JNSF 12-2-235

J. Natn. Sci. Coun. Sri Lanka 1984 **12** (2): 235—250

Studies on the Extraction of Cerium Ions into Systems Containing Saponified Coconut Oil and some of the Acylates Present in Coconut Oil

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(*Date of receipt: 18 November 1982*)
(*Date of acceptance: 17 December 1984*)

Abstract: Among the rare earths, Cerium (Ce) and several of its compounds find a wide range of industrial applications. Cerium is also that most abundant of the rare-earth elements, being found in several minerals (e.g. monazite) in high proportions. It is generally extracted from fractions obtained in the processing of these minerals. Potassium stearate has been used as one of the extracting agents for Ce (IV). In this study, the feasibility of extracting cerium both as Ce (IV) and Ce (III), by precipitation with sodium and potassium salts for stearic, lauric, palmitic, capric, oleic acids; mixture of these acids and saponified coconut oil was investigated. The main objective was to study the extractibility of Ce (III) and Ce (IV) in coconut oil saponified by sodium hydroxide (NaOH); because both coconut oil and sodium hydroxide are available in Sri Lanka, and the method if successful could be economically used on a large scale. The extractibilities of Ce (III) and Ce (IV) ions were determined on a quantitative basis, by their conversion into acylates in each of the above systems over a range of pH values. The results showed that (a) the extent of extraction of Ce (III) and Ce (IV) are reasonably high in the saponified coconut oil, (b) Ce (IV) is best extracted with sodium salts and Ce (III) with potassium salts at a pH value around 5, (c) more than 65% of Ce (III) can be extracted by sodium salts in the pH range of 3.5-6.8 under carefully controlled conditions. Therefore coconut oil saponified by sodium hydroxide can be considered as a promising extracting medium for Ce (IV) ions especially, while the oil saponified by hydroxides of both sodium and potassium is promising for the extraction of Ce (III) ions.

1. Introduction

Triacylates of lanthanum (III) and cerium (III) have been quantitatively precipitated by the reaction of their nitrates or chlorides with an excess of sodium soap in aqueous solution.[1,3] A similar study of lanthanum (III) and cerium (III) chloride using palmitic acid at different molar ratios in benzene, where mono-, di- and tri-palmitates have been isolated, have been reported.[4] Stearic acid has also been used as an extracting reagent[5], for the separation of metallic ions. This extracting reagent has been used to separate cerium from a mixture of rare-earth oxides.[6]

In view of these results and also considering the importance of cerium and its compounds in the context of their industrial application it was considered relevant to study the extractibility of cerium ions by the above-mentioned pure acid soaps and coconut oil soap, at different pH values. A preliminary study using pure fatty acids was necessary in order to understand, by means of the metal complexes formed, the extent of cerium precipitated in the coconut oil soap system, since coconut oil consists of a mixture of fatty acid glycerides and has the following approximate composition.[6]

1.1 Studies on the extraction of Cerium ions

The w/w percentages are given within brackets

1.1.1. Saturated fatty acids

caprylic	$C_7H_{15}COOH$ (9.5%)	capric	$C_9H_{19}COOH$ (7.2%)
lauric	$C_{11}H_{23}COOH$ (47.3%)	nyristic	$C_{13}H_{27}COOH$ (16.6%)
palmitic	$C_{15}H_{31}COOH$ (7.8%)	stearic	$C_{17}H_{35}COOH$ (4.2%)

1.1.2. Unsaturated fatty acids

oleic	$C_{17}H_{33}COOH$ (4.7%)	linoleic	$C_{17}H_{31}COOH$ (2.1%)

Each extracting reagent was in the form of its potassium or sodium salt and the cerium was in the form Ce (III) or Ce (IV) as sulphate.

Extraction of cerium into a coconut oil system is of special significance since this method could be utilized to extract cerium from monazite at an intermediate state in the chemical processing of monazite sand.[2]

2. Experimental

2.1 General

Aqueous solutions of potassium and sodium soaps were prepared separately and solutions of cerium ions were added separately to these solutions. The pH values of the mixtures were adjusted using a pH meter (Corning Model 5) to be in the range 1 to 10. These mixtures were kept overnight and the resulting precipitates were separated. The whole of cerium extracted by the soap was regenerated as sulphate from the precipitate by heating with dilute sulphuric acid, and separating the free fatty acid. A similar procedure was followed in the case of saponified coconut oil, it was observed that the amount of cerium extracted was highly dependent on the pH of the solution.

Several quantitative methods are available for the determination of cerium as Ce (IV). Therefore in order to determine Ce (III) by the above-mentioned procedure; it was oxidised to Ce (IV) using sodium bismuthate ($NaBiO_3$), Ce (III) ions in solution tested for various stages by adding H_2O_2 and ammonium hydrate which gave a yellowish brown cerium perhydroxy precipitate. Cerium was quantitatively determined as Ce (IV) by titrating with ferrous ammonium sulphate, according to the equation:

$$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$$

Three indicators were tried out separately in the determination of Ce (IV) and these were (1) ferroin (2) benzidine/acetic acid (3) N-phenyl anthranilic acid. The most satisfactory one was found to be ferroin which therefore was used for all the determinations.

