Contact Angle and Surface Tension in the Celestite + Alkylic Collector Aqueous Solutions + Air System[†]

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The contact angles of the ternary system celestite + alkylic collector aqueous solutions + air were measured over the range $1.4 \cdot 10^{-5}$ mol·L^{-1} to $5.0 \cdot 10^{-3}$ mol·L^{-1} of alkylic collector at pH between 4 and 11 and at the temperature 20 °C. The surface tension of the aqueous solutions of alkylic collector was also measured to obtain the values of the work of adhesion at the solid−liquid interface. Two different alkylic collectors have been used: sodium dodecyl sulfate and sodium 1-dodecanesulfonate.

Introduction

The variation in surface tension in a flotation bath due to the presence of the surface agents and the modification of pH is of great importance with regard to the wetting phenomenon, owing to the influence both exert on the flotability of solid particles during flotation.

Today it is well-known that surface agents form unimolecular layers at the liquid−gas interface and that this adsorption drastically changes the nature of the interface. Surface tension is, therefore, the property that is most affected.

The surface tension of a liquid and the interfacial tension between two liquids are both quantities that are determined experimentally. In the case of a solid, however, neither the value for the free surface energy nor the value for free interfacial tension with another liquid can be established experimentally. In this case, information on the characteristics of these interfaces is obtained indirectly through the determination of other experimentally achievable quantities. One of the options offering the greatest potential for this purpose is the measurement of contact angles.[1,2]

The flotation is a separation technique based on different physicochemical properties of the surface of solid particles. Since flotation was first developed, many papers have attempted to define the floatability of a body from the results of contact angle measurement. Since experimental conditions differ substantially from naturally occurring flotation, however, such papers have in essence only provided limited explanations of the operation.[3] Furthermore, in flotation, air bubbles only attach to solid particles if they displace water in some way. As a result, wetting phenomena have a considerable impact on the flotation of solid bodies,[4] and thus analysis of the free energy involved in the wetting process enables this process to be described with some degree of accuracy.

This paper examines the modification of the contact angle in the celestite + alkylic collector aqueous solutions + air system when the concentrations of alkylic collector and the pH in the aqueous medium are varied, to obtain characteristic parameters for the solid−liquid interface, with the aid of the surface tension of the solutions.

The alkylic collectors sodium dodecyl sulfate (SDS) and sodium 1-dodecanesulfonate (DSS) have been used. The level of purity required for both collectors is most often defined in terms of the measured surface chemical behavior; however, it is generally accepted that very low levels of a surface active impurity may drastically affect the results.[5−8]

The concentration range of SDS and DSS applied in the present paper is that generally used for the surfactants as flotation agents.

Materials and Methods

Commercially available SDS and DSS purchased from Merck (with a guaranteed minimum purity of 99 %) were used. Both collectors were purified by means of three successive crystallizations of dissolutions of the solute in bidistilled water of resistivity 10 MΩ·cm (Mili-Q quality) and crystallization at 50 °C.

The purified SDS and DSS were dissolved in bidistilled water of resistivity 10 MΩ·cm; the solute was weighed on a Mettler AJ-150 scale with a precision of ± 0.1 mg; and the desired solution volume was obtained by successive dilutions since the concentrations of the agent used are very small. In all cases, the solutions were prepared before the experiments were carried out to avoid possible alterations in the surface agents and hence changes in their properties over time.

NaOH and HCl, supplied by Merck and Probus, respectively, were used as pH modifiers. In both cases, small aliquots of 4 mol·L^{-1} solutions were used to reach the desired pH easily. pH measurements were performed with a Crison 2001 pH-meter having an uncertainty of 0.01.

Measurements of the contact angle of equilibrium were performed by the sessile drop method, which is the most widely used of all direct contact angle measurement methods based on the profile of the drop. This method offers a 2-fold advantage; that is, it requires a very small amount of liquid and scant solid surface.[9] The measurements were made from the reading provided by an ERMA-G1 (goniometric) contact angle measurement of the angle formed by the line tangent to the contour of a drop of solution deposited on a polished surface of celestite mineral ($SrSO_4$). The polished surface of celestite was prepared as follows: a piece of pure mineral was placed inside a mold measuring 20 × 20 × 8 mm^3, and polyester resin was then poured into the mold. Once the resin

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Table 1. Contact Angle, θ/deg, in the Ternary System Celestite + SDS Aqueous Solutions + Air at 20 °C

