JOURNAL OF MATERIALS SCIENCE **29** (1994) 3177–3184

The influence of mixture anionic and non-ionic surfactants on the surface free energy of cassiterite

B. JAŃCZUK, M. L. GONZÁLEZ-MARTÍN, J. M. BRUQUE
Departamento de Fisica, Universidad de Extremadura, 06071 Badajoz, Spain

The measurements of the contact angle were made for water, glycerol, formamide, diiodomethane and bromoform on a cassiterite surface covered with a mixed film of SDS and TX-100 formed by adsorption from solution of SDS and TX-100 at different molar fraction at a constant concentration equal to 2×10^{-4} M. Using the contact angles the dispersion and non-dispersion or Lifshitz–van-der-Waals and acid–base components of the surface free energy of cassiterite covered with a mixed film of SDS and TX-100 were evaluated. These components were compared to those for a "bare" cassiterite surface. Also, the electron-acceptor and electron-donor parts of the acid–base components were determined. On the basis of the measurements and calculations synergetic effects were found in the wettability and surface free energy of cassiterite when it was covered with the mixed film.

1. Introduction

Surfactants are usually applied from mixtures of two or more surface-active substances. Therefore, the influence of the interactions between the surface-active substances on the physico-chemical properties of such compositions, including the adsorption behaviour, is not only of fundamental importance, but it is also of practical interest for the application of surfactants.

There has been much research interest in the interaction between the ionic and non-ionic surfactants used in flotation as well as in their influence on flotation.

Fuerstenau and Yamada [1] have demonstrated the favourable effects on the flotation of corundum of adding non-ionic substances to the sodium dodecyl sulphate solutions. On the other hand, Leja and Schulman [2] have suggested that some additional reagents can improve the flotation process if they can interact with the collector molecules at the solid–liquid interface.

Recent work has shown that the use of mixtures of surfactants provides advantageous synergetic effects [3] and significantly reduces the precipitation in flotation systems [4]. A synergetic effect is caused by the mutual promotion of the coadsorption of anionic and non-ionic surfactants on the mineral surface [5].

A knowledge of the surface free energy is very useful in understanding the interfacial phenomena involved in flotation processes, particularly the mechanisms of air-bubble adhesion to mineral particle and particle aggregation. However, as a result of the adsorption of surfactants the surface free energy of the mineral changes.

Since it is not possible to measure directly the surface free energy of a solid, there are, at present, many indirect methods of measurement based on the heat of immersion [6], the adsorption [7], the zeta potential [8] and contact-angle measurements [7, 9–15].

The method based on contact-angle measurements in solid–liquid-drop–air systems for proper liquids are the most popular [7, 9–15]. There are many different approaches to the evaluation of the surface free energy of a solid from the contact-angle data [7, 9–15]. Among these, the *geometric mean* [7, 9, 16, 17] and the approaches of van Oss *et al.* [13–15] give the most complete information about energetic properties of surfaces.

Thus, by means of contact-angle measurements, the surface free energy of cassiterite covered with a mixed film of sodium dodecyl sulphate and Triton X-100 (and its components: dispersion, non-dispersion or Lifshitz–van-der-Waals and acid–base) have been calculated.

2. Experimental procedure

2.1. Materials

The following liquids were used for contact-angle measurements: water doubly distilled and deionized (W), anhydrous glycerol (G, with a purity of greater than 99.5%, from Merck), formamide (F, with a purity of greater than 99%, from Merck), diiodomethane (D, with a purity of greater than 99%, from Merck) and bromoform (B, with a purity of greater than 99%, from Aldrich).

The cassiterite plates were obtained from mineralogical specimens of cassiterite from Bolivia (Huanuni Mine), they were treated in four different ways before the measurements, as described in [18]. Plates denoted as I were washed several times in

0022–2461

doubly distilled and deionized water, cleaned in an ultrasonic bath for 15 min, and dried at room temperature before measurements. The second and third groups of plates (II and III, respectively) were boiled in HNO_3 60% for some minutes, washed several times in doubly distilled water, cleaned in an ultrasonic bath for 30 min and dried at room temperature (plates II) or at 110 °C (plates III) for 1 h. The fourth group of plates, denoted IV, were boiled in HCl (1 : 1) for some minutes and washed and dried as plates II.

For adsorption sodium dodecyl sulphate (SDS, with a purity of 99%, from Merck) and Triton X-100 (TX-100, with a purity of 98%, from Fluka) were used without further purification.

2.2. Measurements

Mixed aqueous solutions of SDS and TX-100 were made at 2×10^{-4} M and with different molar fractions, x, of TX-100 (from 0 to 1). The pH of the solutions was not controlled.

The cassiterite plates were kept in the mixed aqueous solutions, at each molar fraction, for 24 h. This time was sufficient to ensure the maximum adsorption of SDS and TX-100 onto the cassiterite surface at a given molar fraction.

After equilibration, the plates were dried at room temperature for a long time and, before the measurements, dried at 50 °C for 30 min.

All measurements of the advancing contact angle were made at 20 ± 1 °C by the sessile-drop method [19] using a camera-computer system described elsewhere [18]. For a given system, at least 30 measurements were made, and the accuracy was within $\pm 2°$.

3. Results

The values of the contact angle for water, θ_W, glycerol, θ_G, formamide, θ_F, diiodomethane, θ_D, and bromoform, θ_B, on the four cassiterite plates after equilibration with the mixed solution of SDS and TX-100 are shown in Figs 1 to 5, respectively, as a function of the molar fraction of TX-100 in solution.

