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Influence of tetradecylamine chloride on the surface free-energy components and flotability of barite

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The concept presented by van Oss *et al.* of the surface free-energy components: apolar, (Lifshitz–van der Waals LW), and polar (electron donor/electron acceptor SR) is used in a model system: barite/tetradecylamine chloride (TDACl)–water. The components have been determined for bare, 0.25, and 1.0 TDACl covered barite surfaces. The values were obtained from glycerol (or water) contact angles and by using a method in which zeta potentials were measured for a series of barite/TDACl/*n*-hexane (*n*-hexanol) film samples in water. From the determined surface free-energy components, the values of ΔG for particular samples were calculated. Negative ΔG is the thermodynamic condition for effective flotation. This condition states that the work of water adhesion to the surface must be less than the work of water cohesion. Full agreement between the flotation activity of the samples and the ΔG magnitude was found. We conclude that experimentally determined components are useful quantities for explaining some interfacial phenomena.

1. Introduction

Recently, van Oss *et al.* [1–10] presented a new and, it seems, a very useful approach to the surface free-energy formulation. According to them the non-covalent surface and interfacial interactions consist of a Lifshitz–Van der Waals apolar (LW) component and electron donor/electron acceptor (or Lewis' acid–base) polar (AB) interactions. In many systems the electrostatic interactions can be neglected [1]. Thus, total interaction, γ_i^{TOT}, is a sum of the apolar, γ_i^{LW}, and polar, γ_i^{AB}, range interactions

$$\gamma_i^{\mathrm{TOT}} = \gamma_i^{\mathrm{LW}} + \gamma_i^{\mathrm{AB}} \qquad (1)$$

The γ_i^{LW} involves dispersion (London), induction (Debye), and orientation (Keesom) forces. In most cases, Debye and Keesom interactions contribute a little [4]. Thus the apolar term is largely due to dispersion interactions, and numerically it is equal to the Fowkes' [11] dispersion term.

However, the polar term, in general, results from Lewis' acid–base interaction, or in other words, from electron acceptor (γ_i^+)/electron donor (γ_i^-) interactions. It should be stressed that these interactions are not additive, because they are intrinsically asymmetrical. The polar interactions can be expressed as

$$\gamma_i^{\mathrm{AB}} = 2(\gamma_i^+\gamma_i^-)^{1/2} \qquad (2)$$

Thus, for phases i and j total interfacial free energy reads [4]

$$\gamma_{ij}^{\mathrm{TOT}} = [(\gamma_i^{\mathrm{LW}})^{1/2} - (\gamma_j^{\mathrm{LW}})^{1/2}]^2 + 2[(\gamma_i^+\gamma_i^-)^{1/2} + (\gamma_j^+\gamma_j^-)^{1/2} - (\gamma_i^-\gamma_j^+)^{1/2} - (\gamma_i^+\gamma_j^-)^{1/2}] \qquad (3)$$

or, in the case of solid (s) and liquid (l) phases, it can be expressed by three phase contact angles [4]

$$(1 + \cos\theta)\,\gamma_{\mathrm{l}}^{\mathrm{TOT}} = 2[(\gamma_{\mathrm{s}}^{\mathrm{LW}}\gamma_{\mathrm{l}}^{\mathrm{LW}})^{1/2} + (\gamma_{\mathrm{s}}^+\gamma_{\mathrm{l}}^-)^{1/2} + (\gamma_{\mathrm{s}}^-\gamma_{\mathrm{l}}^+)^{1/2}] \qquad (4)$$

It should be noted that any contribution of the film pressure behind the drop has not been taken into account in this equation. To determine the three components, γ^{LW}, γ^+ and γ^- of a solid or liquid surface free energy, one has to use three liquids, for example, for contact-angle measurements for which the components are known.

Saturated hydrocarbons are known as liquids exposing only the London apolar interaction, γ^{LW}. Aliphatic alcohols show strongly monopolar γ_{s}^- interaction [3, 4], and they can be used for determination of the γ^+ term of another contacted phase. Having determined the two components, even bipolar liquid, like water or glycerol, can be used for determination of γ^- of the other phase.