2.2 Extraction of cerium with free acid soap solution

(i) Preparation of soap solution

Pure acid (8 g) in water (100 ml) was heated to above the melting point (i.e. below 373°K) of the acid and the base MOH (3 g) in water was added to it. The mixture was heated to 373°K; and maintained at this temperature for 2-3 hours, cooled and diluted to make up one litre.

(ii) Preparation of the acetylates of cerium

0.01 M Ce (III) (5 ml) and 0.01 M Ce (IV) (5 ml) were added separately to carboxylate solution (100 ml) of sodium or potassium (0.028 M - 0.040 M). This was the amount of carboxylate solution required for the complete removal of the yellow colour of Ce (IV) ions in the solution. Further 10 ml of the carboxylate solution was then added to ensure an excess. Except in the case of lauric, capric and oleic acid systems in others a white precipitate was obtained. The pH of each solution was adjusted to have specified values in the range 1 to 10 using dilute H_2SO_4. The mixture was shaken thoroughly and left overnight. The precipitate was filtered and washed several times with water and dried. The cerium ions remaining in the aqueous filtrate were determined using ferroin as indicator.

(iii) Extraction of Ce (III) and Ce (IV) from the complex

The precipitate obtained in (ii) was decomposed by heating with dilute H_2SO_4 (50 ml) to just above the melting point of the free acid. When allowed to cool, most fatty acids separated as solids. In cases where the fatty acid was a liquid at room temperature, ice-salt mixtures were used to freeze the fatty acid leaving the Ce (III) and Ce (IV) ions in the dilute H_2SO_4 solution. The solid fatty acids were separated by filtration, and were washed with two 10 ml portions of hot dilute H_2SO_4. All these filtrates were combined and these contained Ce (III) or Ce (IV) ions.

(iv) The determinaton of the Ce (III) and Ce (IV) in the filtrate from (iii) above

The filtrate was directly titrated with 0.0025 M ferrous ammonium sulphate. In the case of cerium in Ce (III) filtrates were estimated after oxidising with sodium bismuthates in dilute H_2SO_4 in the presence of a small quantity of ammonium sulphate. The resulting solution was filtered and the Ce (IV) ions present were determined using ferroin as the indicator.

This procedure was repeated by varying the pH values in the range 1 to 10 for the following component groups:

The equation for the reaction is

$$RCOOH + MOH = RCOOM + H_2O \ (M = Na \text{ or } K)$$

2.3 Extraction of cerium with coconut oil soap solutions

(i) Saponification of coconut oil

MOH (M = Na or K) (15 g) in water (100 ml) was added slowly with continuous stirring (magnetic stirrer was used) to coconut oil (100 ml = 92 g approximately) heated to 373°K. This mixture was heated for a further 3 hours in the case of M = Na, and one hour in the case of M = K, and allowed to cool. Salt water (500 ml) was added to precipitate the soap from glycerol. The solid soap obtained was dissolved in water and made up to one litre.

(ii) Preparation of the cerium complex with the soap solution

0.01 M cerium (III) and cerium (IV) sulphate solutions (5 ml) were added separately into the soap solution (125 ml) prepared as in 2.3 (i). The solutions were cooled in a freezing mixture to a temperature below 278°K, and the pH adjusted as required to lie between 1 and 10. The mixture was left overnight and cooled rapidly in a freezing mixture, then the precipitates were filtered and washed in pre-chilled water. The filtrates were tested for Ce (IV) ions using ferroin indicator. These were found to contain only very small amounts of cerium. Cerium contained in the precipitate was extracted into dilute H_2SO_4 (50 ml). The free oil was re-extracted twice with 10 ml portions of hot dilute H_2SO_4, (10 ml). In each case the oil was removed by solidifying it in a freezing mixture. The amount of cerium present in the total extract was determined by the method as described in 2.1.

3. Results and Discussion

3.1 Stearic acid system — Figures 1 (i) and 1 (ii)

From the results obtained it can be seen that both potassium and sodium soaps have comparable extractibilities with maximum values of 84% at pH 4.5 and 91% at pH 4.0 respectively for Ce (III).

