

Relationship of Structure to Properties of Some Anionic Surfactants as Collectors in the Flotation Process. 1. Effect of Chain Length

N. A. Abdel-Khalek*

Central Metallurgical Research and Development Institute, P.O. Box 87 Helwan, Cairo, Egypt

A. M. A. Omar and Y. Barakat

Egyptian Petroleum Research Institute, Cairo, Egypt

The surface and thermodynamic properties of some synthetic surfactants, as well as their efficiency as collectors in the flotation of petroleum coke, are studied. These surfactants are monoisomeric alkylbenzenesulfonate of different alkyl chains (C12 to C14). The results show that the length of the hydrocarbon chain of these surfactants plays a major role in determining their surface and thermodynamic properties. The values of surface excess concentration (Γ_{\max}) and Gibbs energy of micellization ($\Delta G^{\circ}_{\text{mic}}$) are found to increase with increasing number of carbon atoms in the chain while the values of critical micelle concentration (cmc) are decreased. The results indicate, also, that there is a good relationship between effectiveness of adsorption of a surfactant and its efficiency as a collector. A surfactant of higher Γ_{\max} produces a concentrate of lower ash content and higher flotation yield. Thus, the surfactant with longer alkyl chain (C14) and highest Γ_{\max} value is more selective, as a collector, than others of shorter carbon chain.

Introduction

The mineral industry requires the use of a wide variety of reagents for its operation. These reagents are commonly used as flotation surfactants, grinding aids, flocculants, and dewatering aids. However, flotation surfactants predominate over any other mineral industry chemicals because the flotation process has become the single most important method for separation of minerals from ores.

In flotation practice, mineral selectivity can be achieved through the addition of various reagents that can control the wettability of particular minerals in an ore in the flotation pulp. Flotation reagents are commonly classified into collectors, activators, depressants, frothers, and modifiers. Collectors are surface-active organic reagents that adsorb at the surface of the desired mineral so that it becomes hydrophobic and in turn it can attach to an air bubble. Flotation collectors include reagents such as thiol compounds, alkyl carboxylates, alkyl sulfates, alkylsulfonates, alkyl phosphates, amines, chelating agents, and alkyl phosphonic acids (Fuerstenau and Urbina, 1988).

Selection of a collector (surfactant) with the right structure can greatly enhance selective flotation in any number of practical flotation separations (Smith, 1989). The surface-active properties of a collector are therefore determined, among other things, by its numerous structural characteristics, which include the following (Smith, 1987): (a) the length and number of hydrocarbon chains in the structure, (b) the configuration of the chain or chains including branching and the number and location of double bonds in the chains, (c) the number, type (anionic or cationic), and cross-sectional area of the polar ionic group in the struc-

ture, (d) the position of the ionic group(s) in the structure, (e) the number and nature of nonionic hydrophilic group(s) in the structure, and (f) the presence, position, and type of cyclic group(s) in the structure (Omar and Abdel-Khalek, 1998; Smith, 1989).

As part of a study of the relationships between the chemical structure of well-purified surfactants and their surface and thermodynamic properties, a number of sulfonate surfactants with different hydrocarbon chains, and a benzene ring attached at carbon atom number four, are synthesized and their properties are investigated. These surfactants are monoisomeric alkylbenzenesulfonates. They have the following alkyl chains: 4-phenyldodecylsulfonate (4 ϕ C12), 4-phenyl tridecylsulfonate (4 ϕ C13) and 4-phenyltetradecylsulfonate (4 ϕ C14). The properties of these surfactants are correlated with their efficiency as collectors in the flotation of petroleum coke to be suitable for electrode manufacture.

Materials and Methods

Preparation and Characterization of Surfactants.

