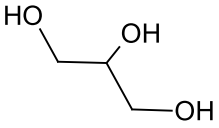
A Study of the Saponification Reaction of Olive Oil

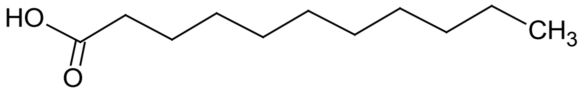
Section A. Introduction

Here in Greece a traditional village craft that has been handed down for generations is the making of soap from olive oil. This process is based on heating olive oil with ashes from wood fires which contain potassium hydroxide. This basic reaction of potassium hydroxide or sodium hydroxide with olive oil is also the basis of laboratory preparations of olive oil soap.

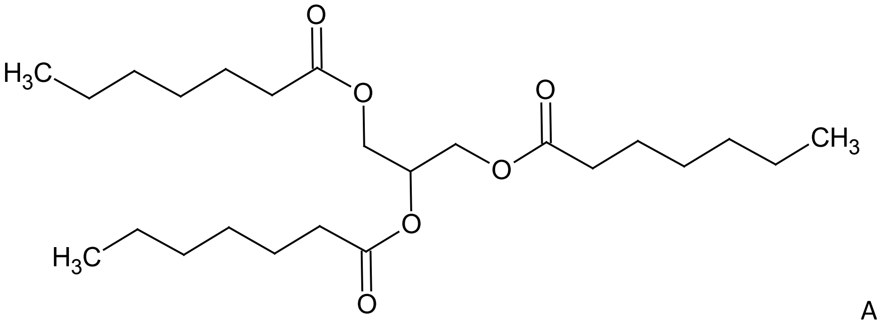
Olive oil is a naturally occurring vegetable oil and it is mainly composed of triglycerides. Also it contains small amounts of free fatty acids, glycerol and other compounds. The general structures of the main components are



Glycerol



Free Fatty Acid



A triglyceride

The chemical composition of a triglyceride like that in olive oil is described in terms of the three fatty acid chains that make up the triglyceride. A fatty acid has the general formula: CH3(CH2)nCOOH. These three fatty chains may not be all the same. There may be small variations in the number of carbon atoms in the main chain and also they may contain C = C double bonds (called unsaturation). In olive oil the main constituent fatty acids in the triglycerides are as follows[1]

Fatty Acid	Molecular Formula	Molar Mass ($gmol^{-1}$)	% Composition in Olive Oil Triglycerides
Oleic Acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	282.5	55 - 83%
Linoleic Acid	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	280.4	3.5 - 21
Palmitic Acid	$CH_3(CH_2)_{14}COOH$	256.4	7.5 - 20%
Stearic Acid	$CH_3(CH_2)_{16}COOH$	284.5	0.5 - 5%
Linolenic Acid	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	278.4	0 - 1.5%

---

[1] Olive Oil Source, http://www.oliveoilsource.com/page/chemical-characteristics. Last accessed 20-9-2012

The most common triglyceride in olive oil is glycerol trioleate with three oleic acid chains and general formula

$$[CH_3(CH_2)_7CH{=}CH(CH_2)_7COO]_3C_3H_5$$

In calculations of % yield later on in this report I will assume that all fatty acid chains were oleic acid. Since the molar masses (except for palmitic acid) are similar this is a fair assumption to make and will make little difference to the calculated yields.

Turning a triglyceride into a soap is called a **saponification** reaction. The reaction can take place with either potassium hydroxide or sodium hydroxide hydrolysing the trioleate to form potassium oleate (or sodium oleate) and glycerol.

The saponification reaction of the major component triglyceride, oleic acid, in olive oil is as follows

$$[CH_3(CH_2)_7CH{=}CH(CH_2)_7COO]_3C_3H_5 + 3\mathbf{M}OH \rightarrow 3CH_3(CH_2)_7CH{=}CH(CH_2)_7COO^- \mathbf{M}^+ + CH_{2(}OH)CH(OH)CH_2OH$$

Oleic acid	*hydroxide*	*oleate salt*	*glycerol*

M is K or Na

The potassium and sodium oleates (or other potassium or sodium salt of a fatty acid) are the compounds that act as soaps.

