

Full Length Research Paper

Thermodynamics of the adsorption of palmitate and laurate soaps onto some metal ore surfaces in aqueous media

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The thermodynamics of the adsorption of sodium-palmitate and sodium-laurate onto galena, hematite and cassiterite surfaces in aqueous media has been studied. The adsorption capacities of the soaps (adsorbates) were determined and the Langmuir, Freundlich and Temkin isotherm models were used to fit the experimental data. The Langmuir isotherm model was the best to describe the adsorption process with the highest correlation coefficient. Evaluation of the complete monolayer adsorption capacity at 29°C using the Langmuir equation showed 0.0506 mmol/g for galena, 0.0494 mmol/g for hematite, 0.0310 mmol/g for cassiterite (for sodium-palmitate adsorption) and 0.0802 mmol/g for galena, 0.0778 mmol/g for hematite, 0.0467 mmol/g for cassiterite (for sodium-laurate adsorption). These values are in the order: galena > hematite > cassiterite. The change in Gibbs free energy, ΔG , enthalpy, ΔH and entropy, ΔS of adsorption were computed and the values indicate that the adsorption processes are spontaneous, exothermic and favoured at low temperature suggesting physisorption as the predominant process.

Key word: Thermodynamics, adsorption, soap, collector reagents, langmuir isotherm.

INTRODUCTION

Thermodynamic studies of the adsorption of palmitate and laurate soaps (adsorbates) onto some metal ores (adsorbents) in aqueous phase were investigated as a prelude to determine the possible use of these soaps as collector reagents in metal ore beneficiation. Molecules of soap possess hydrophobic and hydrophilic parts which can be adsorbed selectively on the surface of the desired mineral particles to reduce wetting by water. 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 that can be described in terms of adsorption isotherm. Such experimental isotherms are useful for a number of applications such as the predictive modeling procedures for analysis and design of adsorption systems (Upendra

and Manas, 2006). The energy changes associated with the adsorption processes as molecules migrate from the bulk phase to the adsorption site and the extent of adsorption depends on some physical parameters such as temperature, pressure, concentration in the bulk phase, and the surface area of the adsorbent, as well as on the nature of the adsorbate and the adsorbent. Various studies have justified the validity of evaluating the effect of these thermodynamic parameters in adsorption process (Arivoli et al., 2008; Abiola and Oforika, 2004; Abdel-aal and Morad, 2001).

In the adsorption of copper, nickel, cobalt and manganese by kaolinite from aqueous solution, Yavuz et al. (2003) observed a small but positive ΔG at low temperature which became negative at high temperature suggesting that the process is spontaneous at such high temperature. Similar results were obtained by Vinod and Anirudhan (2001) for the sorption of tannic acid on zirconium pillared clay which showed the process to be spontaneous, exothermic and the restriction of adsorbate molecules at the surface of the adsorbent. Gaikwad (2004), Gomma and Wahdan (1994) observed similar trend in their studies. Horsfall and Spiff (2005)

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Abbreviations: SSA, Specific surface area; EGME, ethylene-glycol-monethyl ether.

investigated the effects of temperature on the sorption of Pb^{2+} and Cd^{2+} from aqueous solution by caladium bicolour biomass and obtained results which showed that the adsorption process was physical in nature. The purpose of this study is to evaluate the necessary thermodynamic parameters of adsorption process which will be useful in describing the rates, mechanisms and spontaneity or non-spontaneity of the adsorption process. These thermodynamic parameters will then be exploited in the ultimate beneficiation of local ores using sodium-palmitate and sodium-laurate soaps as collector reagents in the froth flotation process which is mainly dependent on the selective provision of hydrophobic surface on the component of the ores.