Three anionic surfactants of sodium salt of monoisomeric alkylbenzenesulfonate were prepared according to recommended procedures as follows (El-Mergawy, 1988; Omar, 1994):

A tertiary carbinol ($\phi\text{RR}'\text{C}-\text{OH}$) of the required chain length was prepared, using alkylphenyl ketone (ϕRCO) and alkylmagnesium bromide ($\text{R}'\text{MgBr}$), where R was C_3H_7 and R' varied between C_8H_{17} and $\text{C}_{10}\text{H}_{21}$. The product (tertiary carbinol) was subjected to a hydrogenation process, using Pd/C in glacial acetic acid, to form linear alkylbenzene ($\phi\text{RR}'\text{CH}$). The latter product was subjected to a sulfonation process, using fuming H_2SO_4 , and a neutralization step, with NaOH, to produce the sodium salt of alkylbenzenesulfonates.

* To whom correspondence should be sent. Current address: Department of Materials Science and Engineering, Engineering Research Center for Particle Science and Technology, University of Florida, Gainesville, FL 32611. E-mail: nagui@ufl.edu.

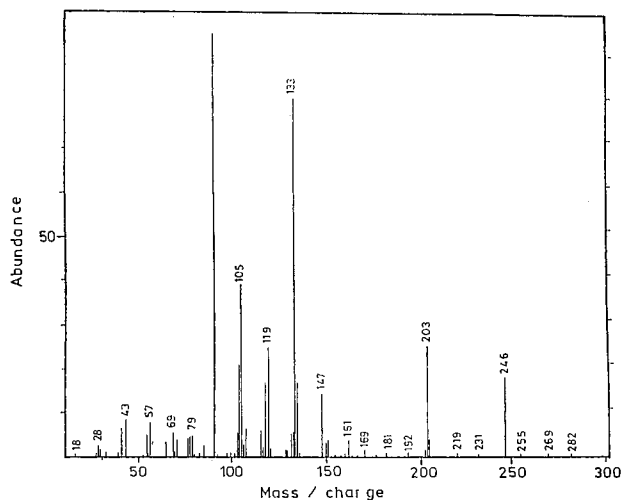


Figure 1. Mass spectrum of 4-phenyldodecane: X-axis, mass/charge; Y-axis, abundance.

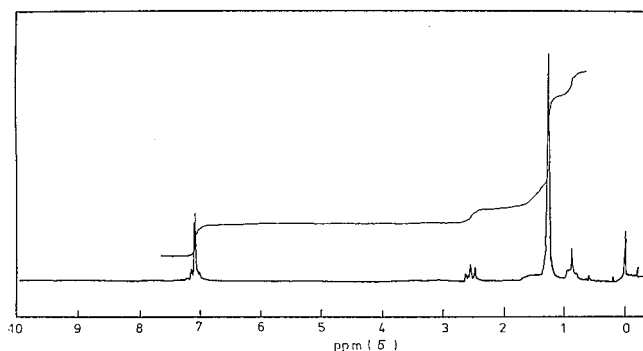


Figure 2. NMR spectrum of 4-phenyldodecane: X-axis, ppm (δ).

Purification of the prepared surfactants was carried out as follows:

(a) Desalting step to remove any traces of hydroxide or organic sulfate. This was performed by shaking the surfactant-2-propanol solution in 250 mL of 30% NaCl solution.

(b) Deoiling step by shaking with 150 mL of *n*-pentane followed by the addition of 25–50 mL of water to facilitate the separation of two layers. The upper layer consisted of *n*-pentane contaminated with unsulfonated alkylbenzene, while the lower layer contained surfactant-2-propanol-water solution. The 2-propanol-water fraction was distilled off at a reduced pressure to obtain the pure sodium alkylbenzenesulfonate (Omar, 1994).