It appears from Figs 1 to 5 that the contact-angle values for all the liquids and plates studied increased slightly in the TX-100 molar fraction range 0–0.6 and then they decreased up to a molar fraction equal to 1.

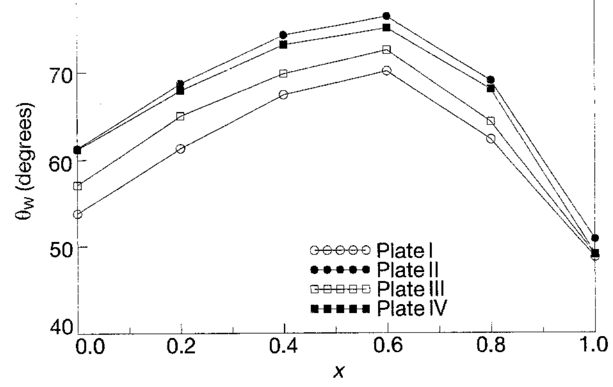

Figure 1 The contact angle for water on cassiterite covered with an SDS + TX-100 mixed film versus the molar fraction, x, of TX-100 in solution.

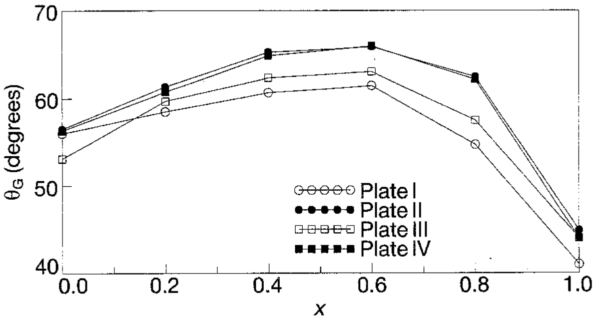

Figure 2 The contact angle for glycerol on cassiterite covered with an SDS + TX-100 mixed film versus the molar fraction, x, of TX-100 in solution.

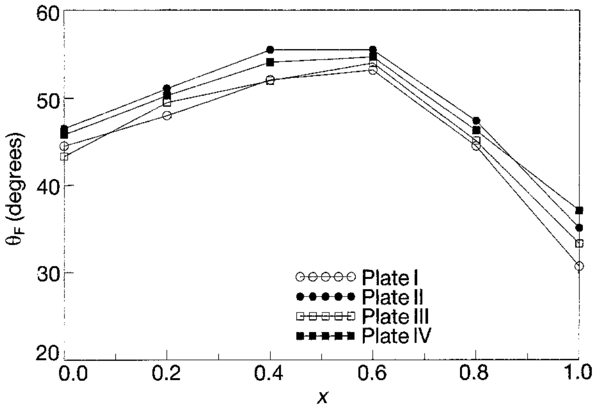

Figure 3 The contact angle for formamide on cassiterite covered with an SDS + TX-100 mixed film versus the molar fraction, x, of TX-100 in solution.

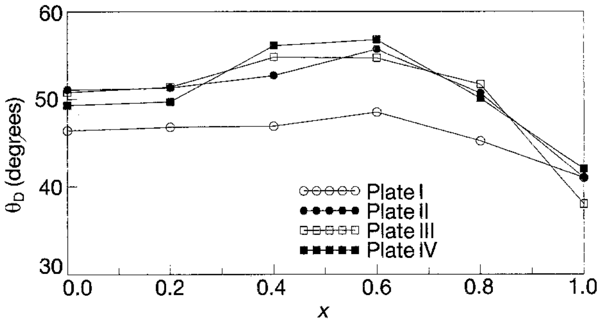

Figure 4 The contact angle for diiodomethane on cassiterite covered with an SDS + TX-100 mixed film versus the molar fraction, x, of TX-100 in solution.

For diiodomethane (Fig. 4) the relationship of the contact-angle as a function of the molar fraction of TX-100 in solution can be divided into two straight linear parts corresponding to the ranges of the TX-100 molar fraction mentioned above.

Also, from Figs 1 to 5 it can be seen that the way of preparing plates before adsorption influences the contact angle for the five liquids used for studies. In the case of diiodomethane and bromoform (Figs 4 and 5) the contact angles measured on plate I are very different than for the other plates. For a given plate, the lowest value of the contact angle at each molar

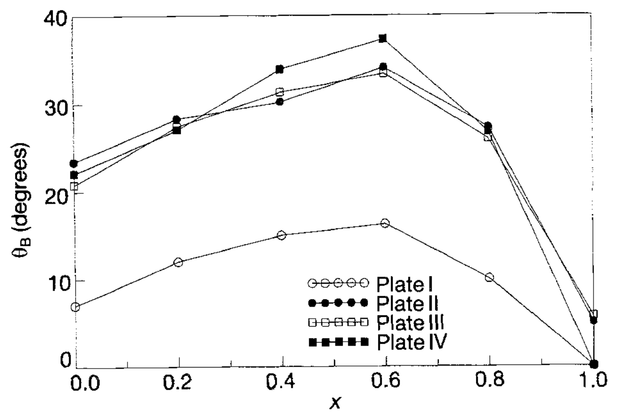

Figure 5 The contact angle for bromoform on cassiterite covered with an SDS + TX-100 mixed film versus the molar fraction, x, of TX-100 in solution.

fraction are observed for bromoform and the highest, with some exceptions for water. It is worth noting that the important difference in the behaviour of plate I from the other plates for the contact angle for diiodomethane and bromoform (Figs 4 and 5).