In this work we applied the concept reported by van Oss *et al.* [1–10] to investigate the possibility of quantitative correlation between changes in solid–liquid interfacial free energy and flotation activity of the mineral.

The flotation process used for benefication of minerals is obviously one of the physicochemical processes that relies on interfacial free-energy differences. Laboratory flotation tests of pure minerals may be used for verification of whether the experimentally determined values of the mineral surface free-energy components have any physicochemical meaning for explanation of the efficiency of the process.

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Thermodynamically, flotation is only possible if a decrease in the specific free energy, ΔG, takes place during replacement of the solid/liquid interface by the solid/gas interface

$$\Delta G = \gamma_{sv} - \gamma_{sl} - \gamma_{lv} < 0 \qquad (5)$$

This is the work of spreading, and as a phenomenological thermodynamic equation it says nothing about the kinetics of the process. However, it shows the necessary condition before flotation occurs.

Equation 6 can be easily derived from Equation 5 showing that the flotation of the mineral, the attachment of a gas bubble to the mineral surface, may take place if the work of water adhesion, W_a, to the solid surface is less than the work of water cohesion, W_c

$$\Delta G = W_a - W_c < 0 \qquad (6)$$

or in terms of apolar and polar interactions, it reads [4]

$$\Delta G = -2\gamma_l^{TOT} + 2\left[(\gamma_s^{LW}\gamma_l^{LW})^{1/2} + (\gamma_s^{+}\gamma_l^{-})^{1/2} + (\gamma_s^{-}\gamma_l^{+})^{1/2}\right] < 0 \qquad (7)$$

Thus, if one knows the components of the mineral surface free energy, the work of water adhesion to the surface and then ΔG can be calculated. Comparison of the calculated interfacial free-energy changes of the system with the flotation properties of the samples (resulting from the surface coverage with a collector) should give information about the validity of experimentally determined components of the mineral surface free energy. To achieve a good flotability of the mineral, the collector should block the polar interaction (short-range hydrogen bonding) of the surface with water molecules, thus diminishing the value of the work of adhesion.

In this paper we have chosen barite/tetradecylamine chloride–water as a model system to test whether a correlation exists between the predictions based on the experimental values of the mineral surface free-energy components and flotation activity changes. The components were determined by contact-angle measurements as well as a method based on zeta-potential measurements [12–20].

The method consists in measurements of zeta potential in doubly distilled water for a series of the mineral samples precovered with known volumes of *n*-alkane for γ_s^{LW} determination [12, 14, 15], and then another series of samples of the same minerals precovered with known volumes of *n*-alcohol for determination of polar interaction of type γ^+ (previously interpreted as non-dispersion component [19]). Having determined γ_s^{LW} and γ_s^+, γ_s^- was determined from contact-angle measurements of water and glycerol drops.

The use of zeta-potential measurements as a method for determination of surface free-energy components was justified by the finding that, in systems with very low ionic strengths (in doubly distilled water) and a non-ionogenic solid, zeta potential is a function of the specific volume of the film deposited on the solid surface [12, 13, 16, 17]. Also, taking into account Lippmann's equation for a polarizable interface combined with Young–Dupre's equation, as done by Holly [21] for a non-conducting solid/liquid interface which relates the electrical surface charge and potential with interfacial free energies and the contact angle, it seemed to us reasonable to consider the observed changes in zeta potential as due to changes in the interfacial solid/liquid free energy resulting from increasing specific volume of the *n*-alkane or *n*-alcohol film [19].

