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RESEARCH ARTICLE

Effect of foreign ions for the determination of metal ion in the presence of surfactants

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Aluminum is the third most abundant metal in the Earth's crust. Despite its ubiquitous nature it is present in small amount in living organisms. Aluminum toxicity has been implicated in the pathogenesis of renal distinct clinical syndromes, including progressive and fatal encephalopathy and bone diseases. In the present study, Al was selected for the analysis by complexometric method. This method was based on the formation of a red colored ternary complex by the reaction of Aluminum with Aluminon (Aurin tricarboxylic acid triammonium salt) in the presence of micellar medium. The ternary complex of Aluminum with the surfactant Triton X-100 shows a maximum absorbance at 530 nm wavelength at pH 4.0 while with the sodium dodecyl sulfate it shows a maximum absorbance at 525 nm and at pH 5.0. The reaction was proceeded by the variation in pH and concentrations of surfactants, aluminon, aluminum. Their effects on the reaction of aluminum with aluminon complex in micellar media were recorded by UV-visible spectrophotometer. The reaction was found to be extremely rapid at room temperature. The system obeys Lambert Beer's law between 0.24 and 21.74 μg/mL concentrations with Triton X-100. The values of slope, intercept and correlation coefficients were 0.07, 0.348 and 0.989, respectively. The concentration varied between 0.24 and 24.14 μg/mL with sodium dodecyl sulfate and the values of slope, intercept and correlation coefficients were 0.029, 0.148 and 0.962, respectively. The foreign ion effect was also tested by keeping the constant concentration of metal ion and determining its concentration in the presence of different foreign ions. The method was also applied for the determination of Al(III) in pharmaceutical formulations and water samples, which showed an excellent resemblance between reported and obtained results.

Keywords aluminum, aluminon, surfactants, SDS (sodium dodecyl sulfate), pharmaceutical formulations and water sample

1 Introduction

Pollution due to chemicals, including heavy metals, may have negative consequences on the biosphere. The most abundant pollutants in the waste water and in sewage sludge are heavy metals [1]. Human activities, such as mining operations and the discharge of industrial wastes have resulted in the accumulation of metals in the environment and eventually results in their accumulation through the food chain, which causes serious ecological and health problems [2]. The availability and annual usage of metals vary widely with the kind of metals. Some metals are abundant and widely used in structural applications. Iron and aluminum are prime examples. Aluminum has a long list of dangers associated with its presence at toxic level. Aluminum is taken into the body by the ingestion of contaminated water and food, wearing antiperspirants that contain aluminum, cooking with aluminum and aluminum alloy pans.

Its toxicity causes speech disorders, chronic fatigue, weakness, skin disorders, breathing problems, and genital abnormalities. Researchers are now exploring the relationship between Alzheimer's disease and the increase in aluminum in the body that many people experience with the age [3].

Beside AAS, a number of other techniques have been reported for metals determination such as NAA, ICP-MS, ICP-AES [4–6]. In the present investigation colorimetric and spectrophotometric methods were adapted [7–10].

In adapting complexometric method among many spectrophotometric determination methods of aluminum, Chromrazurol-S, Pyrocatechol-violet, 8-hydroxyquinoline, Ferron and eriochrome cyanin-S were commonly used as complexing agents [11–15]. However, most of these methods were reported less sensitive. So aluminon is used as a complexing agent which is more sensitive and form water soluble complexes. As a new trend the determination methods for metals have been improved by the introduction of surfactants for the formation of ternary complexes [16–18]. It is also reported that the presence of surfactants has increased the sensitivity, selectivity and stability of the complex. Spectrophotometric method for the determination of economically important metal ions, anions, biologic compounds, drugs and pesticides, etc., at micro level is well known [19]. This is because of certain hypothesis implicating the important role of surfactants in micro determination of

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metals, i.e., the existing methods with less sensitivity could be improved by using surfactants. It is hypothetically believed that the addition of surfactants alone or in combination with spectrophotometric method may have relatively high sensitivity and selectivity [20,21].