The prepared surfactants had different alkyl chains (4 ϕ C12, 4 ϕ C13, and 4 ϕ C14, i.e., sodium salts of 4-phenyldodecylsulfonate, 4-phenyltridecylsulfonate, and 4-phenyltetradecylsulfonate, respectively). Before sulfonation, the structure of the prepared linear dodecyl-, tridecyl-, and tetradecylbenzene was verified from IR, NMR, and mass spectroscopic measurements (Omar, 1994). Mass, NMR, and IR spectra of 4-phenyldodecane, as a representative compound, are shown in Figures 1–3.

Mass spectra was recorded on CED-Du Pont 12-491 mass spectrometer. Figure 1 shows the fragmentation pattern of 4-phenyldodecane. The NMR spectra was measured using a Varian associates model A-60 spectrometer. Figure 2 shows the NMR spectrum of 4-phenyldodecane. Two major resonance bands are apparent. The first at the lower field arises from the hydrogen atoms on the aromatic ring, while the second band at higher field is produced by the hydrogen of the alkyl chain. On the other hand, the IR

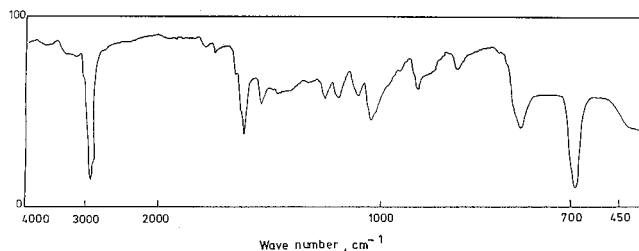


Figure 3. IR spectrum of 4-phenyldodecane: X-axis, wavenumber, cm^{-1} .

Table 1. Chemical Analysis of the Petroleum Coke Sample

| constituents | % | constituents | % |
|-----------------|-------|---------------|-------|
| ash | 1.38 | fixed carbon | 87.20 |
| volatile matter | 14.50 | sulfur | 4.2 |
| nitrogen | 2.0 | | |
| metal content | ppm | metal content | ppm |
| V | 500 | Ti | 14 |
| Si | 410 | Cu | 11 |
| Ni | 380 | Cr | 9 |
| Na | 130 | Mo | 2 |
| Ca | 110 | Co | 1 |
| Fe | 83 | | |

spectrum of 4-phenyldodecane is shown in Figure 3. The intense band at 3000 cm^{-1} is found to be due to the carbon-hydrogen stretching of aromatic protons. The bands between 3000 and 2800 cm^{-1} are found to be associated with aliphatic carbon-hydrogen stretching. The low-intensity bands in the region from 2000 to 1600 cm^{-1} are due to overtones and combination frequencies of aromatic hydrogen vibrations. The band at 760 cm^{-1} is due to the out-of-plane bending of five adjacent hydrogen atoms on the aromatic ring.

Preparation and Characterization of Petroleum Coke Sample. A technological sample of the Belayim petroleum coke, Egypt, was kindly supplied by the Suez Refining Co. The sample was obtained by thermal cracking of heavy petroleum oil. It had a high percentage of aromatics, other cyclic compounds, and asphaltene components. The structure of this type of coke was characterized by a needle-shaped structure with wide unidirectional voids. Yard sampling of thoroughly mixed ore was carried out by coning and quartering methods. Ore pulverization was carried out using a "Wedag" jaw crusher in closed circuit with a 25 mm screen. This was followed by secondary crushing in a "Denver" roll crusher to 100% below 0.5 mm. The product was then dry screened on 0.063 mm sieve the undersize of which was rejected. The fraction $-0.5 + 0.063\text{ mm}$ (representing about 97.5 wt % of the sample) was then subdivided, after thoroughly mixing, into 0.5 kg batches and was stored in closed container as a flotation feed. The chemical analysis of the flotation feed showed that it contains about 87.2% fixed carbon and 14.5% volatile matter. The ash content was 1.38%, while the total sulfur was 4.2%. Ni, V, Si, Ca, and Na were the major (110–500 ppm) metallic inclusions of the coke, whereas Fe, Co, Mo, and Cu were present in minor (1–83 ppm) concentrations as shown in Table 1.