4. Calculations

On the basis of the contact-angle values it is possible to determine the components of the solid surface free energy.

Fowkes suggests that the surface free energy of a solid and a liquid can be divided into the following parts [7]

$$\gamma = \gamma^d + \gamma^i + \gamma^p + \gamma^h \qquad (1)$$

where d, i, p and h denote the dispersion, induced dipole–dipole, dipole–dipole and hydrogen-bond intermolecular interactions, respectively.

From a practical point of view, it is possible to calculate two components – dispersion, γ^d and non-dispersion, γ^n. The non-dispersion component is sum of the γ^i, γ^p and γ^h parts. Thus

$$\gamma = \gamma^d + \gamma^n \qquad (2)$$

Expressing by Young's equation the solid–liquid interfacial free energy as a function of the geometric mean of the dispersion [7] and non-dispersion [16, 17] interactions we can write

$$\gamma_L(\cos\theta_L + 1) + \Pi e_L = 2[\gamma_S^d\gamma_L^d]^{1/2} + 2(\gamma_S^n\gamma_L^n)^{1/2} \qquad (3)$$

where S and L denote solid and liquid, respectively, θ_L is the contact angle, and Πe_L is the spreading film pressure.

van Oss *et al.* [13–15] claim that it is impossible to determine only the γ^d components for polar solids or polar liquids but it is possible to determine the Lifshitz–van-der-Waals component (γ^{LW}). Thus, the γ^{LW} component fulfils the equation [13–15]

$$\gamma^{LW} = \gamma^d + \gamma^i + \gamma^p \qquad (4)$$

However, the γ^h component can be treated as the acid–base component, γ^{AB}. Thus

$$\gamma = \gamma^{LW} + \gamma^{AB} \qquad (5)$$

γ^{AB} can be expressed [13–15] as

$$\gamma^{AB} = 2(\gamma^+\gamma^-)^{1/2} \qquad (6)$$

where γ^+ and γ^- are the electron–acceptor and electron–donor parts of the γ^{AB} component.

Using the van Oss *et al.* [13–15] approach to the solid–liquid interfacial free energy in the Young's equation, we can obtain [13–15]

$$\gamma_L(\cos\theta_L + 1) + \Pi e_L = 2(\gamma_S^{LW}\gamma_L^{LW})^{1/2} + 2(\gamma_S^+\gamma_L^-)^{1/2} + 2(\gamma_S^-\gamma_L^+)^{1/2} \qquad (7)$$

If the Πe_L value is known it is possible to determine the γ_S^d and γ_S^n components from Equation 3 or γ_S^{LW}, γ_S^+ and γ_S^- from Equation 7. It is commonly assumed that the Πe_L value is equal to zero for contact angles higher than zero. In our calculation we have also assumed that $\Pi e_L = 0$.

The contact angle for the cassiterite plates has been measured for five liquids, whose γ_L^d, γ_L^n, γ_L^{LW}, γ_L^+ and γ_L^- are known (Tables I and II) from the literature [7, 15, 20, 21]. In Figs 6 to 9 the average values of γ_S^d, γ_S^n and γ_S are plotted. They are evaluated from Equation 3 using water and one apolar organic liquid (diiodomethane or bromoform), the system denoted system (a), or using two organic liquids (one polar and one apolar) the system denoted as system (b). Also, the average values of γ_S^{LW}, γ_S^+ and γ_S^- evaluated from Equation 7, value of the γ_S^{AB} evaluated from Equation 6, and the value of γ_S evaluated from the liquid systems WGD, WGB, WFD and WFB are plotted for each cassiterite plate in Figs 10 to 13. These systems of liquids were chosen, to safeguard the minimum error in the calculations according to [18].

From Fig. 6, it appears that for cassiterite plates which are not treated by any acids (plates I) before adsorption of the mixture of SDS and TX-100, the dispersion component of the surface free energy does not depend on the molar fraction of TX-100 in the solution. The γ_S^d values obtained from the contact angle for two organic liquids are slightly higher than those from the systems involving water. The non-dispersion component and the total surface free energy depend on the TX-100 molar fraction. The γ_S^n and γ_S values tended to a minimum when the molar fraction increased from 0 to 0.6 and then they increased in

TABLE I Values of the dispersion, γ_L^d, and non-dispersion, γ_L^n, components of the liquid surface tension, γ_L, taken from the literature [7, 15, 20]

Liquid	γ_L^d (mN m^{-1})	γ_L^n (mN m^{-1})	γ_L (mN m^{-1})	Reference
Water	21.8	51	72.8	[7]
Glycerol	34	30	64	[15]
Formamide	39	19	58	[15]
Diiodomethane	50.42	0.38	50.8	[20]
Bromoform	40.55	0.95	41.5	[20]

TABLE II Values of the Lifshitz–van-der-Waals, γ_L^{LW}, electron acceptor, γ_L^+, and electron donor, γ_L^-, components of the liquid surface tension, γ_L, taken from the literature [15, 21]

Liquids	γ_L^{LW} (mN m^{-1})	γ_L^+ (mN m^{-1})	γ_L^- (mN m^{-1})	γ_L (mN m^{-1})	Reference
Water	21.8	25.5	25.5	72.8	[15]
Glycerol	34	3.92	57.4	64	[15]
Formamide	39	2.28	39.6	58	[15]
Diiodomethane	50.8	0.72	0	50.8	[21]
Bromoform	41.5	1.72	0	41.5	[21]

