

"WHAT IS THE EFFECT OF ADDITION OF POTASSIUM, SODIUM AND BARIUM NITRATES ON THE EMULSIFYING ACTION OF SURFACTANTS SODIUM PALMATE AND SODIUM LAURYL ETHER SULPHATE?"

A common problem faced by households with hard water when using soap is lime soaps or soap scum. Calcium or magnesium in hard water replace sodium and react with fatty acid component of soap, forming insoluble scum.²³

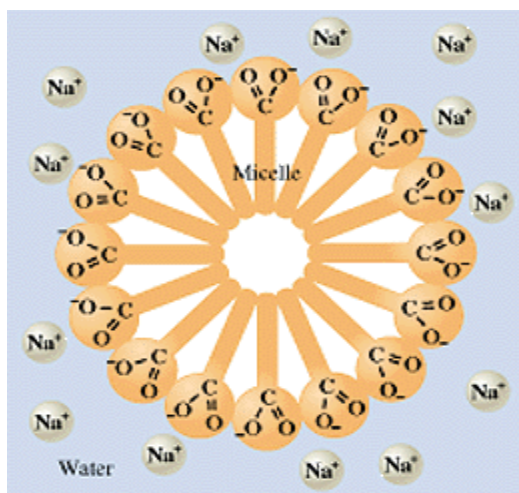
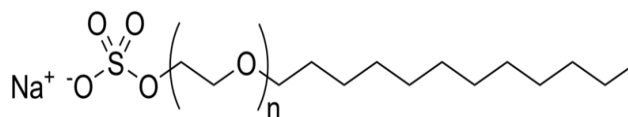


Figure 6: Soap micelle with carboxylate head groups of soap interacting with Na⁺ counter-ions and water²⁴

2.3 Detergent

Detergent is another water-soluble surfactant that combines with impurities and dirt to make them more soluble. It differs from soap in not forming a scum with salts in hard water.²⁵ Detergents contain alkylbenzenesulfonates, a family of compound that is similar to soap.²⁶

An example of detergent is sodium lauryl ether sulphate (SLES), structural formula shown below.



²³ Helmenstine. About.com Chemistry, How Soaps Cleans.

<http://chemistry.about.com/od/cleanerchemistry/a/how-soap-cleans.htm> (Accessed February 14, 2013)

²⁴ New Mexico State University. Solubility.

<http://web.nmsu.edu/~snsm/classes/chem116/notes/solutions.html> (Accessed January 5, 2013)

²⁵ Oxford Dictionaries. Detergent. <http://oxforddictionaries.com/definition/english/detergent> (Accessed February 14, 2013)

²⁶ Salager, Jean-Louis. Surfactants Types and Uses. <http://www.nanoparticles.org/pdf/Salager-E300A.pdf> (Accessed February 14, 2013)

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An EDL consists of three parts: 1) Surface charge - charged ions adsorbed on the micelle surface. 2) Stern layer – counter-ions (charged opposite to the surface charge) attracted to the micelle surface and closely attached to it by electrostatic force. 3) Gouy-Chapman Layer or diffuse layer: a film of the dispersion medium (solvent) adjacent to the micelle. Gouy-Chapman layer comprises free ions with a higher concentration of the counter-ions.⁴⁰ The ions of Gouy-Chapman layer are affected by the electrostatic force of the charged micelle.

