Contact Angle and Surface Tension in the Celestite + Sodium Oleate Aqueous Solutions + Air System

F. Hernáinz* and A. Caro

Department of Chemical Engineering, Faculty of Sciences, University of Granada, 18071-Granada, Spain

The contact angles of the ternary system celestite + sodium oleate aqueous solutions + air were measured in the range 7.3×10^{-6} mol·L^{-1} and 6.2×10^{-4} mol·L^{-1} of sodium oleate at pH between 4 and 12 and at the temperature 20 °C. The surface tensions of the aqueous solutions of sodium oleate were also measured to obtain the values of the work of adhesion at the solid−liquid interface.

Introduction

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]

Flotation is a well-known 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 + sodium oleate aqueous solutions + air system when both the concentrations of sodium oleate 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.

Materials and Methods

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 twofold advantage; that is, it requires a very small amount of liquid and a scant solid surface.[5] 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 mould. Once the resin 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.

Surface tension measurements were performed using the Wilhelmy plate principle,[6,7] considered as one of the most appropiate, 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 × 10 × 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.[8]

The sodium oleate was dissolved in milli-Q quality distilled water. The solute supplied by Fluka (with a guaranteed minimum purity of 99%) was weighed on a METTLER AJ-150 balance. The desired solution concentration was obtained by successive dilutions, since the concentrations of the agent used are very small. In all cases, the solutions were prepared little before the experiments were carried out to avoid possible alterations in the surface agent and hence changes in their properties over time.

Contact angles of equilibrium and surface tension were measured 15 min after the preparation of the solutions. NaOH and HCl, supplied by Merck and Probus, respectively, were used as pH modifiers; in both cases a concentration of 4 mol·L^{-1} was used to reach the desired pH and

* Corresponding author: E-mail: hernainz@goliat.ugr.es. Fax: 34-58-248992. Phone: 34-58-243315.

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Table 1. Contact Angle, θ/deg, in the Ternary System Celestite + Sodium Oleate 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	pH = 12
7.3×10^{-6}	45.0	45.0	46.0	47.5	50.0	50.0	50.0	50.0	48.0
1.4×10^{-5}	45.0	45.0	47.6	48.0	51.0	47.5	50.0	49.0	48.0
4.5×10^{-5}	44.0	45.2	47.0	46.3	46.0	51.0	50.5	49.0	48.0
7.3×10^{-5}	45.5	48.0	51.0	50.0	53.0	52.0	52.0	53.0	52.5
1.4×10^{-4}	48.3	48.7	50.0	52.0	55.0	51.0	50.0	54.0	52.5
4.0×10^{-4}	63.0	63.0	64.1	65.0	65.3	63.6	63.2	60.0	60.0
6.2×10^{-4}	63.0	63.0	70.0	70.0	71.0	68.0	66.5	65.0	65.0

Table 2. Surface Tension, σ/mN·m^{-1}, of Aqueous Solutions of Sodium Oleate 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	pH = 12
7.3×10^{-6}	63.5	64.1	60.4	55.0	56.0	59.9	63.1	61.5	60.2
1.4×10^{-5}	58.0	59.8	57.0	52.3	53.5	55.9	58.6	60.8	56.2
4.5×10^{-5}	53.5	52.8	50.7	45.4	44.4	51.8	53.9	53.1	49.6
7.3×10^{-5}	50.3	49.6	48.9	42.9	40.5	49.6	51.2	50.3	48.0
1.4×10^{-4}	42.2	41.0	35.1	34.2	32.3	36.0	43.3	42.5	36.5
4.0×10^{-4}	35.6	34.9	32.1	31.4	29.9	30.3	39.6	36.6	30.7
6.2×10^{-4}	34.5	33.4	31.8	29.2	28.5	26.8	32.4	31.7	29.0

Table 3. Work of Adhesion per Unit Area, W_{SL}/mN·m^{-1}

	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	pH = 12
7.3×10^{-6}	108.4	109.4	102.3	92.1	92.0	98.4	103.6	101.0	100.5
1.4×10^{-5}	99.0	102.1	95.4	87.2	87.1	93.6	96.2	100.6	93.8
4.5×10^{-5}	92.0	90.0	85.2	76.7	75.2	84.4	88.1	87.9	82.7
7.3×10^{-5}	85.5	82.7	79.6	70.4	64.8	80.1	82.7	80.5	77.2
1.4×10^{-4}	70.2	68.0	57.6	55.2	50.8	58.6	71.1	67.4	58.7
4.0×10^{-4}	51.7	50.7	46.1	44.6	42.4	43.7	57.4	54.9	46.0
6.2×10^{-4}	50.1	48.5	42.6	39.1	37.7	36.8	45.3	45.1	41.2

pH measurements were performed with a CRISON 2001 pH meter.

Results and Discussion

Contact angles of the ternary system celestite + sodium oleate aqueous solutions + air are given in Table 1, as a function of pH and at sodium oleate concentrations between 7.3×10^{-6} mol·L^{-1} and 6.2×10^{-4} mol·L^{-1} at temperature of 20 °C. As the concentration of sodium oleate increases, the contact angle, θ, rises substantially. Thus, at pH = 8 and the sodium oleate concentration 7.3×10^{-6} mol·L^{-1}, the contact angle measures 50°, while, for the same pH but with the sodium oleate concentration 6.2×10^{-4} mol·L^{-1}, the contact angle measures 70°. It is also clear that the pH in the medium has an impact on θ. For all the concentrations of sodium oleate used, as the pH increases, so does the contact angle up to a maximum approaching pH = 8. For higher values, an increase in pH decreases θ. This decrease is greater the higher the concentrations of sodium oleate (6.2×10^{-4} and 4.0×10^{-4} mol·L^{-1}).

Taking into account that the values for θ in alkaline media all fall within 50° and 70°, that is, the limits set by Shaw[9] for flotation to be effective, these solutions may be appropriate for the flotation of celestite with sodium oleate. This seems to be confirmed by the fact that flotation of celestite with sodium oleate is always performed at pH values between 8 and 10.[10−14]

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 the Young's equation[9]

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

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[9]

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

sustituting for $\gamma_{SA} - \gamma_{SL}$ in eq 1

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

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 oleate are shown in Table 2, as a function of pH and sodium oleate concentrations between 7.3×10^{-6} mol·L^{-1} and 6.2×10^{-4} mol·L^{-1} at the temperature 20 °C. The values show that surface tension varied considerably due to variations in both pH and sodium oleate concentration. The minimum values of σ are for a high concentration of sodium oleate and for pH between 8 and 9. According Pugh and Stenius,[15] minimum values for σ often correspond to the optimum conditions for mineral retrieval by flotation.

The work of adhesion per unit area, W_{SL}, is calculated from eq 3, using the values θ and σ from Tables 1 and 2. Table 3 shows the values obtained. As can be seen, W_{SL} falls sharply as the concentration of sodium oleate is increased. The pH of the medium also has a major impact.

The minimum values for W_{SL} (37.2 and 36.8 $mN \cdot m^{-1}$) are achieved at pH values between 8 and 9 at the concentration of sodium oleate 6.2×10^{-4} $mol \cdot L^{-1}$, 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 sodium oleate is achieved in alkaline media at pH values between 8 and 10.

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