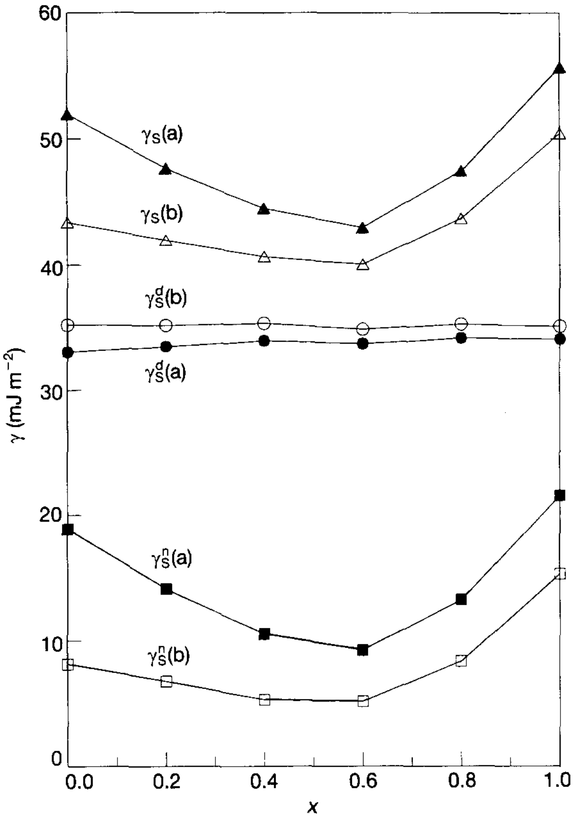

Figure 6 The average value of the non-dispersion component, γ_S^n, the dispersion component, γ_S^d, and the total, γ_S, surface free energy of cassiterite plate I covered with an SDS + TX-100 mixed film versus the molar fraction, x, of TX-100 in solution, for liquid systems (a) and (b).

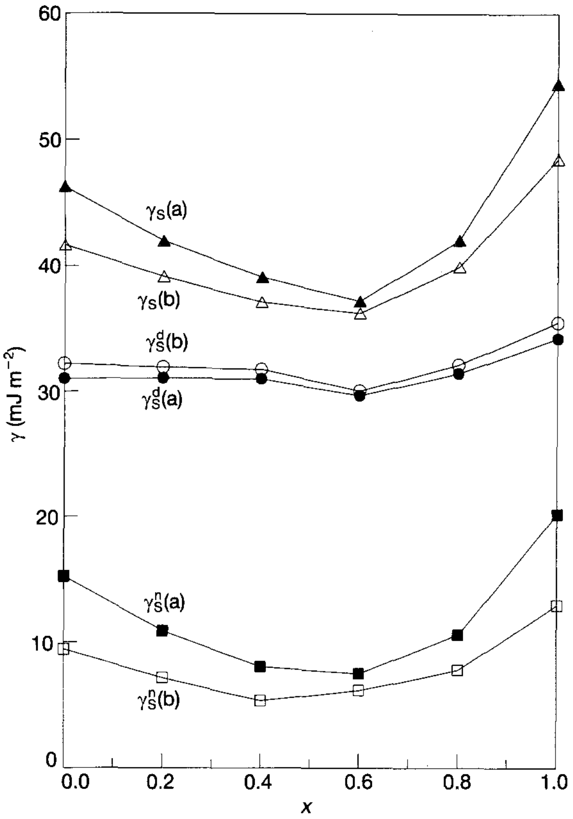

Figure 7 The average value of the non-dispersion component, γ_S^n, the dispersion component, γ_S^d, and the total, γ_S, surface free energy of cassiterite plate II covered with an SDS + TX-100 mixed film versus the molar fraction, x, of TX-100 in solution, for liquid system (a) and (b).

the molar-fraction range 0.6–1. The γ_S^n(b) values were considerably lower than those of γ_S^n(a). Also, the γ_S(a) values were higher than those of γ_S(b); however, the biggest differences were observed at low and high molar fractions of TX-100. For cassiterite plates which were treated by HNO_3 or HCl acids before adsorption of the mixture of surfactants (Figs 7 to 9) γ_S^d, γ_S^n and γ_S decreased in the molar-fraction range for TX-100 of 0–0.6 to the minimum and then increased in the range 0.6–1. The changes of the value of γ_S^d with the molar fraction of TX-100 were considerably smaller than for γ_S^n and γ_S. For all cases, the γ_S^d(a) values were slightly lower than the values of γ_S^d(b), but values of γ_S^n(a) and γ_S(a) were considerably higher than those of γ_S^n(b) and γ_S(b), respectively. The differences between γ_S^n(a) and γ_S^n(b) or γ_S(a) and γ_S(b) were more important at the lowest and highest molar fractions of TX-100 than at $x = 0.5$.

From Figs 10 to 13 it can be seen that for the four kind of plates γ_S^{LW} and γ_S^+ changed only slightly with x, but γ_S^-, γ_S^{AB} and γ_S showed a strong dependence on the TX-100 molar fraction. In each case the minimum value appeared at $x = 0.6$, and the γ_S^+ values were much lower than those of γ_S^-.

Comparing γ_S^d to γ_S^{LW} and γ_S^n to γ_S^{AB} from Figs 6 to 13 it can be seen that the γ_S^d(a) and γ_S^d(b) values were a few mJ m^{-2} higher than those of γ_S^{LW}, but the γ_S^n(a) values were higher and those of γ_S^n(b) were lower than the values of γ_S^{AB}. However the γ_S values obtained on the basis of the contact-angle measurements of the two organic-liquid system, using the geometric mean approach [7, 16, 17], are close in many cases to those obtained from the contact angle of three liquids, including water, on the basis of the van Oss *et al.* [13–15] approach.