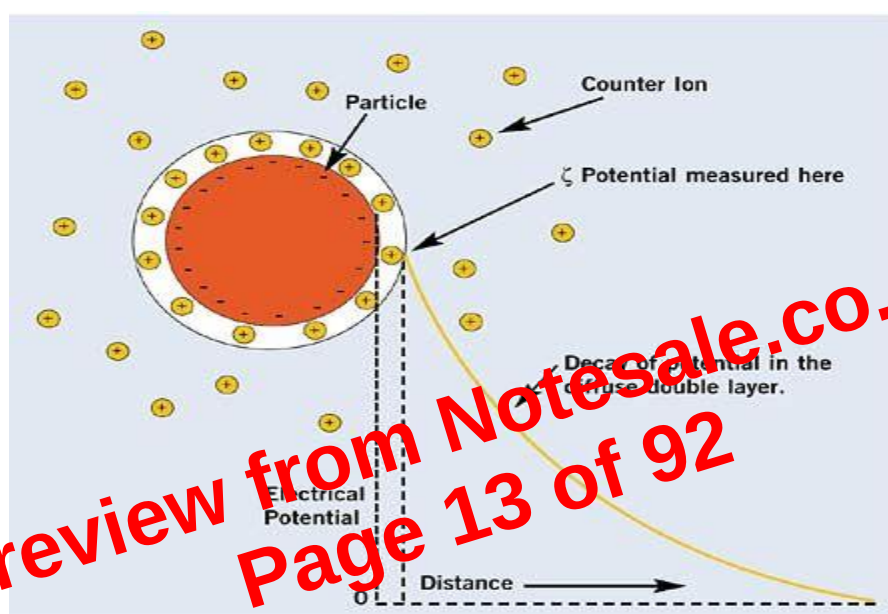


Figure 11: Electric double layer of a negatively charged particle⁴¹

Cation has the effect of compressing the Gouy-Chapman layer of anionic micelles decreasing the thickness of this layer. The extent of compression is dependent on the valence of the cation.⁴² For example, barium ions have two valence compared to sodium ions. Thus, barium ions would be expected to compress the Gouy-Chapman layer of the micelle more than sodium ions.

⁴⁰ Dmitri Kopeliovich, Substances & Technologies. Surfactant.

<http://www.substech.com/dokuwiki/doku.php?id=surfactants> (Accessed January 5, 2013)

⁴¹ Ceramic Industry. Measuring Zeta Potential. <http://www.ceramicindustry.com/articles/measuring-zeta-potential> (Accessed May 23, 2013)

⁴² Paton-Morales, P.; Talens-Alession, F.I. Effect of Competitive Adsorption of Zn^{2+} on the Flocculation of Lauryl Sulfate Micelles by Al^{3+} . *Langmuir* [Online] **2002**, *18*, 8295-9301
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Figure 28: Soap solution with NaNO_3 being heated and stirred for 10minutes

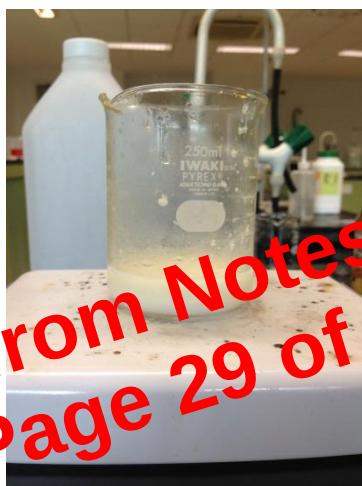


Figure 29: Emulsion of soap solution with NaNO_3 formed after 10minutes of emulsification



Figure 30: Detergent solution with NaNO_3 being heated and stirred for 10minutes

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8. Stir the mixtures again with the magnetic stirrer at stirring scale of 7 and heating scale of 3 for 20 minutes timed with a digital stopwatch.



Figure 34: Soap solution with NaNO_3 being heated and stirred for 20 minutes

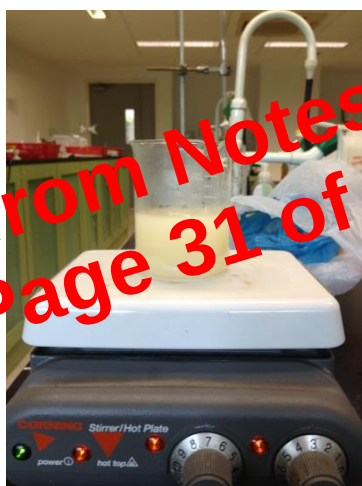


Figure 35: Detergent solution with NaNO_3 being heated and stirred for 20 minutes