The purpose of this study was to synthesise both potassium oleate and sodium oleate based soaps and then to compare their characteristics and properties to see how much the changing from the potassium salt to the sodium salt affects these properties.

Section B. Methodology

There are many descriptions of basic laboratory methods for producing soap from olive oil [2,3,4]. They are all based on heating olive oil in the presence of a concentrated solution of Potassium Hydroxide or Sodium Hydroxide. Because olive oil does not mix with water the solvent used for the reaction is mainly hot ethanol which is a good solvent for olive oil and potassium hydroxide. It is not such a good solvent for sodium hydroxide so some water is added to help the sodium hydroxide dissolve.

From my reading the three common routes are

(i) Heating olive oil with potassium hydroxide in ethanol followed by evaporating off the ethanol to directly form potassium oleate soap.

(ii) Heating olive oil with sodium hydroxide in ethanol and water followed by evaporating off the ethanol and water to directly form sodium oleate soap.

---

[2] Preparation and Properties of Soap, http://www.seattlecentral.edu/faculty/ptran/bastyr/Summer%2006/organic/Organic%20Exp/Experiment4Preparation%20and%20properties%20of%20a%20soap1.pdf, last accessed 20-9-2012

[3] Making Soaps and Detergents, http://www.nuffieldfoundation.org/practical-chemistry/making-soaps-and-detergents, last accessed 20-9-2012

[4] Organic Chemistry Laboratory Procedures, Richard Wheet, Department Of Chemical Technology, Texas State Technical College, 2011, pp 41-43,

http://www.Chemtech.Org/Cn/Cn2123/Organic_Lab_Book.Pdf

(iii) Heating olive oil with potassium hydroxide in ethanol followed by precipitation into saturated aqueous sodium chloride solution to form sodium oleate soap which can be filtered off.

In my study I compared the potassium and sodium soaps prepared by methods (i) and (iii)

Materials

- Extra Virgin Olive Oil (Spa Brand)
- Potassium Hydroxide Pellets
- Sodium Chloride Powder
- Ethanol (95%)
- Liebig Condenser
- Magnetic stirrer hotplate and clamp
- Top pan balance (± 0.01g)
- 500 cm^3 conical flask
- 200 cm^3 volumetric flask
- 100 cm^3 measuring cylinder
- 200 cm^3 measuring cylinder
- 2 beakers (500cm^3)
- 5 beakers (200cm^3)
- 1 graduated pipette (25cm^3)
- 6 conical flasks (250cm^3)
- 5 glass funnels
- 6 petri dishes
- Thermometer
- Glass stirring rod
- Spatula
- Filter papers
- Stopwatch
- Temperature probe
- Brass block with hole for temperature probe

Procedure

Part I: Synthesis of Soaps

1. Using a measuring cylinder 100 cm^3 of olive oil was poured into a 500 cm^3 conical flask and weighed on the top pan balance which had been tared.
2. About 50 grams of potassium hydroxide pellets (a large excess) were weighed on the top pan balance and then added to a 250 cm^3 conical flask. About 150 cm^3 of ethanol was added and the contents gently heated and stirred on the magnetic stirrer hotplate until all the pellets had dissolve.
3. Five petri dishes were pre-weighed and labelled for use later. Also five 200cm^3beakers were prepared with 100 cm^3 of saturated sodium chloride solution. This was done by adding 100 cm^3 of distilled water and adding sodium chloride one spatula at a time with stirring until no more dissolved.
4. The potassium hydroxide solution was added to a 200 cm^3 volumetric flask and made up carefully to the mark with more ethanol.