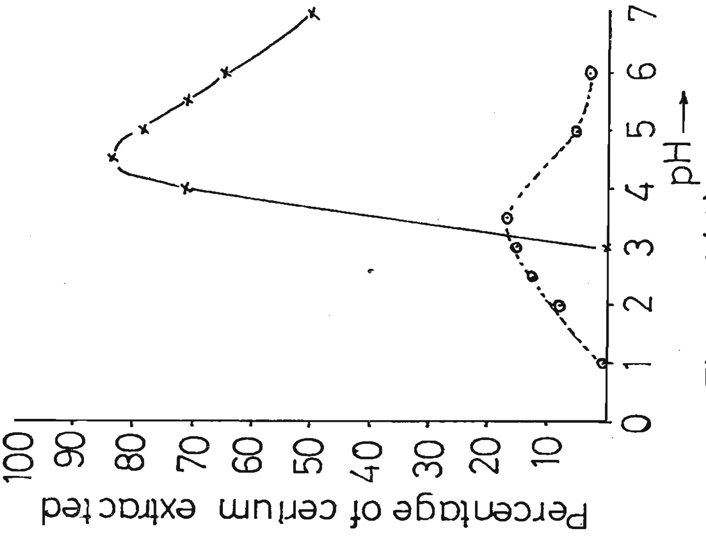

Figure 1 (1)

Cerium extracted into potassium salt of stearic acid $CH_3(CH_2)_{16}COOH$

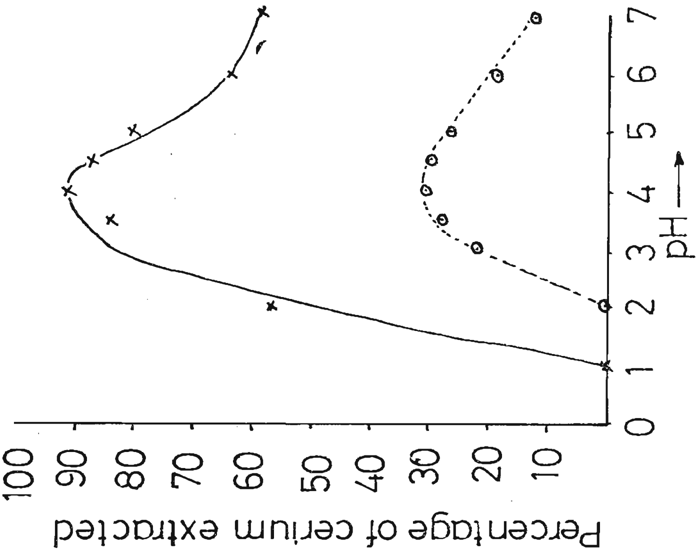

Figure 1 (2)

Cerium extracted into sodium salt of stearic acid

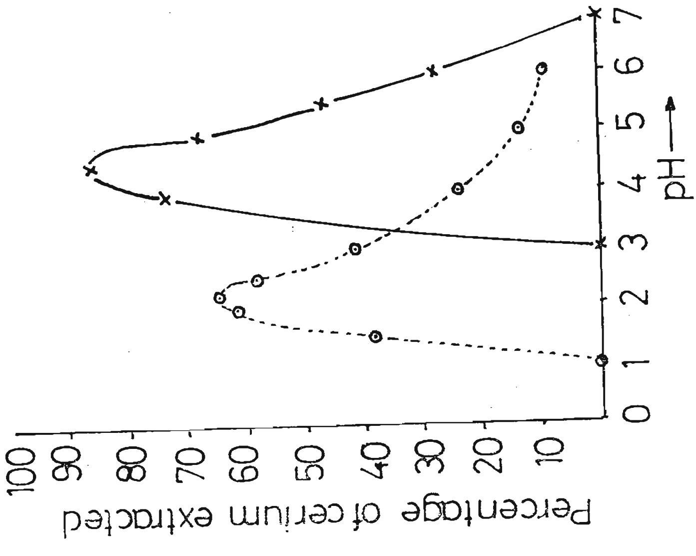

Figure 2(1)

Cerium extracted into potassium salt of Lauric acid $CH_3(CH_2)_{10}COOH$

—— Ce(111)

- - - - Ce(1V)

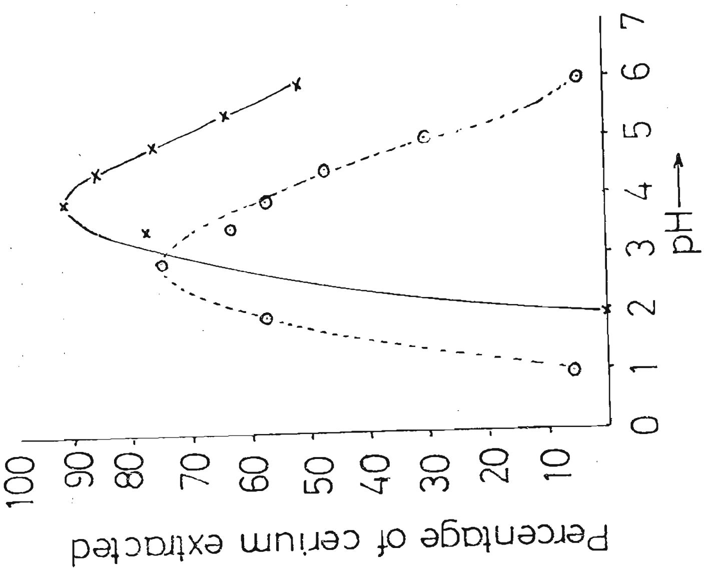

Figure 2(2)