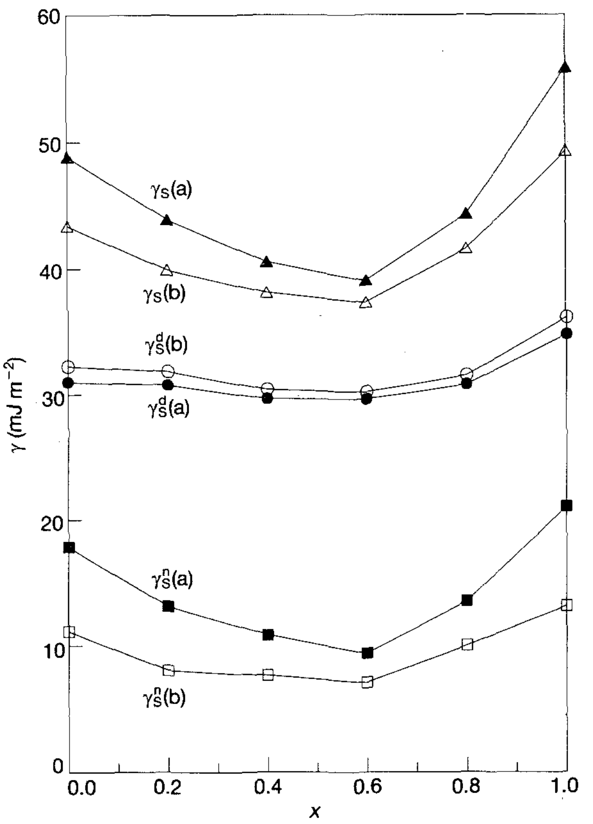

Figure 8 The average value of the non-dispersion component, γ_S^n, the dispersion component, γ_S^d, and the total, γ_S, surface free energy of cassiterite plate III covered with an SDS + TX-100 mixed film versus the molar fraction, x, of TX-100 in solution, for liquid systems (a) and (b).

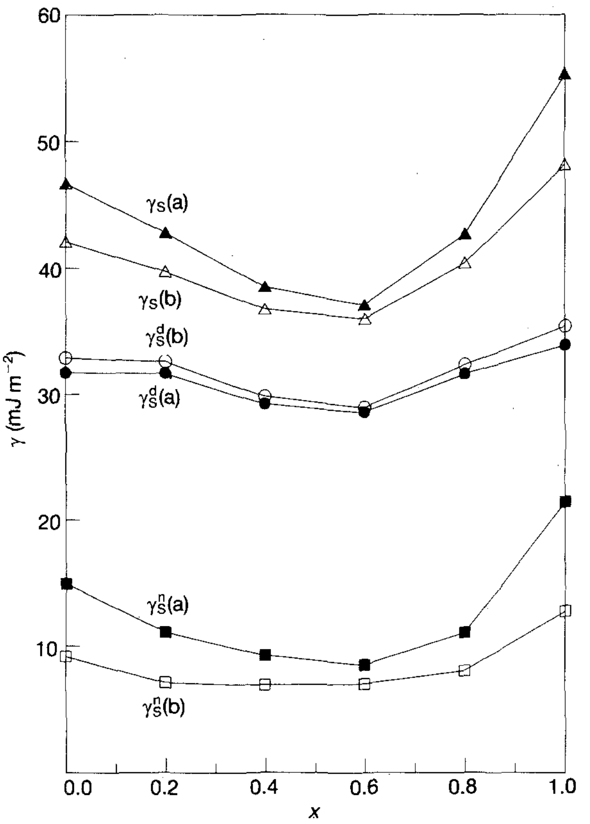

Figure 9 The average value of the non-dispersion component, γ_S^n, the dispersion component, γ_S^d, and the total, γ_S, surface free energy of cassiterite plate IV covered with an SDS + TX-100 mixed film versus the molar fraction, x, of TX-100 in solution, for liquid systems (a) and (b).

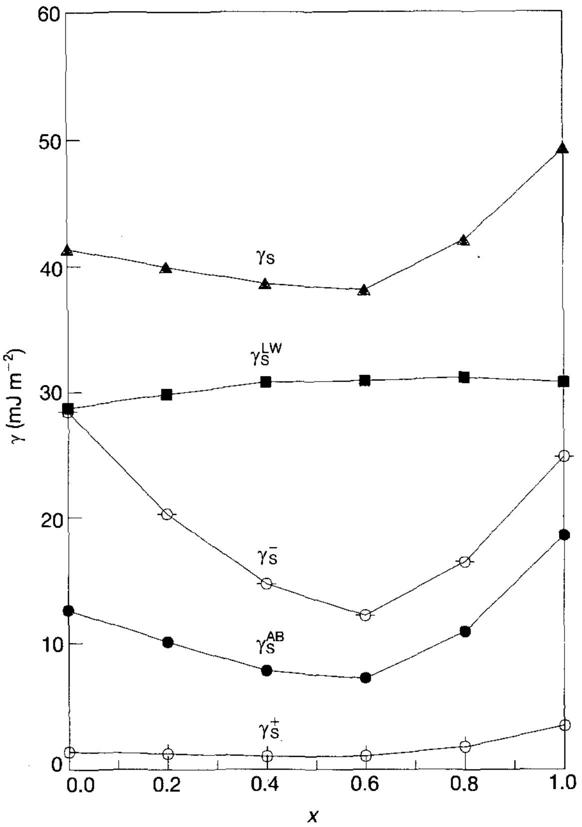

Figure 10 The average value of the Lifshitz-van-der-Waals component, γ_S^{LW}, the electron-acceptor part, γ_S^+, and the electron-donor part, γ_S^-, of the acid–base component, γ_S^{AB}, and the total, γ_S, surface free energy of cassiterite plate I covered with an SDS + TX-100 mixed film versus the molar fraction, x, of TX-100 in solution.