Flotation Experiments. The flotation tests were carried out using a laboratory "Denver D12" flotation cell, with a 5 L container, at 10% solids and at room temperature ($\sim 25^\circ\text{C}$). The sample was conditioned at 1500 rpm with sodium silicate, as an ash depressant, for 5 min. This was followed by another 5 min for conditioning with the surfactant before aeration. The pH was maintained constant at pH 7

Table 2. Effect of Changing the Chain Length on the Surface Properties of the Prepared Surfactants at 25 ± 0.1 °C

| compd | CMC/ 10 ⁻² × mol·L ⁻¹ | γ _{cmc} / mN·m ⁻¹ | Γ _{max} × 10 ⁶ / mol·m ⁻² | A° × 10 ² / nm ² ·molecule ⁻¹ | Π _{cmc} / mN·m ⁻¹ | pC ₂₀ |
|-------|--|--|---|---|--|------------------|
| 4φC12 | 122.8 | 27.84 ^a | 3.435 | 48.338 | 44.14 | 5.143 |
| 4φC13 | 76.3 | 28.42 ^a | 5.208 | 35.215 | 28.42 | 5.021 |
| 4φC14 | 31.6 | 28.07 ^a | 7.235 | 22.950 | 28.07 | 5.081 |

^a ±0.1.

during flotation tests using H₂SO₄ or NaOH (BDH products). The flotation speed was kept constant at 1200 rpm. The froth (concentrate) and the tail fractions were collected, dried, weighed, and analyzed.

Surface Tension Measurements. These measurements were carried out using a "Dagnon Abribot" tensiometer, and the points of intersection were determined using a linear regression analysis technique (Drapper and Smith, 1968). The uncertainties in the measurements of surface tension, temperature, and concentration of surfactants were 0.10, 0.10, and 0.001% respectively. From the surface tension–concentration isotherm, the other surface properties and thermodynamic parameters of surfactants were calculated (Rosen et al., 1982; Abdel-Khalek et al., 1997). Maximum surface excess concentration (Γ_{max}), in mol·m⁻², and area per molecule (A_{min}), in nm², at the aqueous–air interface were calculated from the relationships

$$\Gamma_{\max} = (1/2.303)RT(-d\gamma/d \log C)_T \quad (1)$$

$$A_{\min} = 10^{14}/N\Gamma \quad (2)$$

where $(-d\gamma/d \log C)_T$ is the slope of the γ –log C plot at constant temperature, T , $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, and N is Avogadro's number.

The values of Γ_{max} were taken as a measure for the effectiveness of adsorption of the surfactants at liquid–gas and liquid–solid interfaces (Rosen, 1989).

The surface pressure at the cmc (Π_{cmc}) was calculated from the relationship

$$\Pi_{\text{cmc}} = \gamma_0 - \gamma_{\text{cmc}} \quad (3)$$

where γ₀ is the surface tension of water at zero surfactant concentration and γ_{cmc} the surface tension of the solution at the cmc.

The values of Π_{cmc} were taken as a measure for the effectiveness of surface tension reduction (Rosen, 1989).

The efficiency (pC₂₀) of the surfactant is calculated from the relationship

$$\text{pC}_{20} = \log 1/C_{\Pi=20} \quad (4)$$

where C_{Π=20} is the bulk molar concentration required to reduce the surface tension by 20 mN/m.

Using the cmc values, the Gibbs energy change upon micellization was calculated from the following equation

$$\Delta G^{\circ}_{\text{mic}} = RT \ln \text{cmc} \quad (5)$$

while the Gibbs energy of adsorption was calculated from the following equation (Rosen et al., 1982; Abdel-Khalek et al., 1997):

$$\Delta G^{\circ}_{\text{ad}} = \Delta G^{\circ}_{\text{mic}} - \Pi_{\text{cmc}} A_{\text{cmc}} \quad (6)$$

Results and Discussion

Surface Properties of the Prepared Surfactants.