Consequently, it was possible to treat the zeta potential as an "adsorption parameter". Thus, using Gibbs' adsorption equation

$$\begin{aligned} d\gamma_{sl} &= -\Gamma_i d\mu_i \\ &= -\Gamma_i RT \, d\ln a_i \end{aligned} \qquad (8)$$

and the observed experimental relationship between the zeta potential and the film specific volume, it seems that for these special systems the following relationship can be suggested

$$d\mu_i = RT \, d\ln|\zeta| \qquad (9)$$

Here a_i can be formally defined as the activity of the alkane (or the alcohol) in the water phase or in the film phase, and other symbols have their normal meaning.

If Equation 9 holds, then an empirical equation obtained from Gibbs' adsorption equation for a solid–gas interface

$$\begin{aligned} \pi &= \gamma_s - \gamma_{sf} \\ &= \frac{RT}{V_0 A} \int_0^p v \, d\ln p \end{aligned} \qquad (10)$$

(given for the first time by Bangham and Razouk, see [22]), can be derived

$$\begin{aligned} \pi &= \gamma_s - \gamma_{sf} \\ &= \frac{RT}{V_0 A} \int_{\zeta_0}^{\zeta} v \, d\ln|\zeta| \end{aligned} \qquad (11)$$

where π is the film pressure, γ_s is the bare solid surface free energy, γ_{sf} is the film-covered solid surface free energy, R and T have their usual meanings, V_0 is the molar volume of the film, A is the total surface of the sample, v is the adsorbed volume at the vapour pressure, p, ζ_0 is the zeta potential of the bare solid surface, and ζ is the zeta potential of the sample precovered with the volume v of the film.

Although Equation 11 has not been derived theoretically, we found that it worked in many systems. A comparison of the results obtained by other methods (adsorption [18], contact angles [14, 15], and ellipsometry [20]) support the usefulness of the method.

Another problem is interpretation of the determined film pressure values versus the adsorbed amounts (specific film volumes) in terms of the solid and the liquid surface free-energy components. But it is a general problem of the adsorption isotherms interpretation and it will be discussed later.

2. Experimental procedure

2.1. Materials

Mineralogical specimens of barite from the "Stanisławów" deposit in Poland were used. They were crushed in a corundum mortar and sieved into two fractions: < 0.06 mm for microelectrophoretic measurements, and 0.12–0.3 mm for flotation tests. The fraction for flotation tests was deslimed in doubly distilled water with repeated decantation.

Tetradecylamine chloride was made in our laboratory from tetradecylamine. Methanol of Analar grade was used in these experiments and *n*-hexanol and *n*-hexane were of pure grade. They were used without any further purification, but a chromatography test showed no polar impurities in the *n*-hexane.

2.2. Methods

Zeta potential determinations were done by microelectrophoresis [19, 20]. A glass rectangular cell 100 mm × 20 mm × 1 mm was used. Usually a 10 V cm^{-1} gradient was applied, and the particles were observed under ×210 magnification. The velocity of at least 10–15 particles were recorded in each experiment. Zeta potentials of the barite samples were determined for the following systems.

(i) Barite/TDACl–H_2O. Samples of 0.2 g weighed into glass vials were poured out with 4 ml methanolic solution of tetradecylamine chloride (TDACl) at a desired concentration. Then the methanol was evaporated at 50 °C, and the samples were dried at 60 °C for 1.5 h. After cooling, the samples were dispersed into 100 ml doubly distilled water and zeta potentials were determined.

(ii) Barite/TDACl/*n*-hexane–H_2O, and

(iii) Barite TDACl/*n*-hexanol–H_2O. For these systems a portion (7 g) of barite was added to a methanolic solution of TDACl at such a concentration that was sufficient to cover the barite surface with 0.25, and in another series with 1.0 of a monolayer of TDACl. After evaporation of the methanol and drying, 0.2 g were weighed into glass ampoules, they were then cooled in liquid nitrogen and definite volumes of *n*-hexane or *n*-hexanol were dosed from a Hamilton microsyringe. After additional cooling for a while in liquid nitrogen, the ampoules were sealed with a flame, then heated at 60 °C (*n*-hexane covered samples) and at 110 °C (*n*-hexanol covered samples) for 1.5 h and shaken every 15 min by hand. After cooling, 100 ml of aqueous suspension was prepared of each of the samples.

