Surface and Thermodynamic Parameters of Some Cationic Surfactants

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Three cationic surfactants were prepared by condensing 1-chlorododecane with stoichiometric amounts of either mono-, di-, or triethanolamine. They are: *N*-dodecyl-*N*-mono(hydroxyethyl)ammonium chloride, *N*-dodecyl-*N*,*N*-bis(hydroxyethyl)ammonium chloride, and *N*-dodecyl-*N*,*N*,*N*-tris(hydroxyethyl)ammonium chloride. The surface and thermodynamic properties of these surfactants were investigated to find the relationship between the structure of the hydrophilic portion of such compounds and their efficiency as collectors in the flotation process. The properties studied included surface excess concentration (Γ_{max}), critical micelle concentration (cmc), free energy of micellization ($\Delta G°_{mic}$), and adsorption ($\Delta G°_{ads}$) in addition to the surface tension (γ_{cmc}) at the cmc, effectiveness (Π_{cmc}), and efficiency ($_{p}C_{20}$) of a surfactant to reduce the surface tension of water. The effect of temperature on surface and thermodynamic properties was investigated by making measurements at 25, 35, 45, and 55 °C. The results showed that the number of the hydrophilic portions of the prepared cationic surfactants plays a major role in determining their thermodynamic properties. The values of Γ_{max}, $\Delta G°_{mic}$, and $\Delta G°_{ads}$ were found to increase with increasing number of ethanol groups substituted on the nitrogen atom, from one to three, while cmc and surface area occupied by one molecule (A_{max}) were decreased. The results suggest that the surfactant *N*-dodecyl-*N*,*N*,*N*-tris(hydroxyethyl)ammonium chloride may be preferable as a flotation collector to the other surfactants having a lower number of ethanol groups.

Introduction

Development of new flotation technologies is necessary in view of the limitation of sources of mineral raw materials and the need to treat low-grade ores, especially those that are fine, more complex mineralogically, and more refractory. The difficulties arise when a particular mineral has to be separated from an ore of complex composition or low grade or when the surface properties of the mineral are such as to make the flotation response extremely poor. To overcome this basic drawback in ore flotation, the possibility of using new chelating, modifying agents and/or new surfactants with a strong affinity for minerals themselves has been investigated (Usoni et al. 1971; Nagaraj and Somasundaran, 1981; Nagaraj, 1982; Marabini et al. 1988, 1989).

Thus, the selection of a collector (surfactant) with the correct 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 (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 structure, (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 (Smith, 1987, 1989).

The performance of surfactants in most interfacial process depends mainly on its concentration and orientation at the interface. The modification of the lyophobic and lyophilic groups, in the structure of the surfactant, may become necessary to maintain surface activity at a suitable level. The adsorption of the surfactant at the air−liquid interfaces has been largely recognized to be of great importance from the practical and theoretical points of view (Smith, 1989). The knowledge of thermodynamic parameters of micellization such as $\Delta G°_{mic}$, $\Delta H°_{mic}$, and $\Delta S°_{mic}$ may assist in developing an understanding of the performance of these surfactants as collectors before their application in the flotation processes.

In this paper, three types of cationic surfactants were prepared in the laboratory. They have the same hydrophobic portion but are different in their hydrophilic groups. The surface and thermodynamic properties of these surfactants are determined to evaluate their efficiency as collectors in the flotation process.

Materials and Methods

Three cationic surfactants were prepared by condensing stoichiometric amounts of either mono-, di-, or triethanolamine in aqueous alcohol with 1-chlorododecane (Omar, 1994). The unreacted compound was removed by extraction with petroleum ether (40−60 °C). Each of the pure condensed products was obtained after vacuum evaporation of the solvent used. These products are: *N*-dodecyl-*N*-

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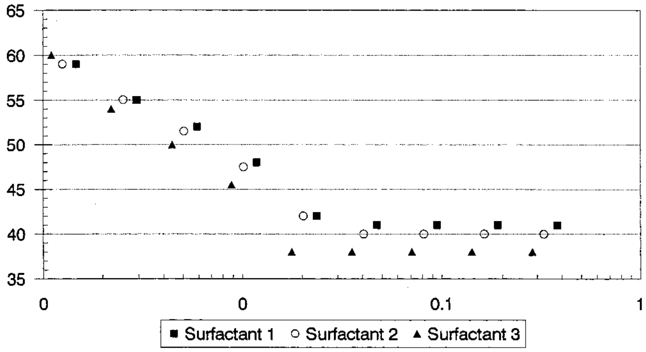