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4.3.1 Detergent

Table 4.3.1.1: Detergent solution

	1	2	3
Initial Vol of HNO_3 / cm^3 $\pm 0.05\text{cm}^3$	0.00	12.20	23.20
Final Vol of HNO_3 / cm^3 $\pm 0.05\text{cm}^3$	12.20	23.20	34.20
Vol of HNO_3 used / cm^3 $\pm 0.10\text{cm}^3$	12.20	11.00	11.00
Readings taken		✓	✓

4.3.2 Detergent - NaNO_3

Table 4.3.2.1: Detergent solution containing NaNO_3

	1	2	3
Initial Vol of HNO_3 / cm^3 $\pm 0.05\text{cm}^3$	0.00	13.00	25.10
Final Vol of HNO_3 / cm^3 $\pm 0.05\text{cm}^3$	13.00	25.10	37.30
Vol of HNO_3 used / cm^3 $\pm 0.10\text{cm}^3$	13.00	12.10	12.20
Readings taken		✓	✓

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4.3.3 Detergent - KNO_3

Table 4.3.3.1: Detergent solution containing KNO_3

	1	2	3
Initial Vol of HNO_3 / cm^3 $\pm 0.05\text{cm}^3$	0.00	13.30	25.60
Final Vol of HNO_3 / cm^3 $\pm 0.05\text{cm}^3$	13.30	25.60	38.00
Vol of HNO_3 used / cm^3 $\pm 0.10\text{cm}^3$	13.30	12.30	12.40
Readings taken		✓	✓

4.3.4 Detergent - $\text{Ba}(\text{NO}_3)_2$

Table 4.3.4.1: Detergent solution containing $\text{Ba}(\text{NO}_3)_2$

	1	2	3
Initial Vol of HNO_3 / cm^3 $\pm 0.05\text{cm}^3$	0.00	15.70	30.70
Final Vol of HNO_3 / cm^3 $\pm 0.05\text{cm}^3$	15.70	30.70	45.70
Vol of HNO_3 used / cm^3 $\pm 0.10\text{cm}^3$	15.70	15.00	15.00
Readings taken		✓	✓

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5. DATA PROCESSING

5.1 Sample Calculation

Only a sample calculation is shown here. All calculations can be found in Appendix C. The general formulas for the calculations can be found in Appendix D.

5.1.1 Control Set

NaOH reacted:

Calculations

$$\begin{aligned}\text{Amount NaOH used} &= \frac{20}{1000} \times 3.000 \\ &= 0.0600 \text{ mol}\end{aligned}$$

Propagation of uncertainties

$$\begin{aligned}\% \Delta \text{ Amount NaOH} &= \left(\frac{0.06}{20.00} \times 100\% \right) + (0.124\%) \\ &= 0.424\% \\ \pm \Delta \text{ amount of NaOH} &= \pm (0.0600 \times 0.424\%) \text{ mol} \\ &= \pm 0.0003 \text{ mol}\end{aligned}$$

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NaOH reacted is $(0.0600 \pm 0.0003) \text{ mol}$

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and Bases (HSAB). HSAB states that hard ligands favour bonding to hard cations, soft ligands correspondingly favour bonding to soft cations. According to the Lewis definition of acid and bases, ligands which are electron donors are bases, while cations which are electron acceptors are acids. The hardness of acid and base is dependent on size and ease of polarizing. The smaller and non-polarizable the acid and base, the harder it is. Hence, hardness of the hexa-aqua univalent ion acids utilized is ordered as $[\text{Na}(\text{H}_2\text{O})_6]^+ > [\text{K}(\text{H}_2\text{O})_6]^+$, with sodium possessing a more extensive hydration shell.