5. The conical flask containing the olive oil was placed on the magnetic stirrer hotplate and the stirring flea was added. A Liebig condenser was set up on top of the flask so that reflux could occur.
6. The olive oil was heated and stirred for a few minutes on the hot plate.
7. The reflux condenser was briefly removed and the 200cm^3 of potassium hydroxide solution quickly added. The condenser was placed back in position and the stopwatch started.
8. After 10 minutes the condenser was briefly removed and a graduated pipette used to remove two lots of 15 cm^3 of reaction mixture. One pipette batch was placed on a pre-weighed petri dish and the other was added to a beaker of saturated sodium chloride and stirred quickly with a spatula.
9. The reaction was continued and the process of taking two batches of reaction mixture repeated every ten minutes until the reaction had completed fifty minutes. Then the stirrer hotplate was turned off and the reaction stopped.
10. The five petri dishes with the reaction mixture (which should be the potassium oleate product) dissolved in ethanol were placed in a fume cupboard and allowed to dry for two days.
11. The white solid (which should be sodium oleate) floating on top of the sodium chloride solution in the five beakers was filtered off using pre-weighed filter papers. The beakers were rinsed with distilled water and filtered as well. The filter papers were allowed to dry for two days.
12. After two days the petri dishes and filter papers were weighed again and the results recorded. To check that drying was complete the weighing was repeated again after one more day immediately before the foaming tests were carried out.

Part II: Characterisation of the Soaps

1. The observations of colour and texture of the soaps was recorded.
2. The yield of the soap samples was measured and recorded
3. The foaming action of the soaps was determined by weighing out 0.5g of soap into a 200 cm^3 measuring cylinder. 50 cm^3 of distilled water was added and the soap dissolved by gently stirring with a glass rod. How easily the soap dissolved in the water was recorded.
4. The measuring cylinder was inverted rapidly five times to cause foaming. The initial volume of foam was recorded.
5. For some samples the stability of the foam was measured by taking measurements of foam height against time
6. The melting temperature of the soaps was attempted to be recorded by placing small flakes of each of the types of soap at the same time on a brass block with thermometer hole (it is used for physics experiments usually) with a temperature probe inserted. The brass block was heated up on a hotplate and the melting behaviour observed.

Section D: Raw Data

Part I: Saponification Reaction

Mass Olive Oil used: 91.94 g (± 0.01g) [Volume Olive Oil: 100 cm^3]
Mass of Potassium Hydroxide: 50.64 g (± 0.01g)
Volume of Potassium Hydroxide/Ethanol solution: 200 cm^3 (± 0.1cm^3)
Temperature of Reflux: 85 °C

Qualitative observations;

The light transparent brown of the olive oil rapidly became a darker brown as it was heated with the ethanol solution of potassium hydroxide.

When the potassium hydroxide was added and the reaction flask was still heating up to reflux a waxy light brown solid was immediately deposited on the colder glass surfaces of the flask and condenser. It dissolved once the hot ethanol started to reach these surfaces.

Extracting the 15 cm^3 batches of reaction mixture was approximate because the solidifying waxy solid inside the graduated pipette obscured the visibility of the liquid level and the reading of the scale.

When the 15 cm^3 batches of reaction mixture were poured onto the cold petri dishes it immediately cooled to a waxy medium brown solid

When the 15 cm^3 batches of reaction mixture were poured into the beakers of sodium chloride solution and stirred a pale cream powdery solid precipitated and floated to the surface of the sodium chloride solution.

Mass Yields of the soaps

Table 1: The mass produced of Potassium Soap left to dry on petri dishes.

	Reaction Time (± 0.1mins)	Mass empty petri dish (± 0.01g)	Mass Petri dish + Potassium Soap After 2 Days (± 0.01g)	Mass Petri dish + Potassium Soap After 3 Days (± 0.01g)	Mass Yield of Potassium Soap (± 0.02g)*
Batch 1	10.0	34.37	41.57	41.53	6.16
Batch 2	20.0	35.80	42.20	42.20	6.40
Batch 3	30.0	35.49	42.09	42.07	6.58
Batch 4	40.0	36.47	41.81	41.79	5.32
Batch 5	50.0	37.90	43.94	43.92	6.02

Table 2: The mass produced of Sodium Soap left to dry on Filter Paper.