Figure 1. Surface tension as a function of concentration for different surfactants at 25 °C. Number of ethyl groups attached to the N-atom: ■, one; ○, two; ▲, three). *X*-axis: *C*/mol·L^{-1}. *Y*-axis: γ/mN·m^{-1}.

mono(hydroxyethyl)ammonium chloride, *N*-dodecyl-*N*,*N*-bis(hydroxyethyl)ammonium chloride, and *N*-dodecyl-*N*,*N*,*N*-tris(hydroxyethyl)ammonium chloride. The reactions of the preparation process for such surfactants can be represented as follows:

$$H_{25}C_{12}Cl + HOCH_2CH_2NH_2 \rightarrow [H_{25}C_{12}{-}N^{+}H_2{-}C_2H_4OH]Cl^{-}$$

$$H_{25}C_{12}Cl + (HOCH_2CH_2)_2NH \rightarrow [H_{25}C_{12}{-}N^{+}H{-}(C_2H_4OH)_2]Cl^{-}$$

$$H_{25}C_{12}Cl + (HOCH_2CH_2)_3N \rightarrow [H_{25}C_{12}{-}N^{+}{-}(C_2H_4OH)_3]Cl^{-}$$

Surface tension (γ) measurements were carried out using a "Dognon−Abribot" tensiometer, and the points of intersection (cmc) were determined using the linear regression analysis technique (Drapper and Smith, 1968). From the surface tension−concentration isotherm, other surface properties and thermodynamic parameters of the surfactants were calculated at four different temperatures. The amount of material adsorbed per unit area at the interface is calculated indirectly from the surface tension measurements as a function of equilibrium concentration of surfactant in the liquid phase by applying the Gibbs absorption equation (Leja, 1982; Jaycock and Parfitt, 1981; Gendy et al., 1994). The uncertainties in the measurements of surface tension, temperature, and concentration of surfactants are 0.10, 0.10, and 0.001%, respectively.

Results and Discussion

Effect of the Number of the Hydrophilic Groups of the Surfactants on Their Surface Tension and cmc. Figure 1 depicts the effect of changing the concentration of different surfactants on their surface tension at constant temperature (25 °C). These results show that, for each type of surfactant, there is a gradual decrease in the surface tension with increase in concentration for solutions up to a certain level above which a nearly constant value was obtained. Such constant values of surface tension are found to be at 41, 40, and 38 mN·m^{-1} for the surfactants containing one, two, and three ethanol groups attached to their N-atom, respectively. The concentration of surfactant at which the surface tension starts to increase suddenly from its constant value to a higher one is known as the critical micelle concentration (cmc). This value is obtained from measurement by analysis using the least-squares method, to determine the point of intersection of the two lines for each series of experiments. The values of the cmc are 4.55 × 10^{-2}, 3.56 × 10^{-2}, and 2.54 × 10^{-2} mol·L^{-1} for the surfactants containing one, two, and three ethanol groups attached to their N-atom, respectively. This decrease in the values of cmc shows the effect of increasing the number of ethanol groups of the surfactants on its surface tension−concentration relationship. Increasing the number of OH groups, on the N-atom of *N*-dodecylammonium chloride molecules, from one to three causes a gradual reduction in the respective cmc and, in turn, the surface tension. Rosen (1989) has mentioned that the number of ionic groups in the surfactant molecule affects the cmc. Also, the critical micelle concentration in aqueous solution depends not only on the structure of the surfactant but also on the number and kind of counterions in the system (Rosen, 1989). Thus, the greater the number of the hydrophilic (ethanol) groups, the higher the solubility in water and, in turn, the lower the surface tension in solution. Meanwhile, the steric hindrance between the three ethanol groups is expected to be larger in comparison with the other surfactants containing one or two ethanol groups. This steric hindrance may also decrease the cmc.

