

## Effect of Temperature on the Adsorption of Metallic Soaps of Castor Seed Oil onto Haematite

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**Abstract:** This study is based on the effect of temperature on the adsorption of three metallic soaps of castor seed oil onto haematite surface in aqueous medium. The results showed a decrease in adsorption density with increase in temperature to a minimum at 50°C for the various soaps. This can be due to the weakening of attractive forces between adsorbate and the adsorbent. This enhances the tendency of the adsorbate ions to escape from each adsorbent surface to the solution phase, hence desorption may start to occur above this temperature. However, between 60 °C and 70 °C adsorption equilibrium was attained. The maximum adsorption capacity for the adsorbates.

**Keywords:** haematite, Castor seed, temperature, adsorbent, adsorbate.

### 1. INTRODUCTION

Adsorption science has exhibited great potential in many technological and industrial systems such as filtration of impurities from liquid or gases, the bonding of molecules to the solid surface of a heterogeneous catalyst, the segregation of surfactant molecules onto the surface of a liquid, and the migration of ions to the surface of a charged electrode. Temperature is a crucial parameter in adsorption reactions. According to the adsorption theory, adsorption decreases with an increase in temperature, and molecules adsorbed earlier on a surface tend to desorb from the surface at elevated temperatures. But for activated carbon, a different trend is noticed where decreasing viscosity and increasing molecular motion at high temperature allows the uptake of molecules into the pores more easily, causing adsorption to increase as temperature increases. However temperature has not been studied as relevant variable in adsorption experiments. The tests are usually performed at approximately 25-30°C. However, a slight increase in cation uptake by seaweed in the range of 4 to 55°C has been reported (Horsfall and Spiff, 2005.)

Metallic soaps are metallic salts of fatty acids. They are groups of water-insoluble compounds containing alkaline earth or heavy metals combined with monobasic carboxylic acids of 7-22 carbon atoms (Lewkowitsch, 1969). They can be represented by the general formula  $(RCOO)_xM$  where R is an aliphatic or alicyclic radical and M is a metal of valence X. They differ from toilet soaps in their composition and insolubility in water. Their solubility or solvation in a variety of organic solvents accounts for their various uses. Soap molecules bear hydrophobic or hydrophilic parts which can be adsorbed selectively on the surface of the desired mineral particles to reduce wetting by water. Thereby enhance their floatation. The balance of dynamic forces between the concentration of adsorbate in bulk solution with that at the interface for a particular system leads to adsorption equilibrium. Adsorption and its phenomena have received a lot of attention by several investigators who reported the dependence of the process on factors such as temperature, pressure, effective surface area, pH, concentration, ionic charge, ionic strength, nature of adsorbate and adsorbent, (Ahalya *et al.*, 2005, Ahalya *et al.*, 2007, Ai *et al.*, 2006, Arivoli *et al.*, 2008, Babarinde *et al.*, 2006, Bos *et al.*, 1994, Chiou *et al.*, 2003, Cordero *et al.*, 2004, Gardea-Torresdey *et al.*, 1998, Hadjar, *et al.*, 2004, Horsfall *et al.*, 2006, Kim *et al.*, 2005, Krishnan and Anirudhan, 2003, Norde and Anusiem, 1992, Ofor, 1995, Ofomaja *et al.*, 2005, Ogali *et al.*, 2008, Quek *et al.*, 1998, Raghuvanshi *et al.*, 2004, Santamarina *et al.*, 2002, Uzun and Guzel, 2004).

Castor oils derived from castor plant (*Ricinus communis L.*), represents a potential by-product and it is used in many technical, medical and different industrial application like biodiesel productions (Amara and Salem, 2009). Castor oil has over 1000 industrial uses and because of this, its demand increases. A scientific investigation of the crop to improve its oil content will go a long way to meet up with the demand (Sepidar *et al.*, 2009).