Table 2 shows the results of changing the length of the hydrocarbon chain of surfactants on their surface proper-

ties. The length of the hydrophobic chain is changed from C₁₂ to C₁₄, while a phenyl group is fixed at carbon number 4. It is clear that the value of critical micelle concentration (cmc) for these surfactants decreases significantly, from 122.8 × 10⁻² to 31.6 × 10⁻² mol·L⁻¹, with increasing the length of hydrophobic chain from C₁₂ to C₁₄. This behavior is similar to that of all known ionic and nonionic surfactants in aqueous media (Rosen, 1989). This decrease in the cmc with increasing chain length is a result of the lower solubility of the longer chain surfactants. The reduction in solubility promotes the formation of micelles. When the number of carbon atoms in the straight-chain hydrophobic group exceeds 15, the water solubility of most surfactants decreases and the cmc values remain substantially unchanged (Rosen, 1989).

In the meantime, the surface excess concentration at surface saturation (Γ_{max}) is a useful measure of the effectiveness of adsorption of the surfactant at the liquid–gas or liquid–liquid interface, since it is the maximum value to which adsorption can attain. The effectiveness of adsorption is an important factor in determining the properties of surfactants such as foaming, wetting, and emulsification, since tightly packed coherent interfacial films have different interfacial properties than loosely packed, noncoherent films (Rosen, 1989). The calculated values of Γ_{max} for the prepared surfactants are changed from 3.435 × 10⁶ to 7.235 × 10⁶ mol·m⁻² with increasing the carbon chain from 12 to 14 (Table 2). Some authors have mentioned that a change in the length of the hydrophobic group of straight chain ionic surfactants beyond 10 carbon atoms appears to have almost no effect on the effectiveness of adsorption at the aqueous solution–heptane interface and little effect on the effectiveness at the aqueous solution–air interface (Rosen, 1989).

Effectiveness of surface tension reduction, Π_{cmc}, is usually considered to depend on the cohesiveness of the collector molecules (low cohesiveness means high effectiveness), since surface tension reduction requires the presence of molecular dispersed collector molecules at the surface. Comparison of the effectiveness of the prepared monoisomeric sulfonate collectors, given in Table 2, with those reported in the literature (Rosen, 1989; Dahanayaka et al., 1986) of similar carbon chains and hydrophilic head shows that they have a fairly good effectiveness compared with most surfactants of similar efficiency.

Effect of Temperature on the Surface Properties of the Prepared Surfactants. It is well-known that the cmc values of all known ionic surfactants increase with increasing temperature (Rosen, 1989; Abdel-Khalek et al., 1997). With this fact in mind and from the data in Table 3, it is obvious that the cmc values of the investigated sulfonates increase slightly with increasing temperature from 25 to 55 °C. For example, increasing the temperature for the surfactant containing 14 carbon atoms from 25 to 55 °C increases its cmc from 31.6 × 10⁻² to 39.4 × 10⁻² mol·L⁻¹. Consequently, no drastic changes are expected in the behavior of these collectors, within this range of temperature, i.e., during the flotation process. The insignificant influence of temperature variation on γ_{cmc} values shown

Table 3. Effect of Temperature on the Surface Properties of the Prepared Surfactants