	Reaction Time (± 0.1mins)	Mass empty Filter Paper (± 0.01g)	Mass Filter Paper + Sodium Soap After 2 Days (± 0.01g)	Mass Filter Paper + Sodium Soap After 3 Days (± 0.01g)	Mass Yield of Sodium Soap (± 0.02g)
Batch 1	10.0	1.54	6.70	6.63	5.09
Batch 2	20.0	1.51	6.15	6.14	4.63
Batch 3	30.0	1.49	6.43	6.39	4.90
Batch 4	40.0	1.48	6.68	6.64	5.16
Batch 5	50.0	1.51	6.91	6.81	5.30

Part II: Characterising the Soap Products

Determination of Melting Temperature

The melting temperature of the soaps could not be determined because the sample of both potassium and sodium soaps remained solid up until the temperature probe maximum of 210°C. The potassium soap at this temperature appeared unchanged whereas the sodium soap started to turn dark brown at 190 °C.

Study of Foaming Action

(i) Potassium Soap Samples

Trial 1:
Soap Sample: Potassium Soap Batch 1 (see Table 1)
Mass of Soap used: 0.51g

Trial 2:
Soap Sample: Potassium Soap Batch 5 (see Table 1)
Mass of Soap used: 0.53g

Table 3: Foaming Action Data for Potassium Salt Soaps

Trial 1: Potassium Soap Batch 1					Potassium Soap Batch 5			
Time (± 0.1min)	Volume Reading of top of foam (± 5cm^3)	Volume Reading of Base of foam (± 1cm^3)	Volume of Foam (± 1cm^3)		Time (± 0.1min)	Volume Reading of top of foam (± 5cm^3)	Volume Reading of Base of foam (± 1cm^3)	Volume of Foam (± 1cm^3)
0	150	46	104		0	170	47	123
3	140	46	94		3	155	47	108
6	130	46	84		6	145	47	98
9	130	47	83		9	135	47	88
12	120	47	73		12	125	47	78
15	115	47	68		15	120	48	72
18	110	47	63		18	115	48	67
21	105	47	58		21	115	48	67
24	100	48	52		24	110	48	62
27	100	48	52		27	110	48	62
30	95	48	47		30	105	48	57
33	95	48	47		33	100	48	52
36	90	48	42		36	100	49	51
39	90	48	42		39	100	49	51
42	90	48	42		42	95	49	46
45	85	48	37		45	95	49	46

(ii) Sodium Soap Samples

Trial 1:
Soap Sample: Sodium Soap Batch 1 (see Table 2)
Mass of Soap used: 0.52g

Trial 2:
Soap Sample: Sodium Soap Batch 5 (see Table 2)
Mass of Soap used: 0.51g

Table 4: Foaming Action Data for Sodium Salt Soaps

Trial 1: Sodium Soap Batch 1					Sodium Soap Batch 5			
Time (± 0.1min)	Volume Reading of top of foam (± 5cm^3)	Volume Reading of Base of foam (± 1cm^3)	Volume of Foam (± 1cm^3)		Time (± 0.1min)	Volume Reading of top of foam (± 5cm^3)	Volume Reading of Base of foam (± 1cm^3)	Volume of Foam (± 1cm^3)
0	100	47	53		0	85	48	37
3	95	47	48		3	85	48	37
6	95	47	48		6	80	48	32
9	95	47	48		9	80	48	32
12	90	47	43		12	80	48	32
15	90	47	43		15	75	48	27
18	90	47	43		18	75	48	27
21	85	48	37		21	75	48	27
24	85	48	37		24	75	48	27
27	80	48	32		27	70	48	22
30	80	48	32		30	70	49	21
33	75	48	27		33	70	49	21
36	75	48	27		36	70	49	21
39	75	48	27		39	70	49	21
42	70	48	22		42	65	49	16
45	70	48	22		45	65	49	16

Qualitative observations.