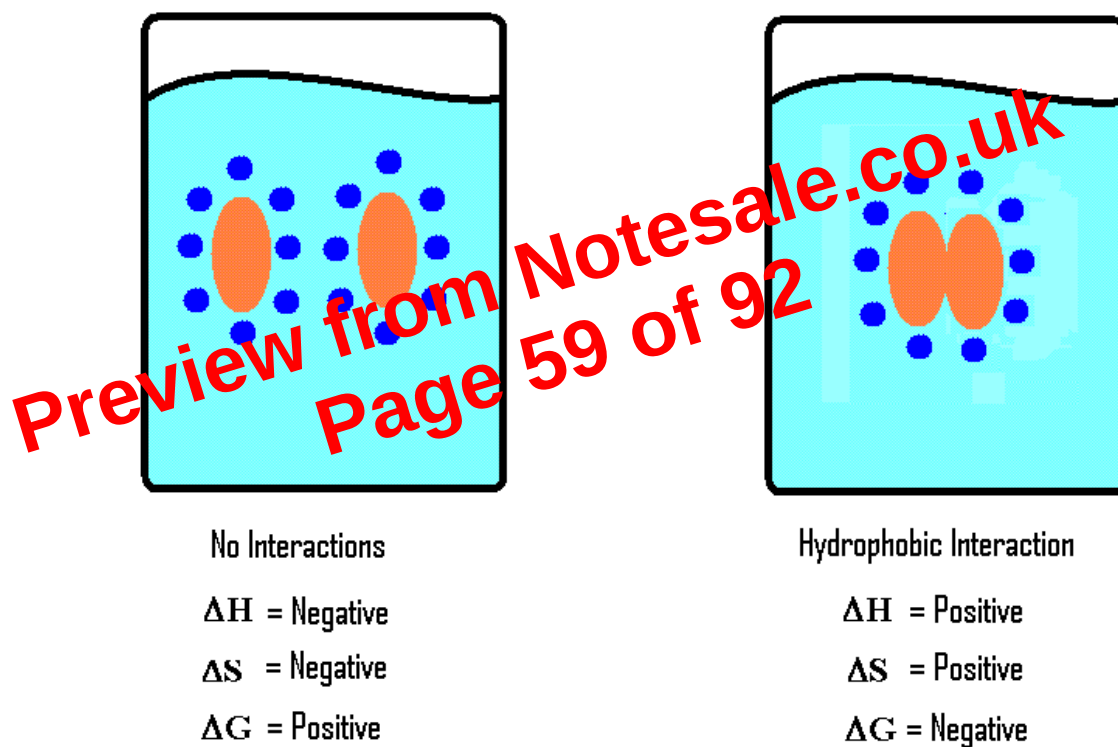


Figure 45: Thermodynamics of hydrophobic interactions⁶⁰

This is evidenced by more exothermic $\Delta H_{\text{hyd}}^{\circ}$ of Na^+ of -416 kJ mol^{-1} compared to -322 kJ mol^{-1} of K^+ . Na^+ is readily hydrated and favours interaction with the

⁶⁰ ChemWiki: The Dynamic Chemistry Textbook. Hydrophobic interactions. http://chemwiki.ucdavis.edu/Physical_Chemistry/Physical_Properties_of_Matter/Intermolecular_Forces/Hydrophobic_interactions (Accessed April 2, 2013)

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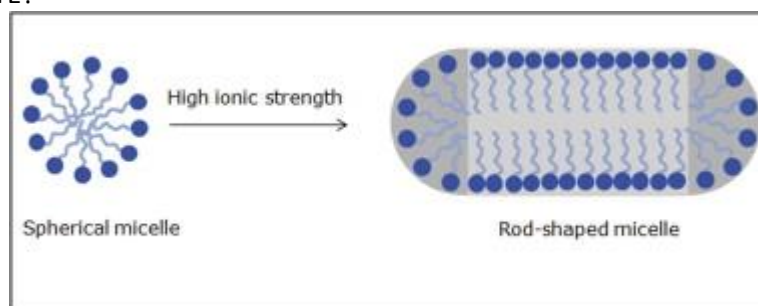


Figure 48: Shape transitions of micelle due to increased ionic strength⁶⁸

6.6 Gibbs free energy

With reference to results obtained, electrostatic energy and binding heat are less endothermic and more exothermic for Ba^{2+} compared to the univalent ions implying that overall enthalpy of micellization for Ba^{2+} is more exothermic. For the comparison between sodium and potassium, differences in binding heat and extensiveness of hydration shell between these ions account for slightly better oil emulsifying ability of potassium ions relative to sodium.

