphite particles and paraffin oil with solution components, especially when stirring of the solution was used, and unfortunately all of that gave unsatisfactory results. Therefore, other coating bath, as shown in Fig. 20b, was employed and discussed in the manuscript.

3.4.1. Study of current efficiency of tin coating versus (pH)-values

Experiments have been carried out at ($V = 2\text{--}5$ V, $i = 3$ mA/cm², $t = 1$ h), and the results have been shown in Table 3.

The relationship between the current efficiency values and (pH)-values have been drawn as in Fig. 21 and reveal that the best current efficiency value is at (pH = 5).

Table 4. Current efficiency values of tin coating versus current density values.

i (mA/cm ²)	Cathode weight (g) before coating	Cathode weight (g) after coating	Tin weight (g)	Current efficiency (BT%)
1	46.4577	46.4589	0.0012	52.68%
2	46.8909	46.8935	0.0026	58.7%
3	46.4367	46.4413	0.0046	69.24%
4	46.9649	46.9720	0.0071	79.77%
5	46.5394	46.5497	0.0103	93.32%
6	46.7461	46.7585	0.0124	93.32%
7	46.4476	46.4537	0.0061	39.13%
8	46.6539	46.6574	0.0035	19.57%

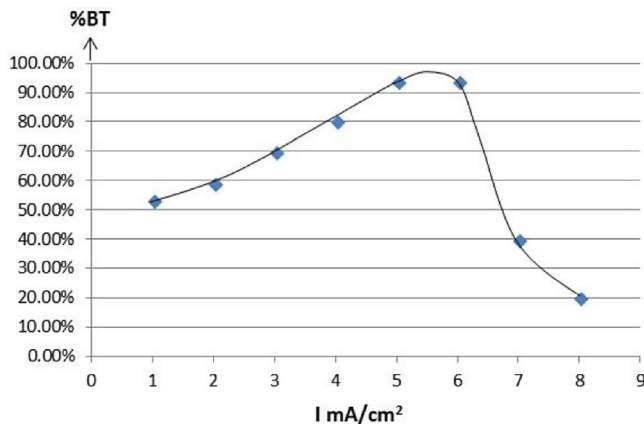


Fig. 22. Curve of current efficiency values of tin coating versus current density values.

3.4.2. Study of current efficiency of tin coating versus current density (i mA/cm²)

Experiments have been carried out at ($V = 2-5$ V, $pH = 5$, $t = 1$ h), and the results have been shown in Table 4.

The relationship between current efficiency values and current density values have been drawn as in Fig. 22 and shows that the best current efficiency value is at ($i = 5.5-6$ mA/cm²).

3.4.3. Study of current efficiency of tin coating versus molarity concentration (C mol/l)

Experiments have been carried out at ($V = 2-5$ V, $pH = 5$, $t = 1$ h, $i = 6$ mA/cm²), and the results are depicted in Table 5.

Table 5. Current efficiency values of tin coating versus molarity concentration values.

C (mol/l)	Cathode weight (g) before coating	Cathode weight (g) after coating	Tin weight (g)	Current efficiency (BT%)
0.01	46.4577	46.4589	0.0012	8.675%
0.02	46.8907	46.8935	0.0028	20.954%
0.04	46.4355	46.4413	0.0058	43.564%
0.06	46.9611	46.9720	0.0109	81.983%
0.08	46.5382	46.5497	0.0115	86.785%
0.1	46.7462	46.7585	0.0123	92.342%
0.12	46.5529	46.5649	0.0120	90.462%
0.14	46.3770	49.3891	0.0121	91.213%

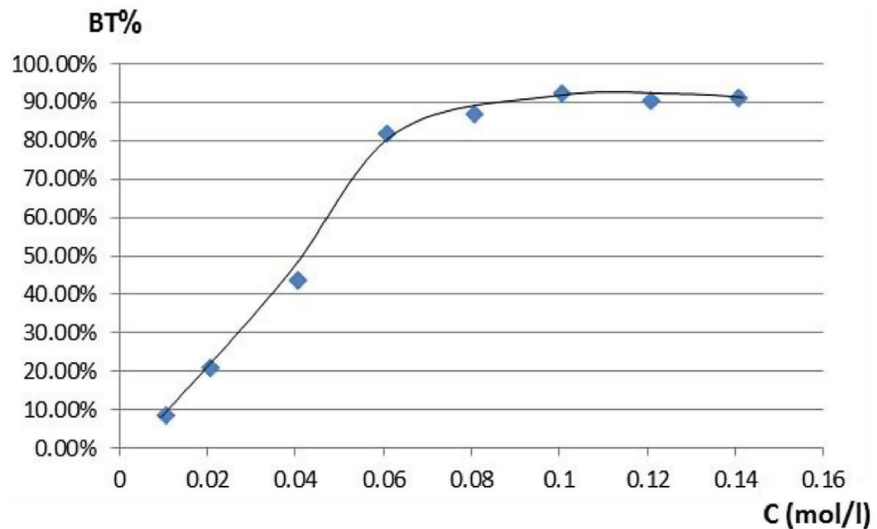


Fig. 23. Curve of current efficiency values of tin coating versus molarity concentration values.