| | $t^a/^\circ\text{C}$ | 4 ϕ C12 | 4 ϕ C13 | 4 ϕ C14 |
|--|----------------------|--------------------|--------------|--------------|
| $\text{CMC} \times 10^{-2}/\text{mol}\cdot\text{L}^{-1}$ | 25 | 122.8 | 76.3 | 31.6 |
| | 35 | 124.3 | 79.6 | 31.6 |
| | 45 | 129.6 | 83.3 | 36.0 |
| | 55 | 132.2 | 87.5 | 39.4 |
| $\gamma_{\text{cmc}}/\text{mN}\cdot\text{m}^{-1}$ | 25 | 27.84 ^b | 28.42 | 28.07 |
| | 35 | 27.31 ^b | 27.93 | 27.60 |
| | 45 | 26.65 ^b | 26.89 | 27.08 |
| | 55 | 25.80 ^b | 26.77 | 26.60 |
| $\Gamma_{\text{max}} \times 10^6/\text{mol}\cdot\text{m}^{-2}$ | 25 | 3.435 | 5.208 | 7.235 |
| | 35 | 2.863 | 3.682 | 4.018 |
| | 45 | 2.787 | 3.208 | 3.383 |
| | 55 | 2.610 | 2.789 | 2.977 |
| $A^0 \times 10^2/\text{nm}^2\cdot\text{molecule}^{-1}$ | 25 | 48.338 | 76.3 | 31.6 |
| | 35 | 57.986 | 79.6 | 31.6 |
| | 45 | 63.614 | 83.3 | 36.0 |
| | 55 | 69.969 | 87.5 | 39.4 |
| $\Pi_{\text{cmc}}/\text{mN}\cdot\text{m}^{-1}$ | 25 | 44.14 | 28.42 | 28.07 |
| | 35 | 39.69 | 27.93 | 27.60 |
| | 45 | 38.36 | 26.89 | 27.08 |
| | 55 | 37.21 | 26.77 | 26.60 |
| pC ₂₀ | 25 | 5.143 | 5.021 | 5.081 |
| | 35 | 5.146 | 5.138 | 5.318 |
| | 45 | 5.188 | 5.162 | 5.313 |
| | 55 | 5.143 | 5.179 | 5.281 |

^a ± 0.1 . ^b ± 0.1 .

in Table 3 indicates that both cmc and γ_{cmc} are solubility-dependent properties.

For ionic surfactants, it is well-known that factors that cause an increase in solubility with temperature (reflected in most cases by an increase in cmc) also work to decrease the effectiveness of adsorption, Γ_{max} (Rosen, 1989; Dahanayaka et al., 1986). For the employed sulfonates, Γ_{max} decreases with increasing temperature but their cmc values increase. For example, the 4 ϕ C12 sulfonate collector has Γ_{max} values of 3.435, 2.863, 2.787, and 2.610 ($\text{mol}\cdot\text{m}^{-2} \times 10^6$) at 25, 35, 45, and 55 $^\circ\text{C}$, respectively. For collectors of the same basic structure, the decrease in Γ_{max} becomes more pronounced by increasing the chain length of the hydrophobic tail. It can be seen from the data in Table 3 that, within the same temperature range, the Γ_{max} value decreases from 5.208 to 2.789 and from 7.235 to 2.977 ($\text{mol}\cdot\text{m}^{-2} \times 10^6$) for 4 ϕ C13 and 4 ϕ C14, respectively.

It is also seen from Table 3 that an increase in temperature results in an increase in A_{min} presumably owing to the increased thermal motion. The calculated efficiency and effectiveness values for the employed sulfonate collectors are also presented in Table 3. Insignificant changes have been observed in these values by changing temperature from 25 to 55 $^\circ\text{C}$, since temperature has a rather minor effect on these quantities. For instance, the 4 ϕ C12 sulfonate collector has effectiveness values of 44.14, 39.69, 38.36, and 37.21 at 25, 35, 45, and 55 $^\circ\text{C}$, respectively. This collector has efficiency values of 5.143, 5.146, 5.188, and 5.143 at the same temperatures, respectively. Many investigators (Rosen, 1989) have reached a general conclusion that increasing effectiveness tends to decrease efficiency and vice versa.