	θ/deg							
c/mol·L^{-1}	pH = 4	pH = 5	pH = 6	pH = 7	pH = 8	pH = 9	pH = 10	pH = 11
$1.4\cdot10^{-5}$	54.5	54.0	53.0	52.0	52.0	52.0	52.0	53.0
$7.3\cdot10^{-5}$	55.0	54.0	52.0	52.0	50.0	52.0	52.0	52.5
$1.4\cdot10^{-4}$	57.0	57.0	55.0	57.0	60.0	55.0	56.0	56.0
$6.2\cdot10^{-4}$	67.0	65.0	65.0	64.5	64.5	64.5	64.5	64.0
$1.0\cdot10^{-3}$	70.0	69.0	65.0	69.0	68.0	68.0	68.0	67.0
$5.0\cdot10^{-3}$	71.1	70.6	65.2	69.0	68.4	68.0	68.2	67.1

Table 2. Contact Angle, θ/deg, in the Ternary System Celestite + DSS Aqueous Solutions + Air at 20 °C

	θ/deg							
c/mol·L^{-1}	pH = 4	pH = 5	pH = 6	pH = 7	pH = 8	pH = 9	pH = 10	pH = 11
$1.4\cdot10^{-5}$	60.9	58.5	57.0	56.7	57.0	57.0	57.0	56.0
$7.3\cdot10^{-5}$	61.0	58.5	57.0	57.0	57.0	57.0	57.0	56.0
$1.4\cdot10^{-4}$	61.0	60.0	60.0	58.0	58.0	58.0	59.0	58.0
$6.2\cdot10^{-4}$	62.0	59.0	60.0	59.0	60.0	58.0	59.0	60.3
$1.0\cdot10^{-3}$	63.0	60.0	59.0	60.0	60.0	58.0	59.5	60.0
$5.0\cdot10^{-3}$	62.0	60.0	59.5	60.0	58.0	58.0	60.0	60.0

Table 3. Surface Tension of Aqueous Solutions of Sodium Dodecyl Sulfate at 20 °C

	σ/mN·m^{-1}							
c/mol·L^{-1}	pH = 4	pH = 5	pH = 6	pH = 7	pH = 8	pH = 9	pH = 10	pH = 11
$1.4\cdot10^{-5}$	67.9	67.9	68.3	68.4	68.5	68.5	68.5	68.6
$7.3\cdot10^{-5}$	64.4	65.7	66.4	66.8	67.4	67.5	67.6	67.6
$1.4\cdot10^{-4}$	61.2	61.4	62.0	62.9	64.2	65.0	66.5	66.7
$6.2\cdot10^{-4}$	51.8	52.4	53.4	54.5	59.4	54.6	55.0	55.3
$1.0\cdot10^{-3}$	49.2	50.2	50.1	50.5	50.5	51.1	51.2	50.8
$5.0\cdot10^{-3}$	32.0	32.2	32.5	32.7	32.8	33.0	32.9	32.6

Table 4. Surface Tension of Aqueous Solutions of Sodium 1-Dodecanesulfonate at 20 °C

	σ/mN·m^{-1}							
c/mol·L^{-1}	pH = 4	pH = 5	pH = 6	pH = 7	pH = 8	pH = 9	pH = 10	pH = 11
$1.4\cdot10^{-5}$	68.5	68.5	68.5	69.1	69.1	69.0	68.3	68.9
$7.3\cdot10^{-5}$	65.0	68.0	68.0	68.5	68.8	68.5	68.4	68.3
$1.4\cdot10^{-4}$	59.5	62.7	66.8	66.9	66.4	66.9	66.9	66.2
$6.2\cdot10^{-4}$	53.5	56.8	58.0	59.0	58.5	58.0	58.2	57.8
$1.0\cdot10^{-3}$	49.7	52.1	52.6	52.4	52.8	53.6	54.0	54.0
$5.0\cdot10^{-3}$	40.0	40.3	40.4	40.2	40.5	40.3	40.8	40.6

Table 5. Work of Adhesion per Unit Area, W_{SL}/mN·m^{-1} (SDS)