Solubility: By comparison the potassium soap was much more water soluble than the sodium soap. The sodium soap needed about 15 minutes stirring to dissolve completely in room temperature water while the potassium soap dissolved completely in about one minute.

Appearance of foam: The potassium soap foam had showed much larger bubbles particularly at the top of the foam. The larger bubbles burst quite easily which made the early foam volume drop more quickly. The sodium soap foam was a more dense foam with smaller bubbles

Section E Discussion of Results

(a) The yield of the saponification reaction:

If I assume that all the fatty acids in olive oil are oleic acid i.e. the olive oil if glycerol trioleate, then I can calculate the % yield of the potassium and sodium oleate formed based on the reaction equation

$$[CH_3(CH_2)_7CH{=}CH(CH_2)_7COO]_3C_3H_5 + 3\mathbf{M}OH \rightarrow 3CH_3(CH_2)_7CH{=}CH(CH_2)_7COO^- M^+ + CH_2(OH)CH(OH)CH_2OH$$

which shows that one mole of Glycerol Trioleate forms three moles of the metal salt of the fatty acid.

Molar Mass of Glycerol Trioleate = 885.4 gmol^{-1} (5)
Molar Mass of Potassium Oleate = 320.6 gmol^{-1} (6)
Molar Mass of Sodium Oleate = 304.4 gmol^{-1} (7)

Mass of Olive Oil initially in 300 cm^3 reaction mixture = 91.94 g (±0.1g = ±0.1%)
Mass of Olive Oil in initially 15 cm^3 reaction mixture = 91.94 × (15 ÷ 300) = 4.60g (± 0.1%)
Moles of Olive Oil in 15 cm^3 reaction mixture = 4.60 ÷ 885.4 = 0.00520 (± 0.1%)

Maximum moles of Potassium or Sodium Oleate formed in 15 cm^3 reaction mixture = 0.00520 × 3
= 0.0156 (± 0.1%)

So maximum Mass Yield of Potassium Oleate = 0.0156 × 320.6
= 5.00g (± 0.1%)

So maximum Mass Yield of Sodium Oleate = 0.0156 × 304.4
= 4.75g (± 0.1%)

We can use these theoretical maximum yields to calculate the % yields because % yield = (Experimental Yield ÷ Theoretical Maximum Yield) × 100

Table 5: Percentage Yields of Potassium and Sodium Soaps

Potassium Soap				Sodium Soap		
Reaction Time (± 0.1mins)	Mass Yield (± 0.02g)	% Yield		Reaction Time (± 0.1mins)	Mass Yield (± 0.02g)	% Yield
10	6.16	123%		10	5.09	107%
20	6.40	128%		20	4.63	97%
30	6.58	132%		30	4.90	103%
40	5.32	106%		40	5.16	109%
50	6.02	120%		50	5.30	112%