MATERIALS AND METHODS

The metal ores used in this investigation are galena (obtained from Enyigba-Abakiliki, Nigeria) contained 59.3% lead, hematite (obtained from Itakpe, Nigeria) contained 76.9% iron and cassiterite (obtained from Jos, Nigeria) contained 58.7% tin. The samples were crushed in the laboratory jaw and roll crushers. Gravimetric method of jigging and tabling was employed in removing siliceous materials, while magnetic separation method was used in separating magnetic materials from the ore sample. Sieve analyses were performed using the British standard sieve plates to obtain samples of galena 65 micron, hematite 70 micron and cassiterite 65 micron. Mineralogical analysis of the ore samples was performed with volumetric and spectrophotometric (Buck scientific atomic absorption spectrophotometer model 205A) methods of analyses. Solutions of reagents were prepared with distilled deionised water, 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-monethyl ether (EGME) method (Cerator and Lutenegeger, 2002). Soap preparation was performed by saponification reaction (Tooley, 1976).

Determination of thermodynamic parameters

0.5 g sample galena was added to 40 mL of 0.2 mmol/L soap solution in a conical flask. The capped flask was agitated in a mechanical shaker (120 oscillations per min.) for 1 h to attain equilibrium adsorption. The mixture was centrifuged, decanted and filtered to obtain a clear filtrate. The equilibrium conductance of the clear filtrate was measured and the equilibrium soap concentration was determined from the calibration curve. The adsorption capacity (q_e) in mol/g, was determined after the experiment was repeated at different concentrations and temperatures. The experiments were repeated using hematite and cassiterite.

Data evaluation

The concentration of soap samples were obtained from the calibration plots of the metal soaps based on Kohlrausch law equation in Equation.1 (Ibezim-Ezeani and Anusiem, 2009; Atkins, 1998).

$$\Lambda_m = \Lambda_m^o - KC^{\frac{1}{2}} \quad (1)$$

Where Λ_m is the molar conductivity, Λ_m^o is the limiting molar

conductivity, C is the concentration of the solution and K is a constant. The adsorption capacity (q_e) at equilibrium in mol/g, was determined using the mass balance equation (Ibezim-Ezeani and Anusiem, 2010) expressed as Equation 2.

$$q_e = \frac{V}{m} (C_o - C_e) \quad (2)$$

Where C_e is the soap concentration in solution (mol/L) at equilibrium, C_o is the initial soap concentration in solution, V is volume of initial soap solution used (L), and m is mass of adsorbent used (g). The adsorption capacities were used in the isotherm equation plots. Linearized form of some adsorption isotherm models (Vikrant and Pant, 2006; Ho et al., 2005, 2001; Abiola et al., 2004; Cordero et al., 2004; Horsfall et al., 2004; Onyango et al., 2004; Haghseresht and Lu, 1998; Muhammad et al., 1998) used for data analyses are presented in Equation 3. (Langmuir), Equation 4 (Freundlich) and Equation 5 (Temkin).

$$\frac{C_e}{q_e} = \frac{1}{X_m b} + \frac{C_e}{X_m} \quad (3)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4)$$

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \quad (5)$$

The constants b, K_f and K_T are the Langmuir, Freundlich and Temkin isotherm constants, respectively. X_m is the maximum adsorption capacity upon complete coverage of the adsorption sites. $1/n$ is a measure of the surface heterogeneity, with values between 0 and 1, b_T is related to the adsorption intensity, R is the gas constant and T is temperature in Kelvin. Thermodynamic parameter ΔH , ΔG and ΔS are calculated from the variation of Langmuir equation constant, b (L/mol) with change in temperature, T, using equations 6 to 9 (Kim et al., 2005; Krishnan and Airudhan, 2003).

$$\ln b = \ln b' - \frac{\Delta H}{RT} \quad (6)$$

$$\ln b = \frac{-\Delta G}{RT} \quad (7)$$

$$\ln b' = \frac{\Delta S}{R} \quad (8)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (9)$$

The plot of $\ln b$ against $1/T$ is linear and ΔH , ΔS and ΔG can be computed from the slope and intercept of such plots. The coefficient of determination, R^2 measurements were used in this study to ascertain the reliability of this data and best fitting models (Chase and Brown, 1992).