## 2. MATERIALS AND METHODS

Ore containing samples of haematite obtained from Itakpe, Nigeria (76.9% iron) were crushed in the laboratory using jaw and roll crushers. Gravimetric method of jigging and tabling was employed in removing siliceous materials, while magnetic separation was used in separating magnetic materials from the ore sample. Sieve analyses were performed using the british standards sieve plates to obtain sample of haematite-70 micron. Mineralogical analysis of the ore sample was performed with volumetric and atomic absorption spectrometric (Buck Scientific atomic absorption spectropotometer model 205A) methods. Solutions of the reagents were prepared with distilled deionised water and sodium hydroxide and hydrochloric acid solutions were used for pH adjustments. BDh chemical reagents analar grade (of not less than 98% purity) were used in this study. Determination of specific surface area (SSA) was done by the ethylene-glycol-monoethyl ether (EGME) method (Cerator and Lutenegger, 2002)

### 2.1. Soap Preparation

The 50g castor seed oil was added to each 50ml of 30% potassium hydroxide, calcium hydroxide and aluminium hydroxide, and 30ml of ethanol was added into each of the 600ml beakers, then heated at 90°C for 1h in water bath with vigorous stirring until creamy-pasty soaps are formed. The 50ml of hot saturated sodium chloride solution was then added to each of the pasty soaps with vigorous stirring for short period and allowed to cool overnight. The soaps cake formed on the surface of the 'lye' were removed and air dired and stored in plastic containers (Tooley, 1976)

### 2.2. Calibration Studies

The electrical conductance of 25cm<sup>2</sup> soap (potassium, calcium and aluminium soaps of castor seed oil) solutions of different concentrations were measured at 29oC and pH 7.31, using an Electronic conductivity meter (model-90 check-mate deluxe field system-corning). From the result, a calibration graph of the soap conductance was plotted against the square root of soap concentrations based on the Kohlrausch law equation (Atkins, 1998);

$$\Lambda_m = \Lambda^o_m - KC^{\frac{1}{2}} \tag{1}$$

Where  $\Lambda_m$  is the molar conductivity,  $\Lambda^o_m$  is the limiting molar conductivity, C is the concentration of the solution and K is a constant.

## 3. RESULTS AND DISCUSSION

Calculations from experimental results and sample analysis show that specific surface area (SSA) of haematite is 118.5m<sup>2</sup>/g. this value is in agreement with that obtained by Ibezim-Ezeani and Anusiem (2009), for haematite using the same method.

**Table1.** Chemical Composition of haematite (Fe<sub>2</sub>O<sub>3</sub>)

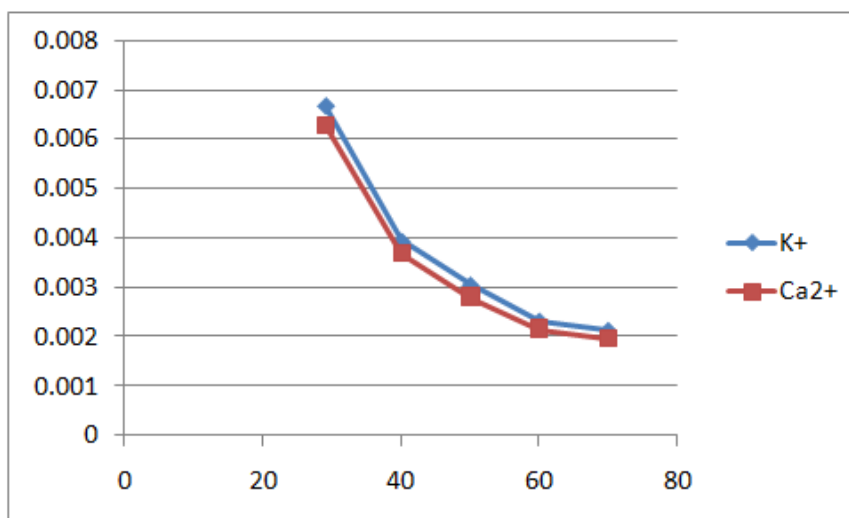
Chemical Composition	Haematite (%)
Fe <sup>3+</sup>	76.9
S <sup>2-</sup>	0.1
Al <sup>3+</sup>	4.1
Si <sup>4+</sup>	8.3
Mg <sup>2+</sup>	0.4
Ca <sup>2+</sup>	0.3
P <sup>3-</sup>	0.1
Ti <sup>4+</sup>	0.2
Mn <sup>2+</sup>	0.1

**Table2.**  $K^+$  Castor seed oil soap adsorption density at different temperatures for haematite

Temperature (°C)	Initial $K^+$ Castor oil soap g/litre	Equilibrium conductance ( $\mu$ S/cm)	Equilibrium( $K^+$ ) Castor soap concentration (g/l)	$K^+$ Castor adsorbed per gram of haematite (g)	Adsorption density of $K^+$ castor oil soap per $m^2$ Haematite surface g/g
29	1.0	58	2.07	7.93	0.00669
40	1.0	91	5.31	4.69	0.00395
50	1.0	97	6.37	3.63	0.00306
60	1.0	103	7.23	2.77	0.00233
70	1.0	104	7.46	2.54	0.00214