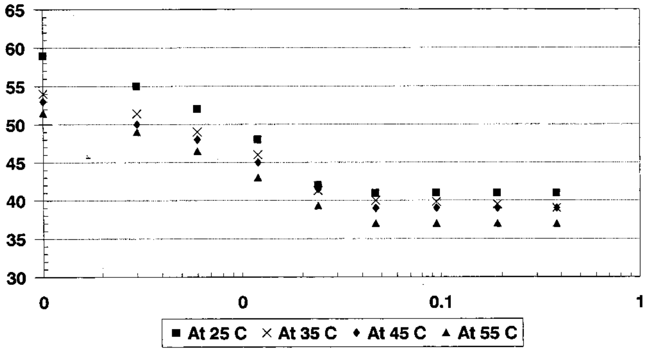

Figure 2. Surface tension vs concentration of *N*-dodecyl-*N*-mono(hydroxyethyl)ammonium chloride. Temperature: ■, 25 °C; ×, 35 °C; ♦, 45 °C; ▲, 55 °C. *X*-axis: *C*/mol·L^{-1}. *Y*-axis: γ/mN·m^{-1}.

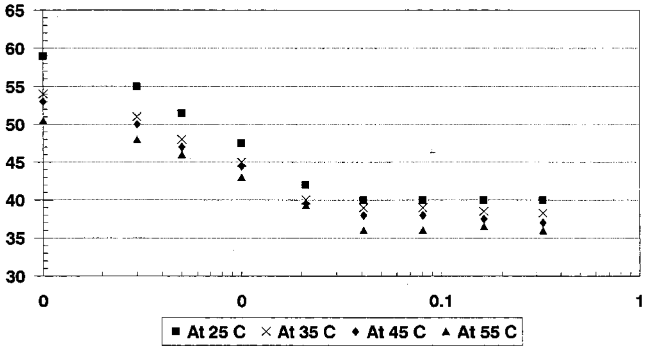

Figure 3. Surface tension vs concentration of *N*-dodecyl-*N*,*N*-bis(hydroxyethyl)ammonium chloride. Temperature: ■, 25 °C; ×, 35 °C; ♦, 45 °C; ▲, 55 °C. *X*-axis: *C*/mol·L^{-1}. *Y*-axis: γ/mN·m^{-1}.

Effect of Temperature on the Surface Tension−Concentration Relationship. Figures 2−4 show the effect of changing the temperature on the surface tension−concentration relationship for the surfactants containing one, two, and three ethanol groups substituted on the hydrophilic head (N-atom), respectively. The results clearly indicate that for each type of surfactant, and at constant concentration, the surface tension gradually decreased with increasing temperature. Meanwhile, a significant item regarding ionic surface active substances is their behavior in aqueous solutions above and below a certain temperature denoted as the Krafft point. Smith (1989) mentioned

Table 1. Surface Properties of the Quaternary Ammonium Compounds at Different Temperatures

compd[a]	t/°C	cmc × 10^{-2}/mol·L^{-1}	γ_{cmc}/mN·m^{-1}	Γ_{max} × 10^6/mol·m^{-2}	$A°$ × 10^2/nm^2·mol^{-1}	Π_{cmc}/mN·m^{-1}	pC_{20}
1	25	4.55	41	1.929	86	30	2.19
1	35	4.93	40	1.627	102	25	1.80
1	45	5.31	39	1.527	108	24	1.72
1	55	5.69	37	1.433	115	23	1.51
2	25	3.56	40	2.488	66.74	31	2.31
2	35	3.88	39	1.777	93.47	26	2.01
2	45	4.21	38	1.656	100.1	25	1.89
2	55	4.53	37	1.522	109	23	1.64
3	25	2.54	38	2.911	57	33	2.34
3	35	2.82	36	2.113	77	29	2.24
3	45	3.11	35	1.814	91	28	2.15
3	55	3.39	33	1.751	94	27	2.07

[a] Compound 1: $[H_{25}C_{12}-N^+H_2-C_2H_4OH]Cl^-$. Compound 2: $[H_{25}C_{12}-N^+H-(C_2H_4OH)_2]Cl^-$. Compound 3: $[H_{25}C_{12}-N^+-(C_2H_4OH)_3]Cl^-$.