Cerium extracted into sodium salt of Lauric acid

—— Ce (111)

-·-·-Ce(1V)

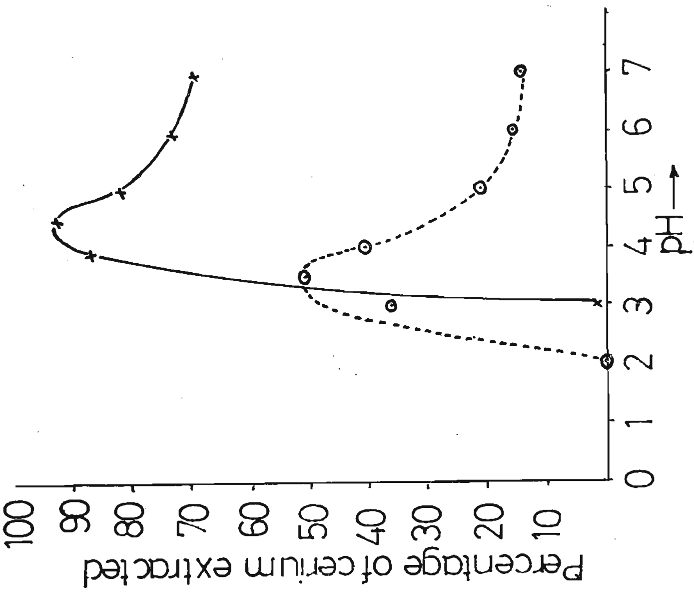

Figure 3(1)

Cerium extracted into potassium salt of Palmitic acid $CH_3(CH_2)_{14}COOH$

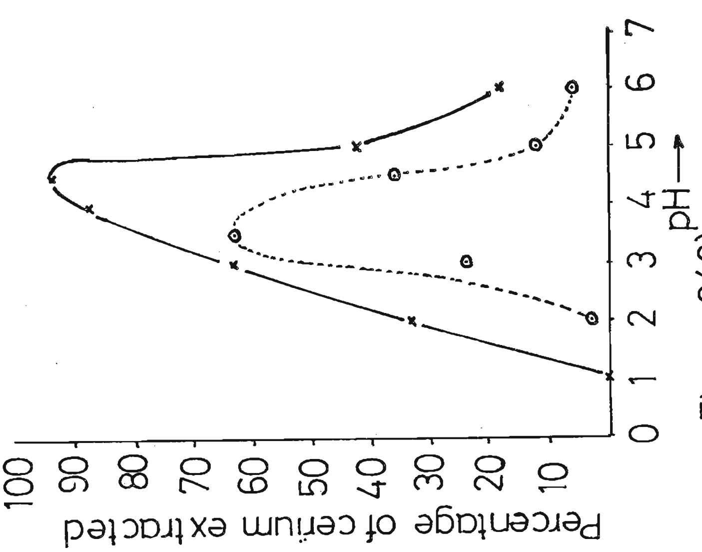

Figure 3(2)

Cerium extracted into sodium salt of Palmitic acid

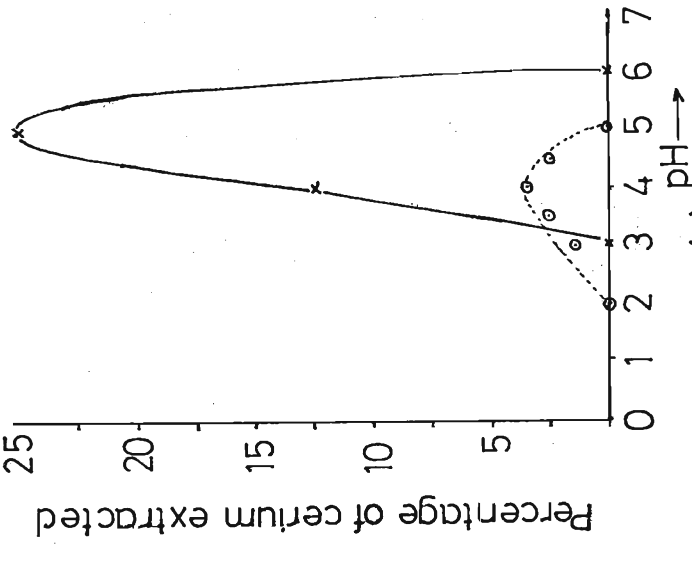

Figure 4(1)

Cerium extracted into potasium salt or capric acid $CH_3(CH_2)_8COOH$

— Ce(111)

---- Ce(IV)