Some Thermodynamic Parameters of the Prepared Surfactants. Table 4 depicts the results of calculation of both the Gibbs energy of micelle formation (ΔG_{mic}) and Gibbs energy of adsorption (ΔG_{ad}) for surfactants at different temperatures. It is clear that ΔG_{mic} appears to become more negative with increasing temperature from 25 to 55 $^\circ\text{C}$ regardless of the length of the hydrophobic alkyl group in the surfactant. This may be attributed to the fact that the amount of water structured by the hydrophobic

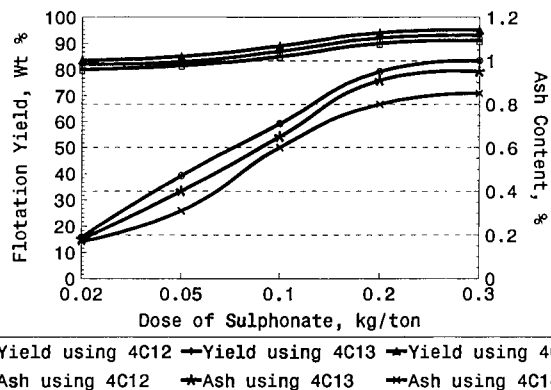


Figure 4. Effect of changing the dosage of the surfactants of different alkyl chain lengths on percent ash and yield of concentrates: X-axis, dose of surfactant, $\text{kg}\cdot\text{ton}^{-1}$; Y1-axis, flotation yield %; Y2-axis, ash content %. □, yield % using C12; ◆, yield % using C13; ▲, yield % using C14; ○, ash % using C12; *, ash % using C13; × ash % using C14.

Table 4. Some Thermodynamic Parameters of the Prepared Surfactants

| | $t^a/^\circ\text{C}$ | 4 ϕ C12 | 4 ϕ C13 | 4 ϕ C14 |
|---|----------------------|--------------|--------------|--------------|
| $\Delta G_{\text{mic}}/\text{kJ}\cdot\text{mol}^{-1}$ | 25 | -32.28 | -33.51 | -35.64 |
| | 35 | -33.77 | -34.70 | -36.84 |
| | 45 | -35.17 | -35.92 | -37.69 |
| | 55 | -37.09 | -36.31 | -38.63 |
| $\Delta G_{\text{ad}}/\text{kJ}\cdot\text{mol}^{-1}$ | 25 | -45.13 | -43.25 | -41.07 |
| | 35 | -48.83 | -45.89 | -46.64 |
| | 45 | -51.70 | -47.96 | -48.90 |
| | 55 | -50.44 | -50.64 | -50.85 |

^a ± 0.1 .

chain and the amount of water bound by the sulfonate headgroup in the nonmicellar species decrease with increasing temperature (Rosen, 1989). ΔG_{mic} values become significantly more negative with increasing the length of the alkyl chain from C12 to C14. This may indicate that the amount of water, structured by the tail group, decreases with increase of collector hydrophobicity.

The data in Table 4 reveal also that ΔG_{ad} values are negative. These negative ΔG_{ad} values indicate that adsorption of these collectors at the aqueous solution-air and the aqueous solution-solid interfaces is spontaneous (Rosen, 1989). In the flotation process, properties that deal with the adsorption of collector molecules at aqueous solution-solid interfaces are highly considered.

Flotation Efficiency of the Prepared Alkylbenzene-sulfonates. Optimization of different operating parameters that affect floatability of Egyptian petroleum coke has been conducted before, using the surfactant 4 ϕ C12 as a collector (Abdel-Khalek et al., 1997). The optimum conditions are as follows: pH 7, dosage of sodium silicate, as a depressant for the gangue fraction, $1.0 \text{ kg}\cdot\text{ton}^{-1}$, and pulp density 10 wt %. These conditions are applied to study the efficiency of the prepared surfactants as collectors in the flotation process. The dosage of surfactants is changed from 20 to $300 \text{ g}\cdot\text{ton}^{-1}$. Figure 4 illustrates the effect of changing dosage of surfactants on their efficiency to reduce percent ash content. The results indicate that the ash content decreases from 1.38% in the feed samples to 0.45%, 0.40%, and 0.35% in the concentrates obtained by using just $50 \text{ g}\cdot\text{ton}^{-1}$ of 4 ϕ C12, 4 ϕ C13, and 4 ϕ C14, respectively. It can be seen that the selectivity of separation improves with application of the surfactant of longer chain C14 as a collector. Similar results have been mentioned by other authors in flotation of alumina with some alkylbenzene-