RESULTS AND DISCUSSION

Specific surface area of adsorbents

Calculations from experimental results and sample

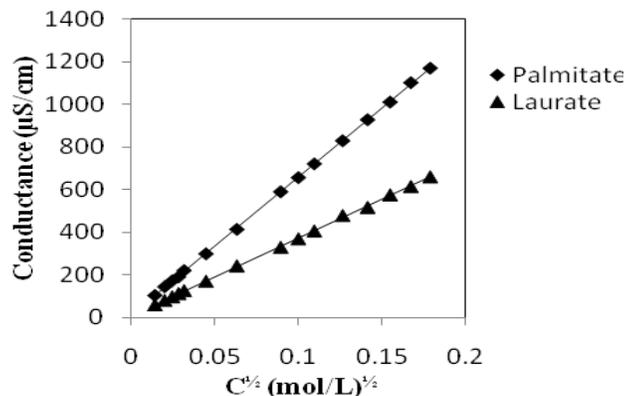


Figure 1. Plot of conductance versus soap concentration.

Table 1. Comparison of coefficient of determination (R^2) For the Isotherms.

Metal ore	Sodium-palmitate adsorption			Sodium-laurate adsorption		
	Langmuir	Freundlich	Temkin	Langmuir	Freundlich	Temkin
Galena	0.9989	0.9552	0.9952	0.9803	0.9471	0.9796
Hematite	0.9971	0.9498	0.9925	0.9977	0.9642	0.9961
Cassiterite	0.9968	0.9067	0.9590	0.9855	0.8582	0.9144

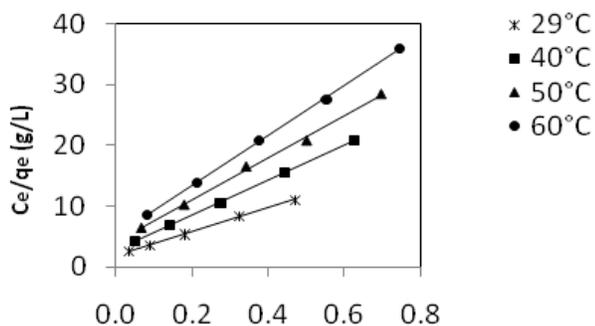


Figure 2. Langmuir isotherms for sodium-palmitate adsorption onto galena at different temperatures and concentrations.

analysis show that the specific surface area of galena is $128.7\text{m}^2/\text{g}$, hematite is $118.5\text{m}^2/\text{g}$ and cassiterite is $88.1\text{m}^2/\text{g}$. These values indicate that the surface area is in the order: galena > hematite > cassiterite. It is expected that if the specific surface area is the primary factor for adsorption, that the adsorption capacity will be greatest for galena. Ho (2006), Horsfall et al. (2004), Horsfall and Abia (2003) reported increased adsorption capacity with increasing surface area in their various studies.

Calibration of conductometer

Plots of the conductance of sodium-palmitate / sodium-

laurate against the square root of initial soap concentrations are linear (Figure 1). This was used for subsequent determination of concentration of the soaps in the various experiments.

Adsorption isotherm

The Langmuir, Freundlich and Temkin isotherm models were considered as possible models to identify the isotherm that best describes the equilibrium adsorption data. The comparison of the coefficient of determination, R^2 , for the three isotherm models is presented in Table 1. From our results, the Langmuir isotherm model with the highest R^2 values best described the adsorption process. This model assumes the formation of monolayer of adsorbate molecules on the adsorbent surface with all adsorption sites being energetically equivalent and that there is no migration or interaction between adsorbed ions on the surface area (Adamson, 1976; Langmuir, 1918). The Langmuir isotherm model was therefore used to analyze our equilibrium data at various temperatures and concentrations and presented in Figures 2 to 4 for sodium-palmitate and Figures 5 to 7 for sodium-laurate. The Langmuir constants X_m (the maximum adsorption capacity upon complete coverage of available adsorption sites), and b (related to energy / intensity of adsorption) for the sodium-palmitate and sodium-laurate adsorption are presented in Tables 2 and 3, respectively. The change in enthalpy, ΔH , Gibbs free energy, ΔG , and entropy, ΔS of adsorption were therefore calculated from