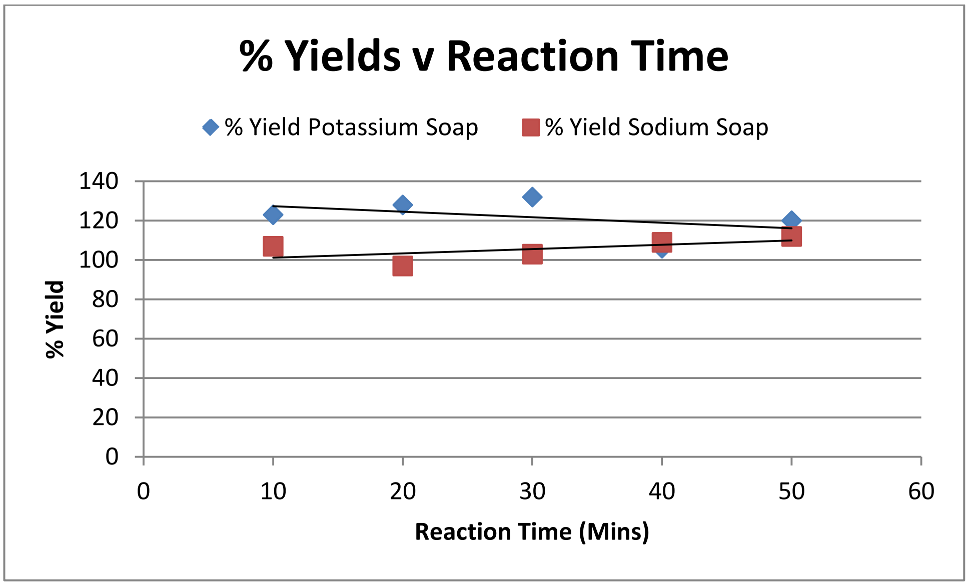
Graph 1: % Yield v reaction Time for Saponification Reaction

---

[5] http://www.sigmaaldrich.com/etc/medialib/docs/Sigma/Product_Information_Sheet/1/t7140pis.Par.0001.File.tmp/t7140pis.pdf, last accessed 30-9-2012

[6] http://www.sigmaaldrich.com/catalog/product/aldrich/60420?lang=en&region=GR, last accessed 30-9-2012

[7] http://www.sigmaaldrich.com/catalog/product/sigma/o7501?lang=en&region=GR, last accessed 30-9-2012



The yields of the saponification reactions indicated that the reaction was completed in the very first 10 minutes in both cases since the mass yield reached close to the maximum value within the first 10 minutes as seen in Tables 1, 2 and 5 and graph 1 above. Any variation up or down in the mass yield of each batch is explainable by the uncertainty in the batch volume of 15 cm^3 due to the solidifying waxy solid in the graduated pipette obscuring the liquid level when extracting the reaction mixture from the reaction flask. The fact that the mass yield stayed constant means that we can be confident that the soap produced is the final product and not a mixture of unreacted olive oil and the potassium or sodium soaps.

There are two other interesting trends to note. One is that the % yield of Potassium Soap is significantly higher on average than the sodium soap and secondly its yield is well above 100%. How is this possible?

One factor to exclude when explaining the high yields is that the samples were still wet with ethanol or water. I had weighed them after drying twice and the two readings were close enough together to state that very little solvent was still evaporating. Also the samples were dry to the touch.

The sodium soap percentage yields were only a little above 100% and this can be explained by some trapped sodium chloride from the precipitation step. The powdery, granule-like feel to the sodium soap supports that there may be some sodium chloride mixed in. Another possible product of the saponification reaction was also the glycerol and there could be some unreacted potassium hydroxide. However these possible impurities would mainly have been left in the aqueous phase during precipitation and should not be present in large amounts in the dried soap left on the filter paper.

The potassium soap was recovered only be evaporation of the solvent and the soap would contain in addition to the potassium oleate both unreacted potassium hydroxide and the glycerol produced in the saponification reaction. The presence of glycerol might explain the waxy texture of the potassium soap in contrast to the dry powdery feel of the sodium soap.