sulfonates where their adsorption is found to increase with increasing chain length from 8 to 14 (Somasundaran et al., 1984). On the other hand, higher recovery of concentrates, at the expense of their quality, have been obtained by increasing collector dosage. Flotation of the coke sample using small dosage ($20 \text{ g}\cdot\text{ton}^{-1}$) of any of these surfactants gives the best selectivity where concentrates of only 0.15–0.20% ash content, with percent ash removal of 87.7–91.3%, are obtained. From Figure 4 it may be concluded that sodium 4 ϕ C14 sulfonate, among the investigated anionic surfactants, is more selective as a collector since it gives a concentrate of the highest recovery and lowest ash content. It seems that the separation process, in terms of grade and recovery, improves with application of the surfactant of longer chain, C14, as a collector.

The results in Figure 4 indicate, also, that the three surfactants behave, in general, similarly with a slight increase in process recovery with increasing the chain length of collector. For example, at a fixed dosage of $20 \text{ g}\cdot\text{ton}^{-1}$, the 4 ϕ C14 sulfonate collector gives a concentrate having an ash content of 0.18% with a yield of 83.12% as compared with 0.19% ash content and 80.0% recovery in case of 4 ϕ C12 collector. In fact, this is in agreement with the results of surface properties of these collectors, which show that the differences in the values of surface tension, γ_{cmc} , and efficiency of surface tension reduction pC_{20} are very small (Table 2).

However, the relatively higher effectiveness of adsorption, Γ_{max} , of collector 4 ϕ C14 than 4 ϕ C12 (and the less surface area occupied by a single molecule of the former) may be in favor of such slightly better flotation results obtained with this collector of longer chain length. In the meantime, the more negativity of Gibbs energy of micellization, ΔG_{mic} , of this surfactant as compared with others should be taken into consideration. The general trend of increasing floatability with increasing the negativity of Gibbs energy of other surfactants has been reached before (Abdel-Khalek et al., 1997; Omar, 1994).

Chemical analysis of the obtained concentrates indicates that the carbon content is significantly improved to $\sim 96.1\%$ in comparison with 87.2% in the feed. This clearly confirms the good selectivity obtained in the flotation process while using such prepared surfactants. This, also, may encourage their application as collectors in the flotation of other minerals.

Conclusions

For the employed anionic collectors, factors that cause an increase in water solubility are indicated by an increase in cmc and also work to decrease the effectiveness of adsorption (Γ_{max}) at the liquid–solid interface.

For the prepared surfactants, each having the same basic structure, increasing the chain length of the hydrophobic tail enhances their tendency for adsorption at the interface, i.e., increases Γ_{max} values.

For sodium alkylbenzenesulfonate collectors, ΔG_{mic} appears to become more negative with increasing temperature regardless of tail length. Meanwhile, the negative ΔG_{ad} values of these collectors indicate that the adsorption of such collectors, at the interface, is spontaneous.

The required dosage of these surfactants for flotation of an Egyptian petroleum coke sample is small ($\sim 20 \text{ g}\cdot\text{ton}^{-1}$). Flotation of the coke sample using a small dosage of any of these surfactants, and in the presence of $1 \text{ kg}\cdot\text{ton}^{-1}$ of sodium silicate at pH 7, gives the best selectivity where concentrates of only 0.15–0.20% ash content, with percent ash removal of 87.7–91.3%, are obtained from a feed containing 1.38% ash content.

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