2 Materials and method

2.1 Instrument

UV-visible spectrophotometer (HELIOS) and digital pH meter were used.

2.2 Reagents

All the chemicals used were of analytical (AR) grade and double distilled water was used throughout the present study.

2.3 General procedure

Stock solution of 1×10^{-2} mol/L $AlCl_3$ was prepared by dissolving 0.2414 g of $AlCl_3\cdot6H_2O$ in 100 mL distilled water. Standard solution of 5×10^{-3} mol/L aluminon was prepared by dissolving 0.2367 g of it in ethanol and was made up to 100 mL by adding distilled water. Buffer solutions of pH 1–3 were prepared by mixing 0.1 mol/L solutions of HCl and KCl; pH 4–6 Buffers were prepared by acetic acid and sodium acetate; Buffer of pH 7–10 were prepared by adding boric acid and NaOH. Surfactants sodium dodecyl sulfate(SDS), N-cetyl pyridinium chloride monohydrate (NCPC), Triton X-100, Tween 20 and Cetyl trimethyl ammonium bromide (CTABr) were prepared in water.

2.4 Choice of surfactant

The aluminum chloride solution containing 2.414 µg/mL of aluminum was transferred from five 5 mL measuring flasks to five 25 mL measuring flasks. Then 5 mL of (5×10^{-3} mol/L) aluminon was added into them and well mixed. The pH of 4.0 was adjusted by adding 5 mL of acetate buffer to the solutions and adding 1 mL 1×10^{-2} mol/L of sodium dodecyl sulfate, cetyl trimethyl ammonium bromide, N-cetyl pyridinium chloride, Triton X-100 and Tween 20, respectively, in each set and diluting each solution up to the mark with distilled water. Then the solutions were mixed well and scanned by UV-visible spectrophotometer.

2.5 Determination of Al^{+3} in water samples

Different water samples like rain water, ground water and canal water were collected from Karachi and Hyderabad. The samples were stored in metal free polyethylene bottles at 4°C. These water samples were filtered and the contents were dehydrated to nearly dryness and were redissolved in 10 mL of distilled water. Then the solution was transferred to a 25 mL volumetric flask and each sample was spiked with a known amount of aluminum 1.2 and 2.1 µg/mL, respectively. 5 mL of buffer, 0.75 mL of 1×10^{-2} mol/L aluminon and 0.75 mL of 1×10^{-2} mol/L surfactant were added, and distilled water was filled until the volume reached the mark. The absorbance of each set was measured and the concentration of aluminum was determined in water samples.

2.6 Determination of Al^{+3} in pharmaceutical samples

Two commercial pharmaceutical samples Mucaine (suspension containing oxenthazaine with aluminum hydroxide and magnesium hydroxide, Wyeth Pakistan Limited, Karachi, Pakistan) and Trisil tablet (containing aluminum hydroxide plus magnesium trisilicate; Efroze chemical industries, Karachi, Pakistan) were used for the determination of aluminum content. These samples were treated before the analysis: We took 5.0 mL portion of mucaine suspension and digested it with sulfuric acid (2% w/v). Then we increased its volume with deionized water. The solution was filtered to remove the insoluble residues and was made up to 25 mL in a measuring flask and used as a working solution for aluminum determination. The Trisil tablet was grounded in a mortal with piston, and a known weight of about 54 mg was digested with concentrated sulfuric acid. Then we made 25 mL of working solution from it. 5 mL of each working solution was transferred to a 25 mL volumetric flask and added with 5 mL of buffer solution, 0.75 mL of 1×10^{-2} mol/L aluminon and 0.75 mL of 1×10^{-2} mol/L surfactant. Then we made the volume high up to the mark and noted the absorbance for each.