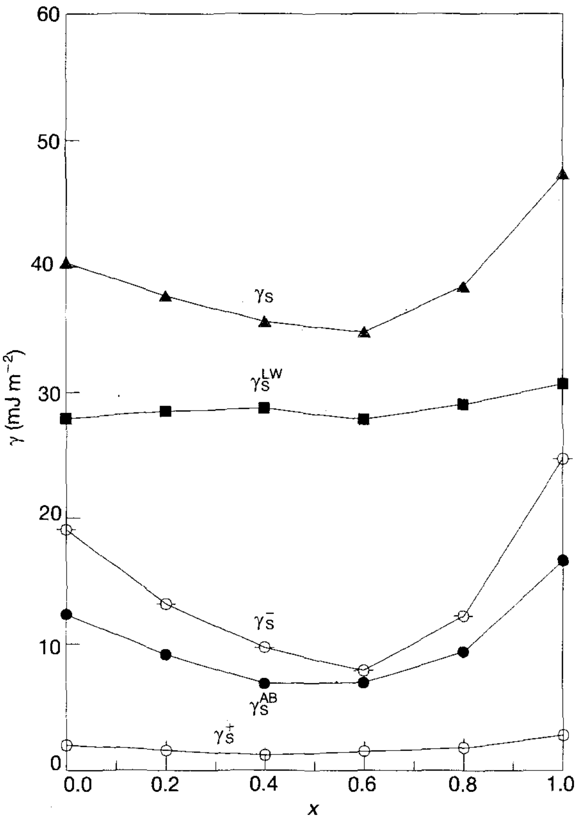

Figure 11 The average value of the Lifshitz–van-der-Waals component, γ_S^{LW}, the electron-acceptor part, γ_S^+, and the electron-donor part, γ_S^-, of the acid–base component, γ_S^{AB}, and the total, γ_S, surface free energy of cassiterite plate II covered with an SDS + TX-100 mixed film versus the molar fraction, x, of TX-100 in solution.

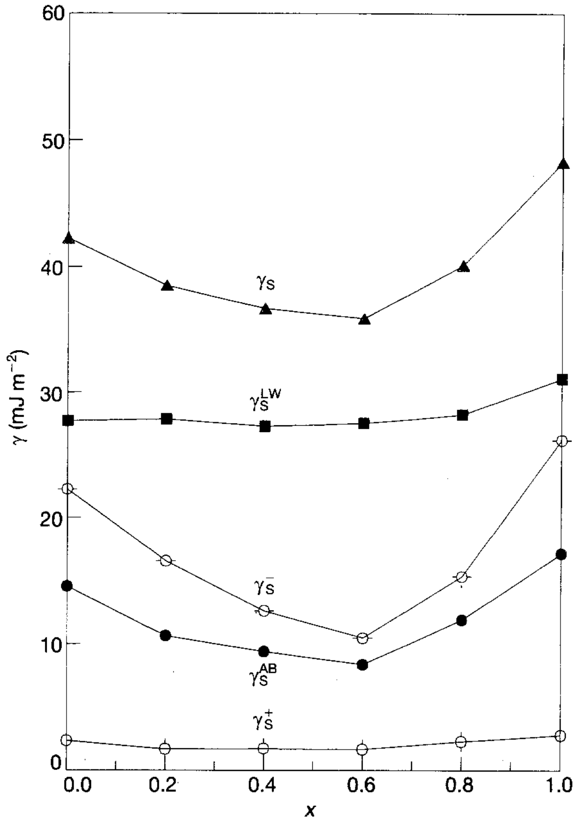

Figure 12 The average value of the Lifshitz–van-der-Waals component, γ_S^{LW}, the electron-acceptor part, γ_S^+, and the electron-donor part, γ_S^-, of the acid–base component, γ_S^{AB}, and the total, γ_S, surface free energy of cassiterite plate III covered with an SDS + TX-100 mixed film versus the molar fraction, x, of TX-100 in solution.