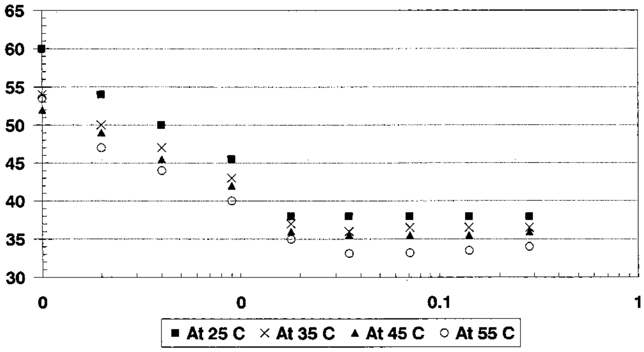

Figure 4. Surface tension vs concentration of *N*-dodecyl-*N*,*N*,*N*-tris(hydroxyethyl)ammonium chloride. Temperature: ■, 25 °C; ×, 35 °C; ▲, 45 °C; ○, 55 °C. *X*-axis: C/mol·L^{-1}. *Y*-axis: γ/mN·m^{-1}.

that the solubility decreases slowly as the temperature is decreased below the Krafft point, but the solubility increases very rapidly with increasing temperature. The Krafft point of many long-chain compounds used in flotation is close to room temperature, and in turn, the ambient temperature is likely to greatly affect their flotation characteristics (Smith, 1989).

Relationship between Temperature and cmc of Surfactants. Table 1 depicts the surface properties of the three surfactants at different temperatures from which it can be seen that the critical micelle concentration (cmc) of each surfactant progressively increased with raising the temperature. For the quaternary ammonium compound that contains one ethanol group substituted on its N-atom, its cmc increased from 4.55 × 10^{-2} mol·L^{-1} at 25 °C to 5.69 × 10^{-2} mol·L^{-1} at 55 °C. Meanwhile, the cmc of the surfactants containing two and three ethanol groups substituted on the N-atom increased from 3.56 × 10^{-2} and 2.54 × 10^{-2} mol·L^{-1} at 25 °C, respectively, to about 4.53 × 10^{-2} and 3.39 × 10^{-2} mol·L^{-1} at 55 °C, respectively. These results are in concordance with that mentioned by other authors (El-Mergaway, 1988; Rosen, 1989). This increase in cmc of the surfactants with raising the temperature could be related to the increase of the thermal motion of such hydrophilic (ethanol) groups and their solubility, which favor micellization.

The results in Table 1 also show that increasing the temperature from 25 °C to 55 °C increases the cmc by about 1.14 × 10^{-2}, 0.97 × 10^{-2}, and 0.85 × 10^{-2} mol·L^{-1} for the surfactants containing one, two, and three ethanol groups, respectively. The cmc of the surfactant that contains one ethanol group is affected to a greater degree by an increase in the temperature than the other surfactants.

Effect of Temperature and Number of Hydrophilic Groups of Surfactants on Their Surface Properties. Table 1 indicates that the number of hydrophilic groups plays an important role in determining the surface excess concentration (Γ_{max}) and the area occupied per molecule (A_{max}) at the aqueous solution−air interfaces. The surface excess concentration (Γ_{max}) at the surface saturation is a useful measure for the effectiveness of adsorption of the collector at the liquid−air, liquid−liquid, and liquid−solid interfaces, since it is the maximum value that, adsorption can attain (Rosen, 1989; Omar, 1994). Increasing the number of the substituted ethanol groups on the N-atom results in a significant reduction in the value of A_{max}. Such increase in the area occupied per molecule is followed by an increase in the surface excess concentration (Γ_{max}). This increase in the values of surface excess concentration (Γ_{max}) with increasing number of ethanol groups is also followed by a slight increase for both the efficiency of reducing the surface tension (pC_{20}) and the effectiveness of surface tension reduction (Π_{cmc}).

The significant decrease in the area occupied by one molecule (A_{max}) for the surfactant (*N*-dodecyl-*N*,*N*,*N*-tris(hydroxyethyl)ammonium chloride) containing three ethanol groups, in comparison with those containing one or two ethanol groups, may be related to the increased intrahydrogen-bonding action between the three hydroxyl groups (OH^-) and interhydrogen-bonding with aqueous solution.

The data in Table 1 show also that the value of the area occupied per molecule (A_{max}) is very sensitive to the temperature where it significantly increased with raising the temperature. This increase in A_{max} with raising the temperature may be related to the increased molecular motion at higher temperatures. Many authors have mentioned that there is a good relationship between efficiency of collector and its surface excess concentration. Increasing Γ_{max} leads to an improvement in the efficiency of the collector (Omar, 1994).