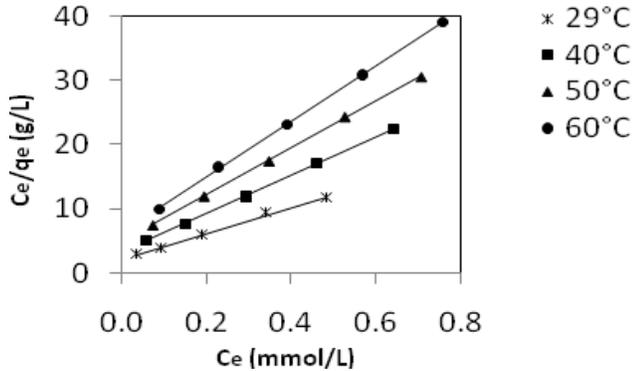


Figure 3. Langmuir isotherms for sodium-palmitate adsorption onto hematite at different temperatures and concentrations.

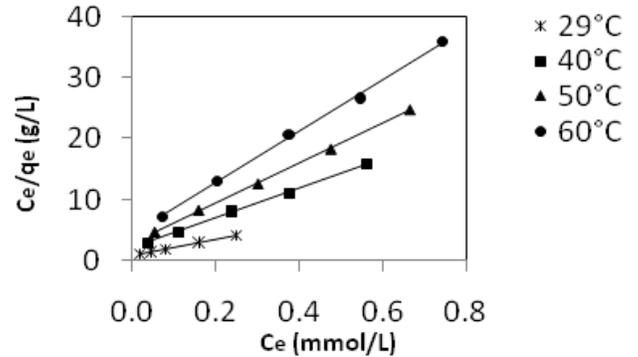


Figure 6. Langmuir isotherms for sodium-laurate adsorption onto hematite at different temperatures and concentrations.

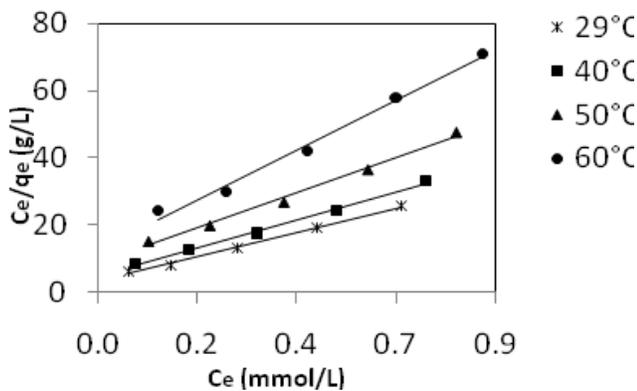


Figure 4. Langmuir isotherms for sodium-palmitate adsorption onto cassiterite at different temperatures and concentrations.

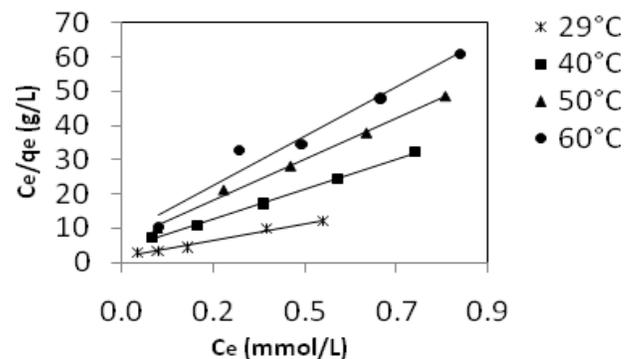


Figure 7. Langmuir isotherms for sodium-laurate adsorption onto cassiterite at different temperatures and concentrations.