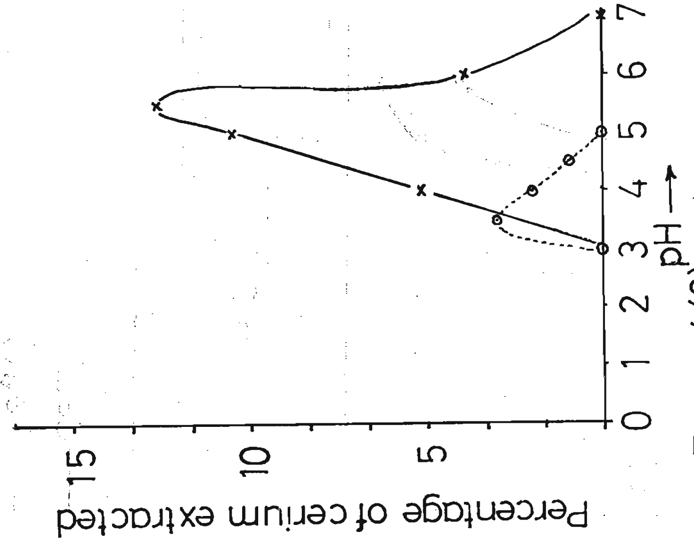

Figure 4(2)

Cerium extracted into sodium salt of capric acid

— Ce (111)

---- Ce (IV)

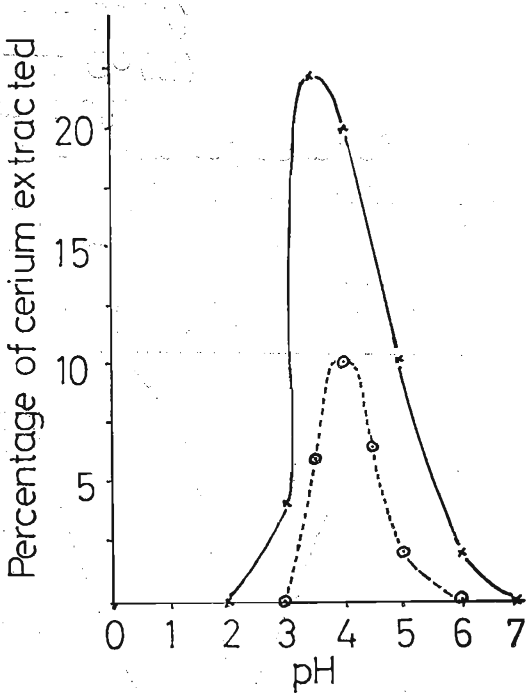

Figure 5(1)

Cerium extracted into potassium salt of Oleic acid $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$

——Ce (III)

----Ce (IV)

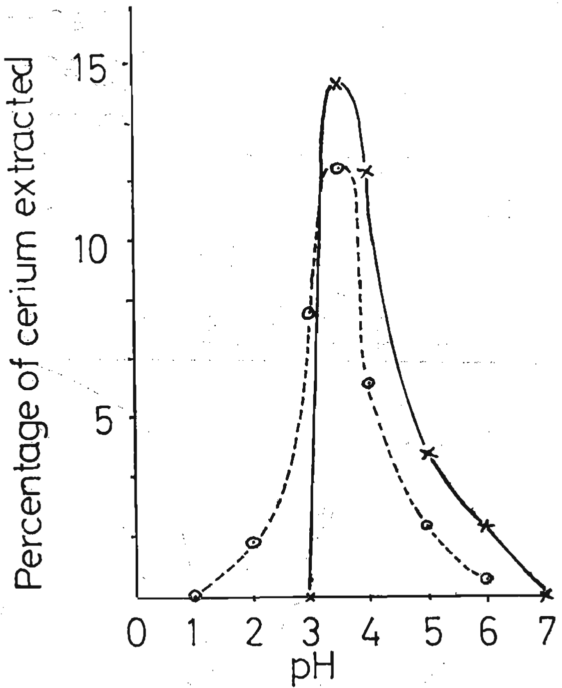

Figure 5(2)

Cerium extracted into sodium salt of Oleic acid

——Ce (IV)

----Ce (IV)

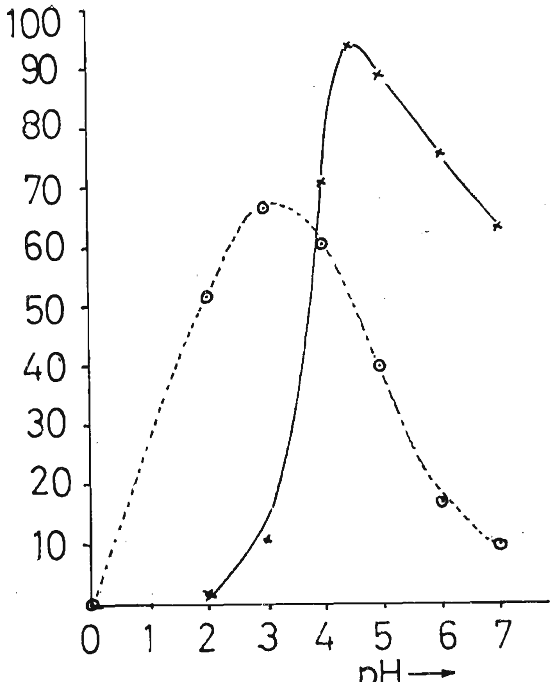

Figure 6(1)

Cerium extacted into potassium salt of acid mixture representing coconut oil.