A reaction is only feasible if the Gibbs free energy, which can be derived from the formula $G = \Delta H - T\Delta S$ whereby G is Gibbs free energy, ΔH is enthalpy change, T is temperature and ΔS is change in entropy, is negative. Hence, a decrease in ΔH (more exothermic) causes a decrease in G . Therefore, formation of micelles is more favourable, CMC decreases. Hence, a smaller number of surfactant molecules are required to form micelles; more oil will be emulsified for the same amount of surfactants. The effects on emulsifying ability differ in the order: $\text{Ba}^{2+} > \text{K}^+ > \text{Na}^+$. This is supported by the data as shown in Graph 6.1.1 and 6.1.2.

⁶⁸ Arunima Chaudhuri, Sourav Halder, Amitabha Chattopadhyay. Organization and dynamics in micellar structural transition monitored by pyrene fluorescence. *Biochemical and Biophysical Research Communications* [Online] **2009**, 390(3), 728-732
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9.2 Appendix B: Standardization of HNO₃ & Concentration of Cations

Concentration Na₂CO₃

Calculations

Amount of Na₂CO₃ used =

$$\frac{26.5010}{22.99 \times 2 + 12.01 + 16.00 \times 3}$$

$$\approx 0.250 \text{ mol}$$

$$\begin{aligned} \text{Concentration of Na}_2\text{CO}_3 &= \frac{0.250}{0.250} \\ &= 1.000 \text{ mol dm}^{-3} \end{aligned}$$

Propagation of uncertainties

$$\begin{aligned} \% \Delta \text{ Amount Of Na}_2\text{CO}_3 \text{ used} &= \pm \left(\frac{0.0010}{26.5010} \right) \times 100\% \\ &\approx \pm 0.00377344\% \end{aligned}$$

$$\begin{aligned} \% \Delta \text{ concentration of Na}_2\text{CO}_3 &= \frac{0.3}{250.0} \times 100\% + 0.00377344\% \\ &\approx \pm 0.12377344\% \end{aligned}$$

$$\begin{aligned} \pm \Delta \text{ concentration of Na}_2\text{CO}_3 &= \pm (1.000 \times 0.12377344\%) \\ &\approx \pm 0.002 \text{ mol dm}^{-3} \end{aligned}$$

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Concentration of Na₂CO₃ utilized is (1.000±0.002)mol dm⁻³

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Table 9.2.1: Mass of NaNO₃

Initial mass of reagent bottle/g $\pm 0.001\text{g}$	2.5771
Final mass of beaker and NaNO ₃ /g $\pm 0.001\text{g}$	2.7473
Mass of NaNO ₃ used/g $\pm 0.002\text{g}$	0.1702

Concentration NaNO₃

Calculations

Amount of NaNO₃ used =

$$\frac{0.1702}{22.99 + 14.00 + 16.00 \times 3}$$

$$\approx 0.002003\text{mol}$$

Propagation of uncertainties

$$\% \Delta \text{ Amount Of NaNO}_3 \text{ used} = \pm \left(\frac{0.0010}{0.1702} \right) \times 100\% \approx \pm 0.5875\%$$