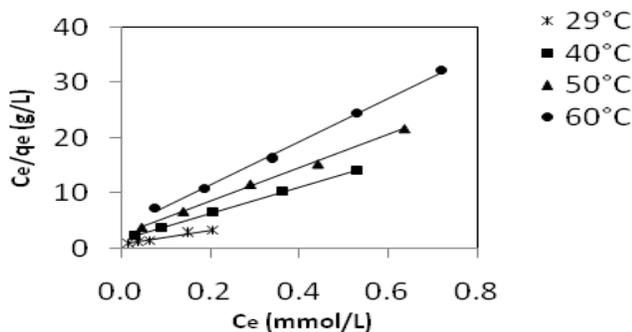


Figure 5. Langmuir isotherms for sodium-laurate adsorption onto galena at different temperatures and concentrations.

the variations of the Langmuir constant, b (L/mol) with change in temperature (Figures 8 and 9 for the sodium-palmitate and sodium-laurate adsorption, respectively) by plotting $\ln b$ versus $1/T$. The values of ΔG , ΔH and ΔS are shown in Table 4.

The negative values of ΔG at 29°C (approximately -23.00 kJ/mol for sodium-palmitate adsorption and -24.00 kJ/mol for sodium-laurate adsorption) indicate that the

adsorption process is to a large extent spontaneous and feasible. The feasibility of the process decreases with increase in temperature judging from the decrease in the values of ΔG with increase in temperature suggesting some structural changes in the adsorbate-adsorbent interaction. Generally, values of ΔG up to -20 kJ/mol are consistent with electrostatic interaction between adsorbate molecules and the adsorbent surface (physical adsorption) while ΔG values more negative than -40 kJ/mol involve charge sharing or transfer from the adsorbate molecules to the adsorbent surface to form a coordinate type of bond which indicates chemical adsorption (Horsfall et al., 2006; Ebenso, 2004). The negative values of ΔH indicate the exothermic nature of the adsorption process which is favoured at low temperature. It is of note that enthalpy change due to chemical adsorption (>40 kJ/mol) is considerably larger than that due to physical adsorption. The ΔG and ΔH values obtained in this study (Table 4) indicate physisorption as the predominant adsorption process.

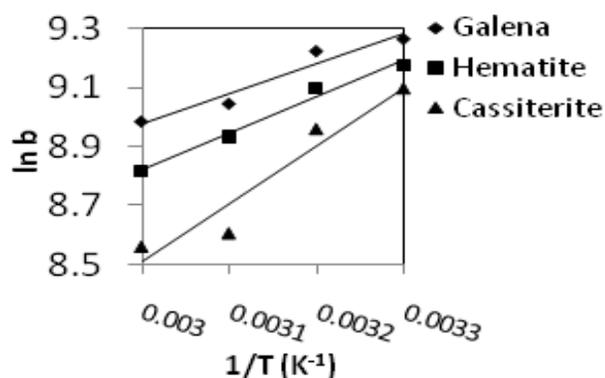
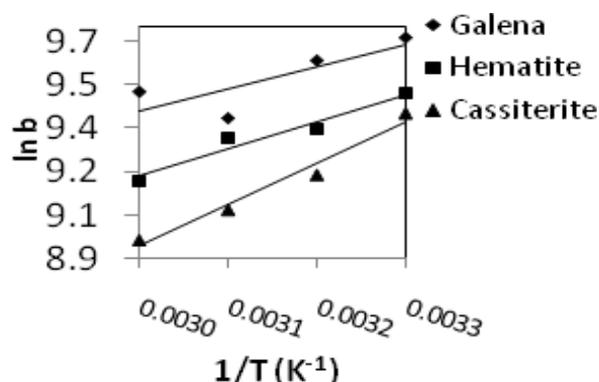
The positive values of ΔS suggest freedom of adsorbate molecules on the adsorbent surfaces confirming predominant physisorption process. In the adsorption processes studied, the values of ΔH and ΔS are higher for the sodium-palmitate when compared to

Table 2. Langmuir constants at different temperatures for sodium-palmitate adsorption.