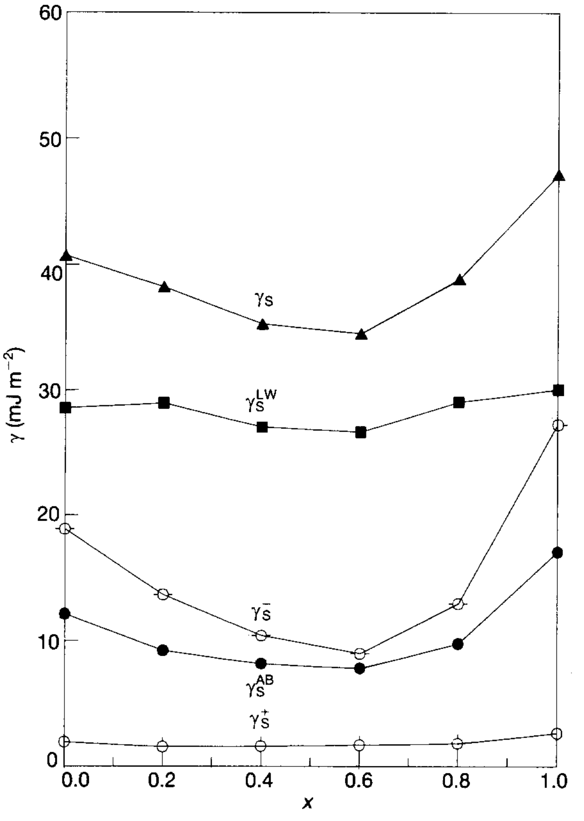

Figure 13 The average value of the Lifshitz–van-der-Waals component, γ_S^{LW}, the electron-acceptor part, γ_S^+, and the electron-donor part, γ_S^-, of the acid–base component, γ_S^{AB}, and the total, γ_S, surface free energy of cassiterite plate IV covered with an SIS + TX-100 mixed film versus the molar fraction, x, of TX-100 in solution.

5. Discussion

The surface of cassiterite not treated by any acid or alkali and well dried is poorly wetted by polar liquids and its surface free energy results mainly from dispersion intermolecular interactions [18]. Under the influence of acids and alkalis, hydrated OH groups were formed on the cassiterite surface [18], they can be dissociated in different ways depending on the pH of the solution in contact with the cassiterite surface.

The pH of the solution of the mixture of anionic and non-ionic surfactants (SDS + TX-100) was not controlled; it ranged from 5.85 to 6, which is slightly lower than the isoelectric point of charge for cassiterite (pH = 6.5) [22]. Therefore, when cassiterite was in contact with such a mixed solution there were only slightly more positive than negative charges on the cassiterite surface. For cassiterite plates I it is possible that the adsorption of SDS and TX-100 molecules takes place mainly as a result of the attractive interfacial free energy, and it is expected that the electrostatic contribution to the free energy plays only a small role in this case. This is confirmed both by the contact angles Figs 1 to 5, plate I and the components of the surface free energy of cassiterite covered with a film of only SDS or only TX-100 ($x = 0$ or $x = 1$) (Figs 6 and 10). The values of the contact angle for polar liquids on the cassiterite/SDS or TX-100 film surface were considerably lower and the values of γ_S^n or γ_S^{AB} (Figs 1 to 3 plate I and Figs 6 and 10) were higher than those for "bare" cassiterite [18] (Tables III to V, i).

Since the surface free energy of cassiterite plate I results mainly from dispersion intermolecular interactions, the interaction between the hydrocarbon chain of SDS or TX-100 should be favourable and the polar "heads" of SDS or TX-100 can be directed

TABLE III Values of the contact angle for water, θ_W, glycerol, θ_G, formamide, θ_F, diiodomethane, θ_D, and bromoform, θ_B, on the cassiterite surface taken from [18]

Plate of cassiterite	θ_W degrees	θ_G degrees	θ_F degrees	θ_D degrees	θ_B degrees
Not treated by acids and dried at room temperature (i)	72	55	44	41	14
Treated by HNO_3 60 % acid and dried at room temperature (ii)	0	14	0	39	0

TABLE IV Values of the dispersion, γ_S^d, and nondispersion, γ_S^n, components of the cassiterite surface free energy, γ_S taken from [18]

Plate of cassiterite	γ_S^d (mJ m^{-2})	γ_S^n (mJ m^{-2})	γ_S (mJ m^{-2})
Not treated by acids and dried at room temperature (i)	36.49	7.41	43.90
Treated by HNO_3 60% and dried at room temperature (ii)	33.65	40.98	74.63

TABLE V Values of the Lifshitz–van-der-Waals, γ_S^{LW}, electron acceptor, γ_S^+, and electron-donor, γ_S^-, components of the cassiterite surface free energy, γ_S, taken from [18]

Plate of cassiterite	γ_S^{LW} ($mJ\,m^{-2}$)	γ_S^+ ($mJ\,m^{-2}$)	γ_S^- ($mJ\,m^{-2}$)	γ_S^{AB} ($mJ\,m^{-2}$)	γ_S ($mJ\,m^{-2}$)
Not treated by acids and dried at room temperature (i)	35.43	1.97	6.39	7.10	42.53
Treated by $HNO_3$60% and dried at room temperature (ii)	30.12	5.03	50.38	31.84	61.96

outwards from the cassiterite surface and then hydrated, which leads to an increase in the wettability of polar liquids and in the contribution of polar intermolecular interactions to the surface free energy of cassiterite plates I covered with SDS or TX-100 film, in comparison to "bare" cassiterite plate (not treated by any acids).

The hydration of cassiterite plate I/SDS or the TX-100 film surface was confirmed by the important divergences among the γ_S^n, γ_S^- and γ_S^{AB} values determined on the basis of the contact angles for the systems of liquids involving water (system (a)) and those only involving only organic liquids (system (b)). This problem was discussed in more detail in our previous paper [18]. It is worth noting that the molecules of polar liquids such as water, glycerol and formamide interact with the hydrated surface in a different way to the apolar molecules (diiodomethane and bromoform).

The molecules of polar liquids, and also water molecules, of course, can penetrate into a hydrated film, but the molecules of apolar liquids cannot. Therefore, the equilibrium state of the system cassiterite plate I/SDS or TX-100 film–polar-liquid drop–air is described by a different energetic state of the cassiterite under the polar-liquid drop than in the system cassiterite/SDS or TX-100–apolar liquid drop–air under the apolar liquid drop. Also, the assumption that $\Pi e_L = 0$ is uncertain.