(b) Characteristics of the Synthesised Soaps

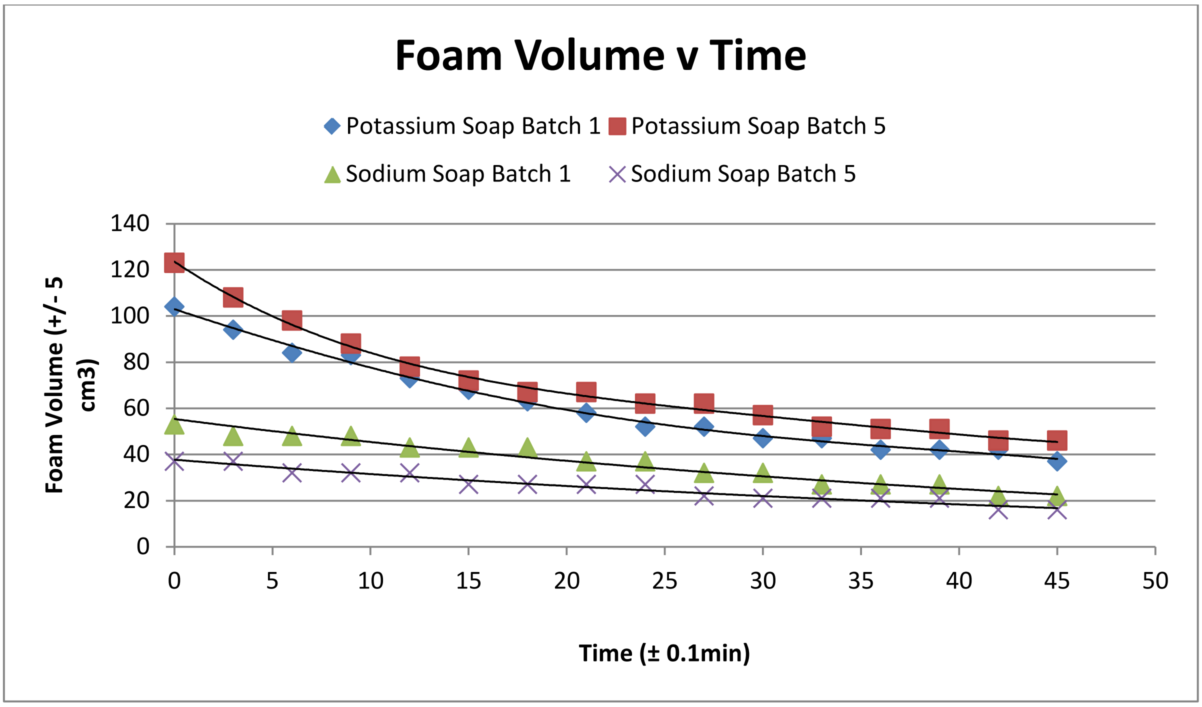
When changing the alkali metal ion in the oleate there was a significant change in the nature of the soap.

The behaviour under heating was qualitatively observed. I heated the samples side by side as high as 210 °C. Neither sample melted but the sodium soap displayed significant darkening like charring. The potassium soap was unchanged in appearance and appears to be more stable to heating.

The water solubility at room temperature also appeared significantly different with the potassium soap being much more quickly dissolved in the water. This could be due to the different metal ion present in the oleate or it could be due to the different physical nature of the soap with the potassium soap being softer than the harder granules of the sodium soap.

The foaming action was also significantly different as displayed in Graph 2 below.

Graph 2: Foaming Action of the Soaps



From the graph we see that the potassium soap has greater foaming action with a greater initial volume of foam. My observations indicate that this was due to larger bubbles being formed in the potassium soap rather than a head of a greater amount of bubbles of the same size in both types of soap. Because the bubbles were bigger and big bubbles are less stable and burst first the volume of foam initially reduces at a faster rate in the potassium soap.

Once again it is difficult to know whether the different foaming action was due to the different chemical nature of potassium oleate versus sodium oleate or whether it was due to the different methods of synthesis meaning that the two soaps contained different impurities such glycerol and residual potassium hydroxide in the potassium soaps versus sodium chloride impurity in the sodium soap. It is believable that changing the metal cation could cause a significant effect because the different charge densities of sodium and potassium cations could cause different electrostatic attractions in the foam. However the different impurities such as sodium chloride v glycerol could also affect the stability of the foam bubbles so it is difficult to decide.