	W_{SL}/mN·m^{-1}							
c/mol·L^{-1}	pH = 4	pH = 5	pH = 6	pH = 7	pH = 8	pH = 9	pH = 10	pH = 11
$1.4\cdot10^{-5}$	107.3	107.8	109.4	110.5	110.6	110.6	110.6	109.8
$7.3\cdot10^{-5}$	101.3	104.3	107.2	107.9	110.7	109.0	109.2	108.7
$1.4\cdot10^{-4}$	94.5	94.8	97.5	97.1	96.3	102.2	103.6	103.9
$6.2\cdot10^{-4}$	72.0	75.5	75.9	77.9	77.8	78.1	78.6	79.5
$1.0\cdot10^{-3}$	66.0	68.1	71.2	68.5	69.4	70.2	70.3	70.6
$5.0\cdot10^{-3}$	42.3	42.8	46.1	44.4	44.8	45.3	45.1	45.2

had hardened, the piece was placed in a STRUERS polisher of materialographic specimens which used silk cloth polishers impregnated with diamond powder of ever-decreasing grain sizes. The drop of solution was placed on this polished surface with a small syringe. The piston device of the syringe incorporated a micrometer screw to ensure equal sizing of each drop. The time elapsed between the placement of the drop and the measurement of the angle was kept to a minimum to avoid alterations in the drop. Fifteen measurements of the contact angle were performed, and their average was taken for each case. After completion of the measurements, the surface of the mineral was cleaned with distilled water, dried, and then polished manually with a STRUERS silk cloth impregnated with STRUERS DP-Spray HQ diamond powder, with a grain size of 1 μm. The surface was then cleaned again with distilled water and left to dry. The uncertainty was ± 0.1°.

Surface tension measurements were performed using the Wilhelmy plate principle,[10,11] considered as one of the most appropriate, since no hydrostatic corrections are required as in the ring method. Measurements of surface tension were performed with a KRUSS K10 digital tensiometer, with a platinum plate measuring $20 \times 10 \times 0.1$ mm^3. The uncertainty was ± 0.1 mN·m^{-1}. The operative technique is the same as that described in a previous work.[12]

Contact angles of equilibrium and surface tension were measured 15 min after the preparation of the solutions.

Results and Discussion

Contact angles of the ternary system celestite + SDS aqueous solutions + air are given in Table 1, as a function of pH and at SDS concentrations between $1.4\cdot10^{-5}$ mol·L^{-1} and $5.0\cdot10^{-3}$ mol·L^{-1} at a temperature of 20 °C. As the concentration of

Table 6. Work of Adhesion per Unit Area, $W_{\mathrm{SL}}/\mathrm{mN\cdot m^{-1}}$ (DSS)

	$W_{\mathrm{SL}}/\mathrm{mN\cdot m^{-1}}$							
$c/\mathrm{mol\cdot L^{-1}}$	pH = 4	pH = 5	pH = 6	pH = 7	pH = 8	pH = 9	pH = 10	pH = 11
$1.4\cdot10^{-5}$	101.8	104.2	105.8	107.0	106.7	106.5	105.4	107.4
$7.3\cdot10^{-5}$	96.5	103.5	105.0	105.8	106.2	105.8	105.6	106.4
$1.4\cdot10^{-4}$	88.3	94.0	100.2	102.3	101.5	102.3	101.3	101.2
$6.2\cdot10^{-4}$	78.6	86.0	87.0	89.3	87.7	88.7	88.1	86.4
$1.0\cdot10^{-3}$	72.2	78.1	79.6	78.3	79.2	82.0	81.4	81.0
$5.0\cdot10^{-3}$	58.7	60.4	60.9	60.3	61.9	61.6	61.2	60.9

SDS increases, the contact angle, θ, rises substantially. Thus, at pH = 4 and the SDS concentration $1.4\cdot10^{-5}$ mol·L^{-1}, the contact angle measures 54.5°, while for the same pH but with the SDS concentration $5.0\cdot10^{-3}$ mol·L^{-1}, the contact angle measures 71.1°. It is also clear that the pH in the medium has an impact on θ. For all the concentrations of SDS, the maximum values of contact angle are a pH between 4 and 5.

The results show that on the ternary system celetite + SDS aqueous solutions + air the SDS is adsorbed on the surface ore by displacing the water. It will facilitate subsequent adhesion of the air bubble. In all concentrations investigated, the maximum adsorption of SDS on celestite occurs at pH values between 4 and 5 which is where the highest values of the contact angle are found.

Contact angles of the ternary system celestite + DSS aqueous solutions + air are given in Table 2, as a function of pH and DSS concentrations between $1.4\cdot10^{-5}$ mol·L^{-1} and $5.0\cdot10^{-3}$ mol·L^{-1}, at a temperature of 20 °C. The results are similar to those found with SDS, and the maximum values of the contact angle are a pH between 4 and 5. However, with increasing concentration of DSS from $1.4\cdot10^{-5}$ mol·L^{-1} to $5.0\cdot10^{-3}$ mol·L^{-1}, the contact angle varies very slightly in the different pH values investigated.