—— Ce (III)

----- Ce (IV)

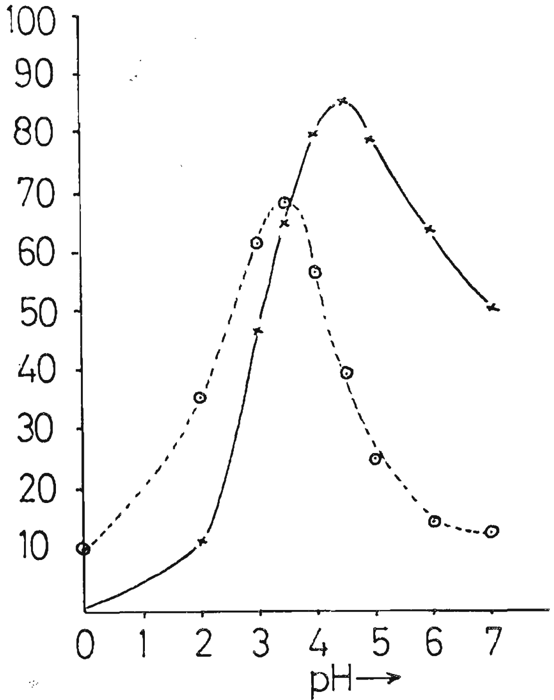

Figure 6(2)

Cerium extracted into sodium salt of acid mixture representing coconut oil.

—— Ce (III)

----- Ce (IV)

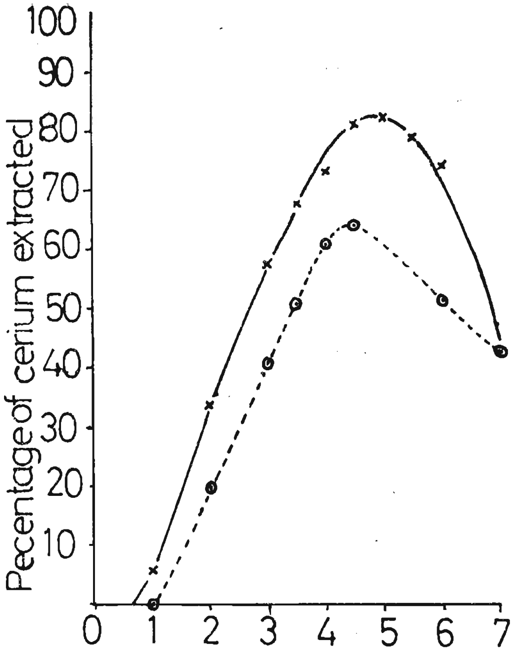

Figure 7(1)

Cerium extracted into potasium salt of coconut oil.

—— Ce (111)

-- --- Ce (1V)

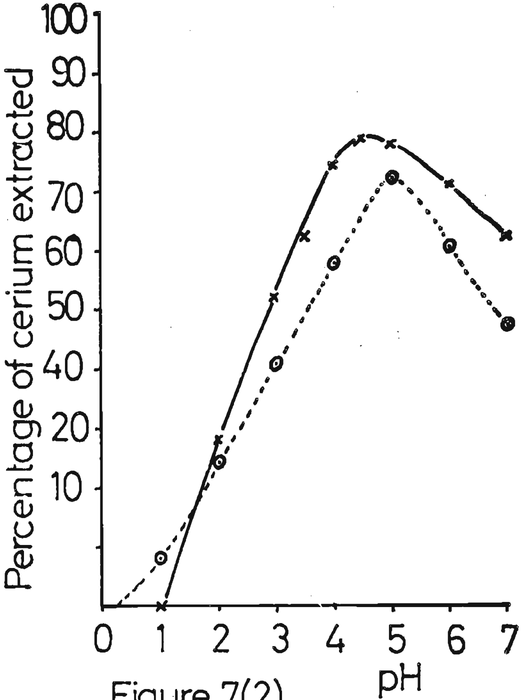

Figure 7(2)

Cerium extacted into sodium salt of coconut oil.

—— Ce (111)

------ Ce (1V)

The extractibility of Ce (IV) is much less, the maximum values in this case being 17% at pH 3.6 and 30% at pH 40 by potassium and sodium soaps respectively.