The presence of a mixed film of SDS and TX-100 on the surface of cassiterite plates I causes an increase in the contact angles for polar and apolar liquids (Figs 1 to 5, plate I) and a decrease in the values of γ_S^n or γ_S^{AB} compared to the values for cassiterite plate I/SDS or TX-100 film surface. This can be related to a change of the orientation of the TX-100 as well as the SDS molecules on the cassiterite-plate-I surface; this orientation leads to a decrease in the degree of hydration of the mixed film on surface, and also to a decrease in the polar-intermolecular-interaction contribution to the surface free energy, in comparison to single SDS or single TX-100 films.

In the case of cassiterite surfaces which were treated by HNO_3 or HCl acids before adsorption (plates II, III and IV), there is an increase in the contact angle for polar liquids (Figs 1 to 3, plates II–IV) and a decrease in the contribution of polar intermolecular interactions (Figs 7 to 9 and 11 to 13) in comparison to surfaces treated by acids but without SDS or TX-100 film (Tables III to V, ii) [18]. On the surface of cassiterite plates II, III and IV, the OH groups were present before SDS or TX-100 adsorption; and, despite the dispersion interactions, the polar intermolecular interactions between SDS or TX-100 molecules and the cassiterite surface play an important role, as a result of which the hydrated heads of SDS or TX-100 are probably directed towards the cassiterite surface bonded to the OH groups, and then there is a decrease in the wettability of the cassiterite/SDS or TX-100 film surface in comparison to the "bare" hydrated cassiterite surface [18]. Also, the non-dispersion or acid–base components of the cassiterite/SDS or TX-100 film surface free energy are lower than for "bare" cassiterite.

When the surface of cassiterite plates II–IV were coated by a mixed SDS + TX-100 film, a further decrease in the wettability and polar components of the cassiterite surface free energy took place. This synergetic effect was probably caused by the mutual promotion of coadsorption of SDS and TX-100 molecules on the cassiterite surface and by the consequently higher bonding of OH groups by these molecules. In this case, in contrast to cassiterite plate I, there is not a reversing of the orientation of the heads of SDS and TX-100 molecules. On the basis of above mentioned studies it can be stated that, from the flotation point of view, the use of mixed solutions of anionic and nonionic surfactants can cause a synergetic effect in the process of adhesion of air bubbles to the mineral surface and an increase in the stability of the mineral–air–bubble aggregate due to the decrease in the contribution of the polar interactions to the mineral surface free energy.

Acknowledgement

The financial support for this work by DGICYT under project No. PB89-0519 is gratefully acknowledged.

References

1. D. W. FUERSTENAU and B. YAMADA, *J. Trans. Amer. Inst. Min. Engs.* **223** (1962) 50.
2. J. LEJA and J. H. SCHULMAN, *Min. Engng Y.* **6** (1954) 221.
3. M. J. ROSEN, Surfactants and Interfacial Phenomena, 2nd Edn. (Wiley, New York, 1989) p. 393.
4. K. L. STELLNER and J. F. SCAMCHORN, *Langmuir* **5** (1989) 77.
5. M. L. GONZÁLEZ-MARTÍN and C. H. ROCHESTER, *J. Chem. Soc. Faraday Trans.* **88** (1992) 873.
6. A. C. ZETTLEMOYER, in "Hydrophobic Surfaces", edited by F. M. Fowkes, (Academic Press, New York, 1969) p. 1.
7. F. M. FOWKES, *Ind. Eng. Chem.* **56** (1964) 40.
8. E. CHIBOWSKI and A. WAKSMUNDZKI, *J. Colloid Interface Sci.* **66** (1978) 213.
9. S. WU, in "Polymer interface and adhesion" (Dekker, New York, 1982).
10. K. L. MITTAL, in "Adhesion science and technology", Vol. 9A, edited by L. H. Lee (Plenum, New York, 1976) p. 129.
11. P. P. J. SELL and A. W. NEUMANN, *Agew. Chem.* **78** (1966) 321.
12. D. LI and A. W. NEUMANN, *J. Colloid Interface Sci.* **148** (1992) 196.
13. C. J. van OSS, R. J. GOOD and M. K. CHAUDHURY, *J. Chromatography* **391** (1987) 53.

14. C. J. van OSS and R. J. GOOD, *J. Dispersion Sci. Technol.* **9** (1988) 355.
15. C. J. van OSS, R. J. GOOD and H. J. BUSSCHER, *ibid.* **11** (1990) 75.
16. D. K. OWENS and R. C. WENDT, *J. Appl. Polym. Sci.* **13** (1969) 1741.
17. D. H. KAELBLE, *J. Adhesion* **2** (1970) 66.
18. B. JAŃCZUK, J. M. BRUQUE, M. L. GONZÁLEZ-MARTÍN and J. MORENO DEL POZO, *J. Colloid Interface Sci.* **161** (1993) 209.
19. A. W. NEUMANN and R. J. GOOD, in "Surface and colloid science", Vol. 11, edited by R. J. Good and R. D. Stromberg (Plenum, New York, 1979) p. 31.
20. B. JAŃCZUK and T. BIAŁOPIOTROWICZ, *J. Colloid Interface Sci.* **127** (1989) 189.
21. B. JAŃCZUK, M. L. KERKEB, T. BIAŁOPIOTROWICZ and F. GONZÁLEZ-CABALLERO, *ibid.* **151** (1992) 333.
22. S. B. BAHACHANDRAM, G. SIMKOWICH and F. F. APLAN, *Int. J. Min. Process.* **21** (1987) 157.

Received 13 July
and accepted 17 December 1993