Also, the results indicate that DSS adsorption on the surface of celestite is better at pH values between 4 and 5, although the effect on the contact angle of the variation in the DSS concentration and the pH is lower than that found with SDS.

The difference between the interfacial free energy per unit area of the solid in equilibrium with liquid-saturated air above it, γ_{SA}, and the interfacial free energy per unit area at the liquid−solid interface, γ_{SL}, is given by Young's equation[9]

$$\gamma_{\mathrm{SA}} - \gamma_{\mathrm{SL}} = \sigma \cos \theta \tag{1}$$

where σ is the surface tension and θ is the contact angle.

The work of adhesion, W_{SL}, or the reversible work required to separate the unit area of the liquid from that of the solid is given by the expression[13]

$$W_{\mathrm{SL}} = \gamma_{\mathrm{SA}} - \gamma_{\mathrm{SL}} + \sigma \tag{2}$$

and substituting for $\gamma_{\mathrm{SA}} - \gamma_{\mathrm{SL}}$ in eq 1

$$W_{\mathrm{SL}} = \sigma(1 + \cos \theta) \tag{3}$$

from which it is apparent that an increase in the surface tension of the wetting liquid always increases adhesional wetting, whereas an increase in the contact angle obtained after wetting may or may not indicate a decreased tendency for adhesion to occur. If the increase in the contact angle (and consequent decrease of cos θ) reflects an increase in γ_{SL}, there is a diminished tendency to adhere. If it reflects merely an increase in σ, there is an increased tendency to adhere. The driving force in adhesional wetting can never be negative and is equal to zero only when the contact angle is 180°, which is never achieved in practice.

Surface tensions for aqueous solutions of sodium dodecyl sulfate are shown in Table 3, as a function of pH and SDS concentrations between $1.4\cdot10^{-5}$ mol·L^{-1} and $5.0\cdot10^{-3}$ mol·L^{-1} at the temperature 20 °C. The values show that surface tension varied considerably due to variation of SDS concentration and, to a lesser extent, due to variation of pH. The minimum values of σ are for a high concentration of SDS and for pH between 4 and 5. According to Pugh and Stenius,[14] minimum values for σ often correspond to the optimum conditions for mineral retrieval by flotation.

In these solutions, the minimum values of surface tension correspond with the greatest adsorption of SDS on the interface. If celestite is present, SDS displaces the water creating hydrophobic surfaces on which air bubbles can adhere.

Surface tension for aqueous solutions of sodium 1-dodecanesulfonate are shown in Table 4, as a function of pH and DSS concentrations between $1.4\cdot10^{-5}$ mol·L^{-1} and $5.0\cdot10^{-3}$ mol·L^{-1} at the temperature 20 °C. The values show that surface tension varies very slightly when pH in the medium is modified. The lowest values for surface tension are generally found in acid media, although there is no great difference when compared with neutral or alkaline media. These results are very similar to those found with sodium dodecyl sulfate (SDS), except at a concentration of $5.0\cdot10^{-3}$ mol·L^{-1} in which the effect of SDS on the surface tension decrease is very high.

The work of adhesion per unit area, W_{SL}, is calculated from eq 3, using the values θ and σ from Tables 1 and 3 for SDS and Tables 2 and 4 for DSS. Tables 5 and 6 show the values obtained. As can be seen, W_{SL} falls sharply as the concentration of SDS is increased with this collector, and the minimum values for W_{SL} ((42.3 and 42.8) mN·m^{-1}) are achieved at pH values between 4 and 5 at the concentration of SDS $5.0\cdot10^{-3}$ mol·L^{-1}, thus causing decreased adhesional wetting of the solid. This also increases the possibilities of the solid adhering to air bubbles and thus being floated. These results agree with the fact that flotation of celestite with SDS is achieved in acid media at pH values less than 6.[15,16]

The results obtained with DSS are similar to those described for SDS, and the minimum values of W_{SL} are also at pH between 4 and 5 at the concentration of DSS $5.0\cdot10^{-3}$ mol·L^{-1}. Also, these results agree with the fact that flotation of celestite with DSS is achieved in acid media.[15,16]

A previous work,[17] using sodium oleate, also found that the minimum values of W_{SL} are in the pH range in which flotation of celestite is carried out with this collector.

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