Conclusion

The main conclusions arising from this study are as follows

(i) The saponification reaction occurs quickly at the reflux temperature. Although the methods of preparation that I read had stated react for at least 20 minutes the reaction according to the yield had reached completion by 10 minutes.

(ii) The soaps were produced in very high yields showing that the saponification reaction is very efficient. The fact that the potassium oleate based soap had a very high yield above 100% is explained by the presence of other substances such as glycerol which is also produced in the saponification reaction and unreacted potassium hydroxide. The precipitation step in the production of the sodium oleate based soap means that glycerol and potassium hydroxide should not be present in high amounts explaining the more reasonable yield close to 100%. There could be some sodium chloride present from the precipitation step.

(iii) The potassium oleate based soap had better stability under heating and was more easily dissolved in water than the sodium oleate based soap. I don't know whether this is due to the different metal cation or whether the different impurities depending on whether the isolation of the soap was by evaporation or precipitation have caused the effects

(iv) The potassium oleate soap had a greater foaming action than the sodium oleate based soap. This could be due to the different charge densities of sodium and potassium cations could causing different electrostatic attractions in the foam. Equally though the different impurities depending on whether the isolation of the soap was by evaporation or precipitation have caused the effects.

Evaluation

The conclusions to this study are not yet very certain because of the simple nature of the methodology and some large random errors arising from the procedure.

The largest random error was probably when I extracted 15cm^3 batches of reaction mixture. The graduated pipette was hard to use because solid soap was precipitating inside it and blocking the pipette and obscuring the readings. This makes the calculated % yields uncertain although because I did repeat readings we can see the general trend in % yields and the conclusion that the yields are very high and that there is a greater yield of the potassium soap than the sodium soap is valid.

The other large random error was in the foam volume reading since bubbles would stuck to the side of the measuring cylinder and give an apparently higher reading. Then if one or two of these bubbles burst the volume would apparently drop suddenly. This would be a significant problem if this investigation was looking in detail at foam stability but for the comparison in foaming action between the potassium and sodium soaps I think the data is sufficiently clear that the potassium soap had a greater foaming action than the sodium soap.

The solubility and melting temperature tests were very quick and the conclusions here are not very solid. More research is needed to draw conclusions on these areas.

The biggest flaw in the methodology was the fact that the potassium and sodium soaps were not isolated the same way and because of this they may contain different other compounds other than the oleate, such as glycerol, potassium hydroxide and sodium chloride. This meant that the different foaming action and solubility behaviour may be due to the different impurities and not due to the difference between the potassium oleate and sodium oleate.

If I had time to improve and extend the investigation I would:

(i) Synthesise the sodium soap by refluxing olive oil with sodium hydroxide dissolve in an ethanol/water mixed solvent. Then I would collect soap by allowing solvent to evaporate from a petri dish just like the potassium soap. This would mean that the impurities would be similar and the comparison of soap behaviours will be a better fair test. This is the most important improvement.

(ii) I should carry out more systematic tests for solubility such as adding soap to water with gentle stirring on the magnetic stirrer and to measure the rate of dissolving and the maximum amount dissolved.

(iii) It is hard to successfully measure the melting temperatures for the soaps because we don't have a thermometer that will go high enough. The literature values for the melting temperatures are: potassium oleate = 235-240 °C [8] and sodium oleate = 232-235 °C [9]. If I can find a temperature probe to go high enough I would repeat the measurements because it will give me confirmation that the soaps are mainly composed of the oleate salts if the melting points are close to literature values.

(iv) I would more carefully repeat the measurement of foaming action several times for each soap sample and I would use a bigger measuring cylinder (we have a 500 cm^3 one at school) and would stir for a set time at a set speed with the magnetic stirrer. This should give more reproducible results to the foaming tests.

---

[8] http://www.chemical-buyers.com/cas-143/143-18-0.html , last accessed 3-10-2012

[9] http://www.chemicalbook.com/ChemicalProductProperty_EN_CB6726306.htm, last accessed 3-10-2012