The extractibility of Ce (III) into potassium soap begins at pH 3.0 increases sharply to a maximum and then decreases gradually while the extractibility into sodium soap begins at pH 1.0 increases to a maximum and decreases thereafter throughout the range, the variation being more uniform. Extractibility of 60% is obtained for both potassium stearate and sodium stearate in the pH ranges 4.0-6.3 and 2.1-6.5 respectively.

The extractibility curve for Ce (IV) with potassium soap increases gradually from pH 1.0 to the maximum and then decreases uniformly while the extractibility into sodium soap begins at pH 2.0 increases to the maximum faster than in the case of potassium salt and then decreases slowly thereafter. Extractibility of 10% is observed in the pH range 2.3-4.4 with the potassium stearate and 20% in the pH range of 2.2-6.0 with the sodium stearate.

3.2 Lauric acid system — Figures 2 (i) and 2 (ii)

Potassium and sodium soaps have comparable extractibility with maximum extraction of 86% at pH 4.5 and 91% at pH 4.0 respectively for the Ce (III).

The extractibilities for Ce (IV) are relatively lower; the maximum values being 65% at pH 2.2 and 74% at pH 3.0 for the potassium laurate and sodium laurate respectively.

The extractibility of Ce (III) into the potassium salt begins at pH 3.0, increases rapidly to a maximum and decreases less rapidly to about 28% at pH 6.0 while the extractibility into the sodium laurate begins at pH 2.0, increases to about 50% at pH 6.0. The two curves for Ce (III) exhibit similar behavioural patterns.

The extractibility of Ce (IV) into the potassium laurate begins at pH 1.0, increases to the maximum and decreases less rapidly reaching about 9% at pH 6.0, while the extractibility into the sodium salt begins around 6% at pH 1.0, increases to a maximum and decreases less rapidly as compared to the potassium salt reaching 6% at pH 6.0. The two extractibility curves for Ce (IV) of the two salts show appreciable dissimilarities notably in the decreasing range. It is clearly evident that the extractibilities of Ce (III) ions are better than those of Ce (IV) ions by both potassium and sodium salts.

3.3 Palmitic acid system — Figures 3 (i) and 3 (ii)

Potassium palmitic extracts Ce (III) ions giving a maximum value of 92% (at pH 4.5) while the sodium palmitate gives only a maximum of 30% (at pH 4.0). The maximum extractibilities of Ce (IV) were much lower by both salts, being 51% (at pH 3.5) for potassium salt and 24% (at pH 4.0) for the sodium salt.

The extractibility curves for Ce (III) ions for the two salts show some similarities although their ranges of values differ. The potassium palmitate begins to extract Ce (III) ions at pH 3.0, increases rapidly to the maximum and decreases very slowly reaching about 73% at pH 6.0, and the sodium palmitate begins the extraction at pH 1.0, rises slowly to the maximum and decreases rapidly thereafter to a value of 6% at pH 6.0.

The extractibility curves of Ce (IV) ions for the two salts have much less in common unlike in the case of Ce (III) except that both show a maximum. The potassium palmitate begins to extract Ce (IV) ions at pH 2.0, the extraction reaches the maximum at pH 3.5 and decreases thereafter less rapidly to reach 16% at pH 6.0, while the sodium palmitate also begins to extract Ce (IV) at pH 2.0. The latter reaches the maximum at a higher pH of 4.0 and then decreases nearly at the same rate as in the case of the potassium salt to about 2% extraction at pH 6.0.

For both Ce (III) and Ce (IV) ions the potassium soap has a better extractibility than the sodium soap. When Ce (IV) acylate is decomposed Ce (III) ions are regenerated and not Ce (IV) ions. These in turn have to be oxidized to Ce (IV) in order to be estimated. The change in the oxidation state of cerium ions provides a valuable insight as to why Ce (III) ions are extracted better than Ce (IV) ions into two salts. The conversion of Ce (IV) into Ce (III) probably occurs during the formation of the acylate.

3.4 Capric acid system — Figures 4 (i) and 4 (ii)

The extractibility of Ce (III) ions by the capriates is lower than for the acylates given in 3.1 to 3.3. The maximum values for potassium salts is 26% at pH 5.0 and for sodium salt is 12% at pH 5.5.

The extractibilities of Ce (IV) ions have maxima of 4% at pH 4.0 for the potassium salt and 3% at pH 3.5 for the sodium salt. The curves for Ce (III) show similarities in that the values are ascending more rapidly than descending with respect to the change of pH values. The extractibility for potassium capriate lies entirely in the pH range 3.0-6.0 and that for sodium capriate lies entirely in the pH range 3.0-7.0 with the zero value at the extremities in both cases.

In the case of Ce (IV) the sodium and potassium salts give extractibility curves which have almost opposite forms with respect to each other. The curve for potassium salt lies in the range pH 2.0-5.0 and shows a rapid descent while that for sodium salt lies in the range pH 3.0-5.0 and shows a rapid ascent and a slow descent.