2.7 Effect of foreign ions

The selectivity of proposed spectrophotometric method was investigated by detecting the absorbance of 9.657 µg/mL aluminum in the presence of various foreign ions. Sodium and potassium salts were used for anionic study, whereas sulfate and nitrate salts were used for cations determination. During the procedure foreign ions concentrations were kept 200 fold in excess as compared to the aluminum concentration.

3 Results and discussion

The aluminum forms a red colored complex with aluminon. In the presence of micelle, an attempt was made to increase the sensitivity of the method, which was significantly improved by the addition of surfactants.

3.1 Choice of surfactant

The maximum enhancement in the absorbance of complex was observed in the presence of Triton X-100, which is a nonionic surfactant compared with sodium dodecyl sulfate, which is a cationic surfactant (Fig. 1). Therefore, these two surfactants were selected as a micellar medium in the proposed procedure.

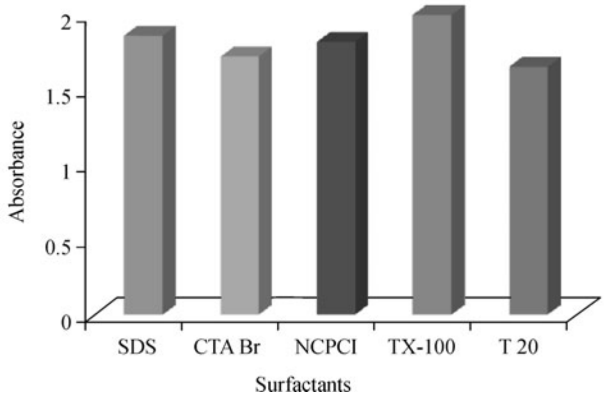

Figure 1 Effect of various surfactants on the Al^{3+}-aluminon system

3.2 Effect of pH

The effect of pH on the formation of aluminum-aluminon complex at pH ranging from 1 to 10 was measured. Triton-X 100 and sodium dodecyl sulfate surfactants were run at pH 4.0 and 5.0. The results show the maximum tendency of complex formation (Fig. 2).

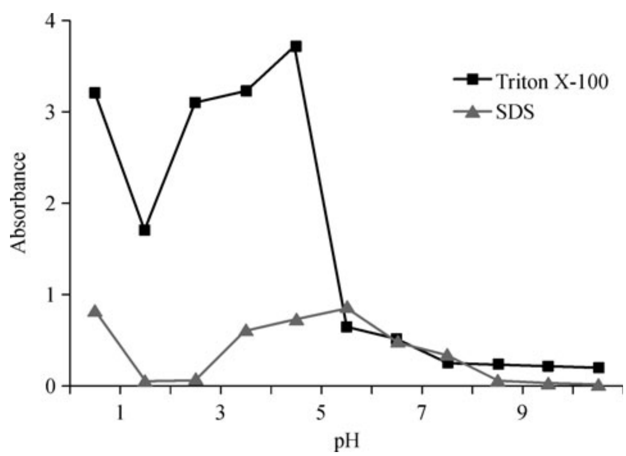

Figure 2 Effect of pH on Al-aluminon-surfactant system

3.3 Calibration curve

This reaction was spontaneous at room temperature showing the formation of ternary complex by the appearance of color. A calibration curve between aluminum ion concentration and absorbance was drawn as shown in Fig. 3, which followed the Lambert-Beer's Law up to the 21.61 µg/mL and 21.72 µg/mL concentrations in the absence and in the presence of Triton X-100 surfactant. The results are represented in Table 1. Whereas in the presence of sodium dodecyl sulfate surfactant the calibration curve was also seen follow the Lambert-Beer's Law up to 21.61 µg/mL and 24.14 µg/mL aluminum concentration as shown in Fig. 3 and Table 1.

3.4 Determination of Al^{+3} in water samples

This method was also applicable for the determination of Al^{+3} ions in water samples. Ground water, rain water and canal water were selected for analysis. The results showed that trace amount of aluminum was present in rain water and ground water while a slightly higher amount was observed in canal water as shown in Table 2.