**Table3.**  $Ca^{2+}$  Castor seed oil soap adsorption density at different temperature for haematite

Temperature (°C)	Initial $Ca^{2+}$ Castor oil g/litre	Equilibrium conductance ( $\mu$ S/cm)	Equilibrium( $Ca^{2+}$ ) Castor soap concentration (g/l)	$Ca^{2+}$ Castor adsorbed per gram of haematite (g)	Adsorption density of $Ca^{2+}$ castor oil soap per $m^2$ Haematite surface g/g
29	1.0	63	2.53	7.47	0.00630
40	1.0	93	5.62	4.38	0.00369
50	1.0	100	6.67	3.33	0.00281
60	1.0	104	7.44	2.56	0.00216
70	1.0	105	7.66	2.34	0.00197



**Fig1.** Plot of adsorption density at different temperatures for  $K^+$  and  $Ca^{2+}$  of Castor seed oil soaps

Tables 2 and 3 show the adsorption densities of  $K^+$ , and  $Ca^{2+}$  soaps of castor seed oil onto adsorbent (haematite) at various temperatures. Fig 1 shows the plot of these adsorption densities as a function of temperature. Fig 1 and tables 2 and 3 show that the adsorption densities decrease with increasing temperature to minimum at 50°C for the various soaps. The decrease in adsorption density with increasing temperature is likely due to the weakening of attractive forces between the adsorbate and the adsorbent. This enhances the tendency of the adsorbate ions to escape from each adsorbent surface to the solution phase, hence adsorption may start to occur above this temperature.

However, between 60°C and 70°C, the adsorption density remains constant. This may be attributable to the denaturation or distortion of the adsorbate molecules. This will cause the structured water molecules surrounding the hydrophobic (non-polar) groups to be disrupted (Anusiem, 1999). These are likely to alter the orientation and effective interaction at the site. Physical adsorption usually decreases with increase in temperature while chemisorption is favoured at higher temperature (Houwing and Salomon, 1965). For physical adsorption, we expect that the adsorption will be higher at the lower temperature than that at higher temperature where as if the process is a chemical

absorption, the reverse is true. (Ebenso, 2003, 2004). The observed decreased temperature in adsorption density suggests that the adsorption on the adsorbent is largely a physical process.

This is in line with the results obtained by Horsfall and Spiff (2005a), Ekpe *et al.*, (2001) and Fouda *et al.*, (2000). However, generally, the adsorption theory suggest that adsorption decreases with increase in temperature and that molecules adsorbed earlier on a surface tends to desorb at elevated temperatures, Sharma and Sharma (2000).

Also at high temperature, the thickness of the boundary layer decreases, due to the increased tendency of the metal ion to escape from the ore surface to the solution phase which results in a decrease in adsorption as temperature increases. (Aksu and Kutsal, 1991).

Considering the various soaps of castor oil, potassium soap has the highest adsorption density followed by calcium soap. This indicates that there is a correlation between the adsorption density and the size to the charge ratio of the cations which are 0.75 and 2.02 for potassium and calcium respectively. Therefore, the smaller the size the charge ratio, the greater the adsorption density. The likely origin of these differences may be related to the increased diffusion rate of smaller ions to the surface of the adsorbent.

#### 4. CONCLUSION

This study has shown the effect of adsorption of potassium, calcium of castor seed oil onto haematite. The results showed that the adsorption densities decrease with increasing temperature to a minimum at 50°C for the various soaps. The decrease in adsorption density with increasing temperature is likely due to the weakening attractive forces between adsorbate and adsorbent. Adsorption equilibrium was attained between 60°C and 70°C. The maximum adsorption capacity for the adsorbate is in the order: potassium soap > calcium soap of castor seed oil which is in the reverse of the size to charge ratio of the cations due to increased diffusion rate of smaller ion to the surface of the adsorbent. The level of adsorption of all the adsorbates on the surface of the adsorbent suggest that all metallic soaps of castor oil in the study show a reasonable degree of surface coverage that may warrant their use as collector reagents in floatation separation of haematite from its ore.

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