3.5 Oleic acid system — Figures 5 (i) and 5 (ii)

Since this was the only unsaturated acylate found in coconut oil in appreciable amounts this was the only system studied. The extractibilities are generally low for Ce (III); the maximum value is 24% at pH 3.5 for potassium oleate and 15% at pH 3.5 for sodium oleate. Ce (IV) has a maximum value of 10% at pH 2.0 for the potassium salt and 12% at pH 3.5 for the sodium salt.

The forms of the extractibility curves of Ce (III) for the two acylates are similar showing a steep ascent up to the maximum and then a gentle descent. The curve for potassium oleate lies in the pH range 2.0-7.0 while that for the sodium salt lies in the pH range 3.0-7.0. The curve of Ce (IV) for the potassium salt lies in the pH range 3.0-6.0 and that for sodium salt lies in the pH range 1.0-6.0. Both curves have similar shapes with comparable ascending and descending parts. The low melting point of oleic acid causes difficulties in handling this system.

3.6 Mixture of acids representing coconut oil — Figures 6 (i) and 6 (ii)

A synthetic mixture of the acids containing capric, lauric, palmitic, stearic and oleic acids approximately in the ratio as found in coconut oil (3.1: 20.8: 3.9: 1.0: 2.8 by weight) was used. Myristic acid could not be used because of its non-availability.

Potassium acylate showed a greater extractibility of both Ce (III) and Ce (IV) than the sodium acylate. For Ce (III) the maximum value with the potassium soap is 94% at pH 4.5 and that with sodium soap is 87% at pH 4.5. The corresponding maxima for Ce (IV) are 72% at pH 3.5 and 69% at pH 3.5 respectively.

The curves for Ce (III) acylates are similar with a much steeper ascent than descent, whereas in the case of Ce (IV) the ascent and the descent are comparable for the mixture of acylates.

It is seen that for a given oxidation state of cerium and for a known mixture of acylates, the variation of the extractibility with pH is almost independent of the nature of the alkali ion.

The extractibilities in these two acylate mixtures are high and are similar to those in the pure lauric, stearic and to a small extent palmitic acid systems, although the percentages of the components differ widely. The effect of the other two low extractibility components is very small.

3.7 Saponified coconut oil — Figures 7 (i) and 7 (ii)

Saponified coconut oil shows high extractibilities for both Ce (III) and Ce (IV). The maximum value for Ce (III) by potassium soap is 83% at pH 5.0 and by sodium soap is 80% at pH 4.5. The corresponding extractibilities for Ce(IV) are 64% at pH 4.5 and 72% at pH 5.0 respectively.

The curve shows that more than 50% of Ce (III) can be extracted by potassium soap in the pH range 2.6-6.8 and more than 65% by sodium soap in the pH range 3.5-6.8. Similarly over 50% extraction of Ce (IV) can be affected by the potassium and sodium soaps in the pH ranges of 3.5-6.2 and 3.5-6.8 respectively.

4. Conclusion

The results show that (a) the extents of extraction of Ce (III) and Ce (IV) are reasonably high in the saponified coconut oil, (b) Ce (IV) is best extracted with sodium salts and Ce (III) with potassium salts at a pH value around 5, (c) more than 65% of Ce (III) can be extracted by sodium salts in the pH range of 3.5-6.8 under carefully controlled conditions. Therefore coconut oil saponified by sodium hydroxide can be considered as a promising extracting medium for Ce (IV) ions especially, while the oil saponified by hydroxides of both sodium and potassium is promising for the extraction of Ce (III) ions. Since the sodium soaps are cheaper than the potassium soaps; especially in Sri Lanka, the use of the former is economically feasible.

There were some experimental difficulties encountered in using coconut oil as compared to the use of pure fatty acid soaps as indicated below:

(i) Due to low efficiency of re-saponificated, coconut oil is difficult to recycle where as pure fatty acid soaps can be recycled with very little loss (5%). This is probably due to the strong nature of the combination of cerium-ions with saponified coconut oil.

(ii) pH measurements are somewhat difficult due to the fatty acid being deposited on the electrodes.

(iii) The acylate is very difficult to filter even at the best extracting pH.

We strongly feel with a further amount of extensive and effective research, these experimental difficulties could be greatly minimized.

The dissimilarity observed in the Figures 6 and 7 may be partly due to the acylates of myristic, caprylic and linoleic acids were not studied due to their non-availability at the time of study.

Even with the above-mentioned experimental difficulties, it could be stated that a reasonably high extractibility of cerium (III) and cerium (IV) can be achieved in coconut oil saponified with sodium hydroxide under carefully controlled conditions. After the above difficulties are overcome with further research, the process has to be carried out on a pilot scale and the details of its economics have to be worked out.

The authors gratefully acknowledge the financial assistance provided by the Natural Resources, Energy and Science Authority of Sri Lanka for the above research work.

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