3.5 Al^{+3} determination in pharmaceutical samples

The proposed amount of aluminum obtained by this determination method is comparable with the certified amount as represented in Table 3. The results showed accuracy and a good selectivity of the method for the determination of aluminum in analgesic samples.

3.6 Effect of foreign ions

3.6.1 Cations effects

It was found that Cd^{+2}, Cu^{+2}, Pb^{+2} and Fe^{+2} interfered slightly in the determination of aluminum, while Cu^{+2}, Zn^{+2} and Ba^{+2} had moderate effects and Cr^{+2}, Co^{+2}, Ni^{+2}, Mn^{+2}, Hg^{+3} and Bi^{+3} had extreme effects in it.

3.6.2 Anions effects

Acetate, citrate and oxalate slightly interfered in the determination of Aluminum, while EDTA and nitrate moderately interfered, and only phosphate interfered extremely as shown in Fig. 4.

4 Conclusion

The proposed spectrophotometric method was adopted for the determination of aluminum metal in the presence of Triton X-100 and sodium dodecyl sulfate surfactants. The application of surface active substances plays an important role in the

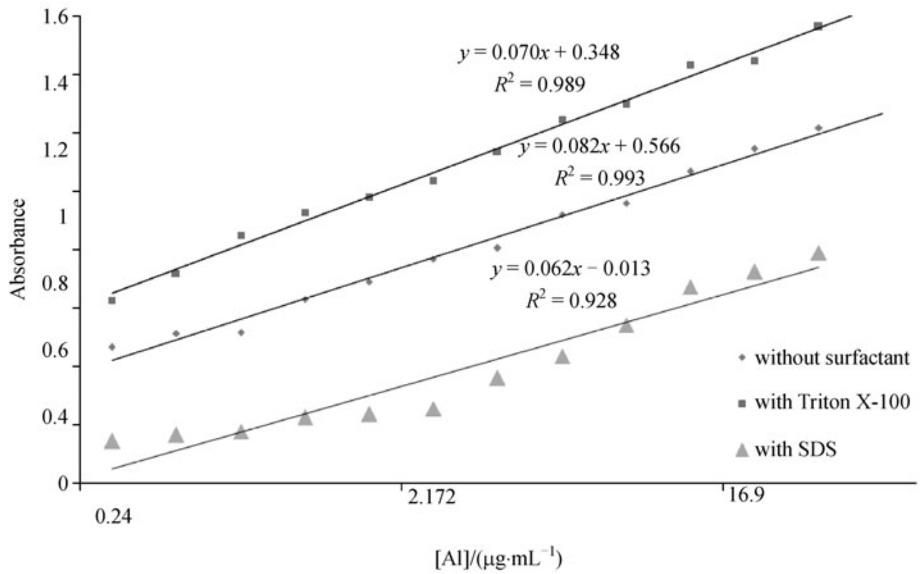

Figure 3 Calibration curves of Al(III)-aluminon and Al-aluminon-surfactant system

Table 1 Characteristics of complex of Al(III)-aluminon in the presence and absence of surfactants

Parameters	Selected values		
	Absence of surfactant	Presence of T X-100	Presence of SDS
Wavelength	525 nm	530 nm	525 nm
Reaction medium	Acetate buffer of pH 4.0–6.0 (preferably pH 4.0)		
Stability/h	10	11	12
Temprature /°C	Temprature (20°C±5°C)		
Beer's Law range /(μg·mL^{-1})	0.24–21.61	0.24–21.72	0.24–24.14
Molar absorbtivity /(L·mol^{-1}cm^{-1})	3.47×10^4	5.79×10^4	4.8×10^4
Regression Eq.	$Y = 0.082x + 0.566$	$Y = 0.070x + 0.348$	$Y = 0.062x - 0.013$
(a) Intercept	0.566	0.348	0.013
(b) Slope	0.082	0.070	0.062
Correlation coefficient	0.933	0.989	0.928
Relative standard deviation /% (Al^{+3}) = 9.65 μg/mL, n = 5	–	3.1	3.0