The relationship between current efficiency values and molarity concentration values have been drawn as in Fig. 23 and suggests that the best current efficiency value is at ($C = 0.1$ M).

3.4.4. Study of current efficiency of tin coating versus the time (t min)

Experiments have been carried out at ($V = 2-5$ V, $pH = 5$, $i = 6$ mA/cm²), and the relationship between current efficiency values and the time have been drawn as in Fig. 24 and it is evident that the best current efficiency value is at ($t = 5$ min).

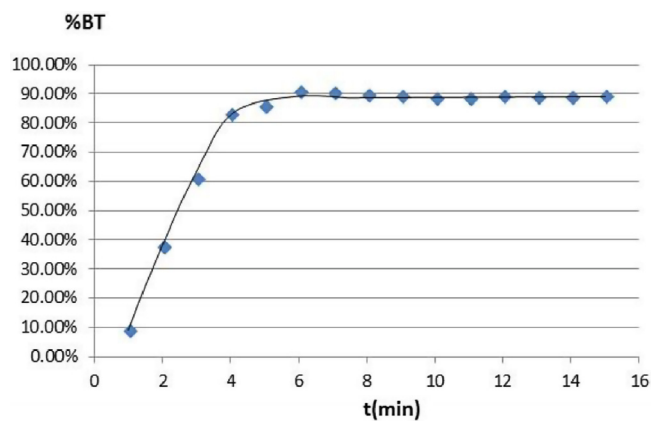


Fig. 24. Curve of current efficiency values of tin coating versus time values.



Fig. 25. Industrial iron electrodes, which has been coated with tin in the appropriate operating conditions.

3.4.5. Calculation of tin film thickness after applying the appropriate operational conditions

The film thickness of tin which covered the industrial iron (steel) surface in the appropriate operating conditions ($V = 2-5$ V, $i = 6$ mA/cm², pH = 5, $t = 5$ min, $C = 0.1$ M) have been calculated by using the following relationship [13]:

$$d = \frac{M_M}{\rho \cdot S}$$

The thickness of the coating film was: $d = 1.273 \times 10^{-4}$ cm = 1.273 μ m.

Deposition rate is given at (5 min) by the Eq. (3).

$$V = d/t = MM/(t \cdot \rho \cdot S) = 0.0114/(5 \times 7.3 \times 13.35) = 14.004 \mu\text{m/h}$$

A good coating tin layer on the industrial iron (steel) has been obtained by using the insoluble dry graphite anodes, and the following conditions is the suitable operating conditions:

$$(V = 2-5 \text{ V, } i = 6 \text{ mA/cm}^2, \text{ pH} = 5, t = 5 \text{ min, } C = 0.1 \text{ M}) \Rightarrow d = 1.273 \mu\text{m}$$

The electro-deposition of tin following our procedure thoroughly described above was applied, as shown in Fig. 25.

4. Conclusion

The physical properties of the aqueous solutions of (alizarin red S – tin(II) chloride) was studied, and the optimal condition for formation the complex have been determined, where pH method, electrical conductivity method and UV/Vis spectral method indicated that the suitable used concentrations are (10^{-5} M) or adjusting the (pH)-value to be (5). In addition, the optimum reaction stoichiometry of formed complex, which is (1:1), was also determined.

The experimental portion of electrodeposition of tin(II) in presence of (ARS) as complex showed that the use of anodic graphite past caused a heavy sludge, and that gave unsatisfactory results. A good results have been obtained when we use insoluble dry graphite as anodes to coat industrial steel with tin, where the following conditions were the suitable operating conditions: ($v = 2-5$ V, $i = 6$ mA/cm², pH = 5, $t = 5$ min, $C = 0.1$ M). Hence, the thickness of plated layer was (1.273 μ m).

Declarations

Author contribution statement

Nour M-S. Ali: Conceived and designed the experiments; Performed the experiments; Wrote the paper.

Prince N. Amaniampong: Analyzed and interpreted the data; Wrote the paper.

Ayman Karam: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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