Temp. (°C)	Galena		Hematite		Cassiterite	
	b (L/mol)	Xm (mmol/g)	b (L/mol)	Xm (mmol/g)	b (L/mol)	Xm (mmol/g)
29	10596.02	0.0506	9674.12	0.0494	8920.61	0.0310
40	10167.38	0.0348	8960.44	0.0336	7772.48	0.0263
50	8494.74	0.0288	7599.19	0.0274	5457.30	0.0210
60	7994.50	0.0242	6763.35	0.0231	5211.02	0.0149

Table 3. Langmuir constants at different temperatures for sodium-laurate adsorption.

Temp. (°C)	Galena		Hematite		Cassiterite	
	b (L/mol)	Xm (mmol/g)	b (L/mol)	Xm (mmol/g)	b (L/mol)	Xm (mmol/g)
29	15746.75	0.0802	12977.58	0.0778	12103.03	0.0467
40	14544.73	0.0423	11480.06	0.0409	9788.57	0.0258
50	11889.72	0.0332	11107.64	0.0306	8690.64	0.0188
60	13039.59	0.0249	9595.36	0.0237	7826.38	0.0156

**Figure 8.** Plot of natural logarithm of langmuir constant at different temperature for sodium-palmitate adsorption.**Figure 9.** Plot of natural logarithm of langmuir constant at different temperature for sodium-laurate adsorption.

that of sodium-laurate. This observation could be due to differences in the molecular structure of the two compounds which are similar with respect to the position of the carboxylate group, but with different numbers of the carbon atoms (the palmitate soap has 16 carbon atoms, while the laurate soap has 12 carbon atoms). This difference in the length of carbon chain could induce a steric effect. The longer chain of the palmitate soap / its bulkier nature may hinder the proper orientation of the soap and thereby decrease the ease of its migration to the active sites which could lead to coverage of fewer adsorption sites, while the laurate soap bearing smaller carbon-chain may diffuse faster in the aqueous medium and thereby enhance higher surface coverage. Also in all the experimental cases, the values of ΔH and ΔS for the adsorbents are in the order: galena > hematite > cassiterite. This trend is consistent with the values of their specific surface area, confirming the importance of surface area in the evaluation of the dynamics and

feasibility of the process for a given application.

Conclusion

This study has demonstrated that the sodium-palmitate and sodium-laurate adsorption onto galena, hematite and cassiterite in aqueous phase is feasible. Results obtained show that our data fits the Langmuir isotherm model suggesting the formation of monolayer with energetically equivalent adsorption sites and with no lateral interaction between the adsorbed molecules on the adsorbent surface. Thermodynamic data analysis revealed that the adsorption process is spontaneous, exothermic, physical in nature and related to the specific surface area of the adsorbent. Our results suggest that the locally produced soaps can be exploited as collector reagents in designing an appropriate froth flotation system for harnessing galena, hematite and cassiterite from their ores.

Table 4. Thermodynamic parameters for the adsorption processes.

Adsorbent	ΔH (kJ/mol)	ΔG at 29°C (kJ/mol)	ΔS (J/K/mol)
Galena (sodium-palmitate)	-8.52	-23.34	49.08
Hematite (sodium-palmitate)	-10.30	-23.12	42.46
Cassiterite (sodium-palmitate)	-16.35	-22.90	21.70
Galena (sodium-laurate)	-6.38	-24.23	59.11
Hematite (sodium-laurate)	-7.81	-23.80	52.95
Cassiterite (sodium-laurate)	-11.86	-23.57	38.76

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