Effect of Structure of the Surfactant and Its Temperature on Its Thermodynamic Properties. Table 2 shows the values of $\Delta G°$, $\Delta H°$, and $\Delta S°$ of micellization and adsorption of three surfactants at different temperatures (25−55 °C). These results indicated that the values of $\Delta G°_{mic}$ are all negative for the three surfactants and at different temperatures as well. This means that the micellization process for these surfactants is spontaneous ($\Delta G°_{mic} < 0$).

The results in Table 2 indicated also that the value of $\Delta G°_{mic}$ appears to increase (from −7.65 to −9.10 kJ·mol^{-1}) with increasing number of ethanol groups (from one to three) attached to the hydrophilic head, with the net result of −0.6 kJ/mol/ethanol group. Such increase in the value of $\Delta G°_{mic}$, with increasing number of ethanol groups, could be related to the reduction in the degree of hydration of

Table 2. Thermodynamic Parameters of the Surfactants at Different Temperatures

compd[a]	t/°C	$\Delta G°_{mic}$/kJ·mol^{-1}	$\Delta H°_{mic}$/kJ·mol^{-1}	$\Delta S°_{mic}$/kJ·mol^{-1}	$\Delta G°_{ads}$/kJ·mol^{-1}	$\Delta H°_{ads}$/kJ·mol^{-1}	$\Delta S°_{ads}$/kJ·mol^{-1}
1	25	−7.65	5.16	0.043	−10.23	−7.25	0.04
1	35	−7.70	5.54		−10.25	−7.12	
1	45	−7.75	5.92		−10.36	−7.18	
1	55	−7.81	6.29		−10.46	−7.18	
2	25	−8.26	5.746	0.047	−10.33	−3.18	0.024
2	34	−8.32	6.156		−10.75	−3.35	
2	45	−8.37	6.576		−10.88	−3.24	
2	55	−8.43	6.986		−10.94	−3.07	
3	25	−9.10	5.80	0.05	−10.98	−2.01	0.03
3	35	−9.13	6.27		−10.37	−2.13	
3	45	−9.17	6.73		−11.72	−2.18	
3	55	−9.23	7.17		−11.76	−1.93	

[a] Compound 1: $[H_{25}C_{12}-N^{+}H_2-C_2H_4OH]Cl^{-}$. Compound 2: $[H_{25}C_{12}-N^{+}H-(C_2H_4OH)_2]Cl^{-}$. Compound 3: $[H_{25}C_{12}-N^{+}-(C_2H_4OH)_3]Cl^{-}$.

the ethanol group upon micellization as a result of steric hindrance.

Also, increasing the temperature from 25 to 55 °C seems to cause $\Delta H°_{mic}$ to become more positive and $\Delta G°_{mic}$ to become slightly more negative.

On the other hand, the results in Table 2 also reveal that the values of $\Delta G°_{ads}$ of all surfactants, and at different temperatures as well, are all negative. This indicates that the adsorption of these surfactants at the aqueous solution−air and the aqueous−solid interfaces are also spontaneous (Rosen, 1989). Meanwhile, the value of $\Delta G°_{ads}$ of *N*-dodecyl-*N*,*N*,*N*-tris(hydroxyethyl)ammonium chloride is slightly more negative in comparison with the other two surfactants. This suggests that the former surfactant may be preferable as a collector in the flotation processes to the other two quaternary ammonium chlorides. The technical evaluation of these surfactants as collectors in the flotation process of some Egyptian ores (e.g., barite, white sand, and feldspar) is under investigation.

Conclusions

Changing the hydrophilic portion of some prepared cationic quarternary ammonium surfactants by increasing the number of ethanol groups substituted on their nitrogen atom of the head from one to three reflected some changes in their surface and thermodynamic properties as follows:

(1) It increases surface excess concentration, Γ_{max}, as well as the negativity of both the free energy of micellization, $\Delta G°_{mic}$, and adsorption, $\Delta G°_{ads}$. Meanwhile, the critical micelle concentration (cmc) and surface area occupied per molecule (A_{max}) are decreased.

(2) Increasing the temperature appears to cause a decrease in surface excess concentration, while the surface area occupied per molecule, A_{max}, increases. This is accompanied by an increase in the values of both the free energy of micellization, $\Delta G°_{mic}$, and adsorption, $\Delta G°_{ads}$, at the aqueous solution−air interface.

(3) The results suggest that the surfactant *N*-dodecyl-*N*,*N*,*N*-tris(hydroxyethyl)ammonium chloride may be preferable as a flotation collector to the other quaternary ammonium salts of lower numbers of ethanol groups.

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