Table 2 Determination of Al^{+3} in different environmental water samples

Water samples	Concentration of Al^{+3} /(μg·mL^{-1})	
	Added Al^{+3}	Found Al^{+3}
Rain water Karachi	1.200	1.203
	2.100	2.103
Ground water Karachi	1.200	1.210
	2.100	2.110
Ground water Tando Allahyar	1.200	1.208
	2.100	2.107
Canal water Tando Allahyar	1.200	1.230
	2.100	2.140

Table 3 Al^{+3} in pharmaceutical formulations

Pharmaceutical formulations	Certified value /(μg·mL^{-1})	Proposed value /(μg·mL^{-1})
TRISIL(tablet)	0.323	0.319
Mucaine Suspension	0.322	0.320

Al-aluminon complex formation and creates better conditions to enhance the sensitivity of the method. The aluminum metal in water samples and pharmaceutical products was also determined. The excessive use of aluminum metal in ordinary life emphasizes the need to estimate the aluminum metal content in environmental and pharmaceutical samples. The determination of Al metals was done by complex metric method by adopting spectrophotometric technique. The introduction of surfactants Triton X-100 and sodium dodecyl sulfate enhances the sensitivity of the method. The results from the present investigation represent that Triton X-100

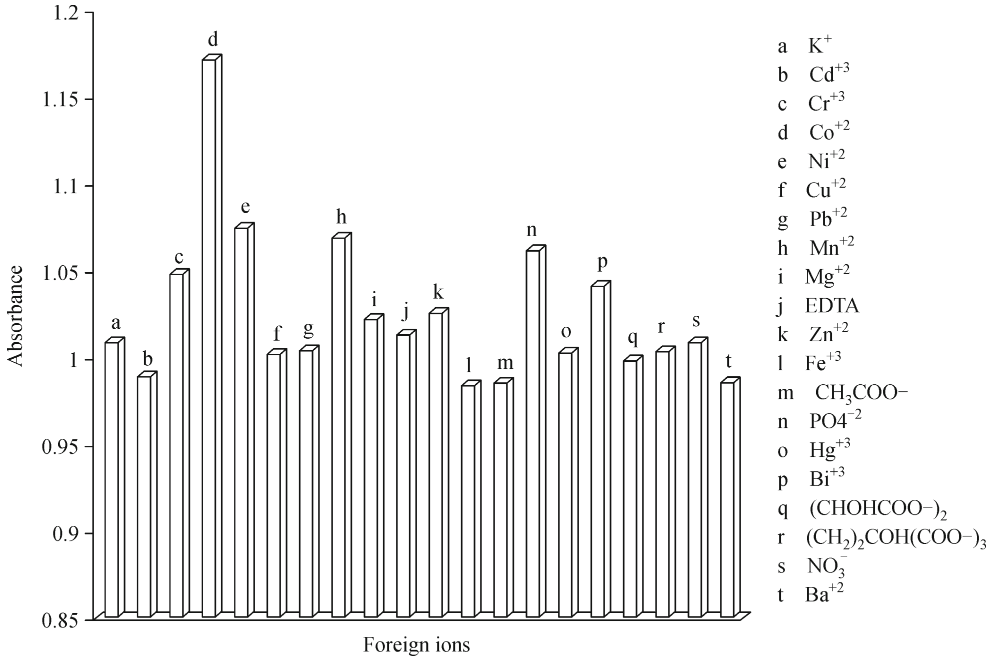

Figure 4 Effects of foreign ions in determination of aluminum

shows a better selectivity compared to sodium dodecyl sulfate surfactant. While Al concentrations in water samples show appreciable amount of Al as represented in literature. By proceeding on such methods we can improve the sensitivity of the determination of metal complexes like Al and other metals. This method can be applied on industrial scale to check the accuracy and precision of procedure.

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