$\% \Delta$ concentration of NaNO₃

$$= \frac{0.06}{20.00} \times 100\% + 0.5875\%$$

$$\approx \pm 0.8875\%$$

$$\text{Concentration of NaNO}_3 = \frac{0.002003}{0.02000}$$

$$= 0.100\text{mol dm}^{-3}$$

$\pm \Delta$ concentration of NaNO₃

$$= \pm (0.100 \times 0.8875\%)$$

$$\approx \pm 0.001\text{mol dm}^{-3}$$

Concentration of NaNO₃ utilized is $(0.100 \pm 0.001)\text{mol dm}^{-3}$

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Soap – Ba(NO₃)₂ solution

Calculations

$$\text{Volume of HNO}_3 \text{ used} = \frac{14.60 + 14.60}{2} \\ = 14.60 \text{ cm}^3$$

$$\text{Amount of HNO}_3 \text{ used} = \frac{14.60}{1000} \times 2.005 \\ \approx 0.02928 \text{ mol}$$

$$n(\text{excess NaOH}) = 0.02928 \text{ mol}$$

$$\text{Amount of NaOH reacted} = 0.0600 - 0.02928 \\ = 0.03073 \text{ mol}$$

$$\text{Amount un-emulsified oil} = 0.03073 \div 3 \\ \approx 0.01024 \text{ mol}$$

$$\text{Amount emulsified oil} = 0.01525 - 0.01024 \\ \approx 0.00501$$

Propagation of uncertainties

$$\pm \% \Delta \text{ Vol. Of HNO}_3 \text{ used} = \pm \left(\frac{0.10 + 0.10}{2} \right) \\ = \pm 0.10 \text{ cm}^3$$

$$\pm \% \Delta \text{ Amount of excess NaOH} = \pm \% \Delta \text{ amount of HNO}_3 \text{ used}$$

$$\pm \% \Delta (\text{excess NaOH}) = \frac{0.10}{14.60} \times 100\% + 0.919\% \\ \approx \pm 1.604\%$$

$$\pm \Delta \text{ amount of NaOH reacted} = \pm (0.0003 + 1.604\% \times 0.02928) \\ \approx \pm 0.0007696$$

$$\pm \Delta \text{ amount of un-emulsified oil} = \pm 0.0007696 \div 3 \\ \approx \pm 0.0002565 \text{ mol}$$

$$\pm \Delta \text{ amount of emulsified oil} \\ = \pm (0.00022 + 0.0002565) \\ \approx \pm 0.00048 \text{ mol}$$

Amount of emulsified oil is $(0.00501 \pm 0.00048) \text{ mol}$

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Detergent – Ba(NO₃)₂ solution

Calculations

$$\text{Volume of HNO}_3 \text{ used} = \frac{15.00+15.00}{2} \\ = 15.00\text{cm}^3$$

$$\text{Amount of HNO}_3 \text{ used} = \frac{15.00}{1000} \times 2.005 \\ \approx 0.03008\text{mol}$$

$$n(\text{excess NaOH}) = 0.03008\text{mol}$$

$$\text{Amount of NaOH reacted} = 0.0600 - 0.03008 \\ = 0.02993\text{mol}$$

$$\text{Amount un-emulsified oil} = 0.02993 \div 3 \\ \approx 0.009975\text{mol}$$

$$\text{Amount emulsified oil} = 0.01525 - 0.009975 \\ \approx 0.00528\text{mol}$$

Propagation of uncertainties

$$\pm\% \Delta \text{ Vol. Of HNO}_3 \text{ used} = \pm \left(\frac{0.10+0.10}{2} \right) \\ = \pm 0.10\text{cm}^3$$

$$\pm\% \Delta \text{ Amount of excess NaOH} = \pm\% \Delta \text{ amount of HNO}_3 \text{ used}$$

$$\pm\% \Delta (\text{excess NaOH}) = \frac{0.10}{15.00} \times 100\% + 0.919\% \\ \approx \pm 1.586\%$$

$$\pm \Delta \text{ amount of NaOH reacted} = \pm (0.0003 + 1.586\% \times 0.02346) \\ \approx \pm 0.0007769\text{mol}$$

$$\pm \Delta \text{ amount of un-emulsified oil} = \pm 0.0007769 \div 3 \\ \approx \pm 0.0002590\text{mol}$$

$$\pm \Delta \text{ amount of emulsified oil} \\ = \pm (0.00022 + 0.0002590) \\ \approx \pm 0.00048\text{mol}$$

Amount of emulsified oil is (0.00528±0.00048)mol