Flotation tests of the barite samples in doubly distilled water were performed in a single-bubble Hallimond's tube with a volume of about 100 ml and with a nitrogen flow rate of 20 ml min^{-1}. The barite samples used for the tests were 1.5 g in weight and were floated with 100 ml nitrogen, or, if a sample floated completely, the volume of nitrogen required was recorded. Prior to the flotation tests the barite samples had been covered with TDACl according to the procedure described in (i). After each of the tests had been completed, TDACl concentration was determined in the "post-flotation" water.

Determination of TDACl in post-flotation water was made by the Few [23] method in which a colour complex formed with Tropeoline in 1:1 ratio is then extracted into chloroform and the solution is analysed spectrophotometrically at 485 nm wavelength. Previously determined calibration curves were used.

Interfacial tension measurements of water–*n*-hexanol were conducted by a volume-drop method at 20 °C. Additionally, the surface tensions of water and *n*-hexanol have also been measured by the same method at 20 °C.

Contact angles were measured on the barite pellets by the sessile drop method. The pellets were obtained from the barite powder by pressing it between two stainless steel plates under a pressure of 150 kG cm^{-2}. Prior to pressing the powder surface had been covered with TDACl from methanolic solution by evaporation of the methanol. The total content of TDACl in the solution was sufficient to cover the powder with 0.25 or 1.0 statistical monolayer of TDACl. Advancing contact angles of a sessile drop of glycerol or water at 20 ± 0.5 °C were measured using a goniometer–telescope system with ×25 magnification. Several drops, 1–2 μl in volume, were settled on the surface and the contact angle value was read out immediately.

3. Results and discussion

Barite possesses a hydrophilic surface which is manifested by almost complete spreading of a water drop on it, and also it should appear in its low natural flotability in water. The results of the flotation tests of the barite samples are shown in Fig. 1. As can be seen, the natural flotability of the bare barite sample is really low. It amounts to only about 10%. Moreover, from this figure it can also be seen that even one statistical TDACl monolayer does not lead to complete flotation of the sample. It floats only in about

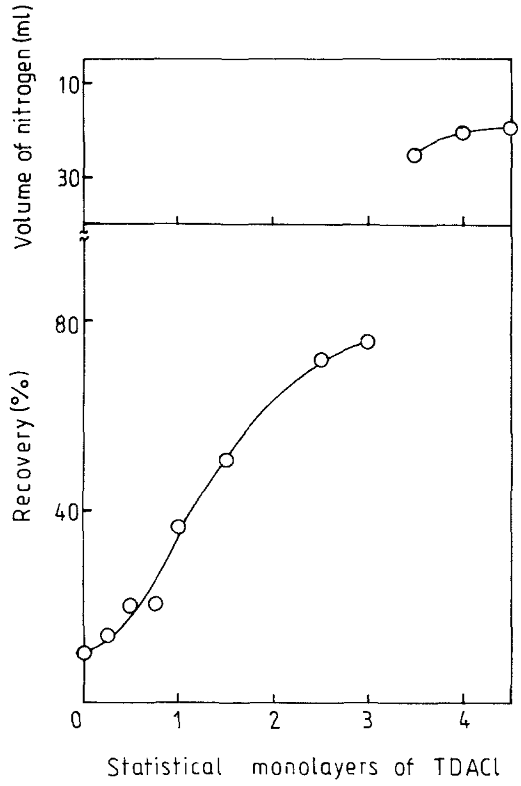

Figure 1 Flotation recovery of barite in doubly distilled water as a function of the number of statistical tetradecylamine chloride (TDACl) monomolecular layers deposited on the barite surface.

40%. Obviously such coverages of the surface should decrease the polar (hydrogen bonds) interactions, and thus increase the flotation. The question is whether any quantitative relationship holds between the magnitudes of the surface energy components and flotability.

Both cationic and anionic collectors can be used to float minerals of the kind such as barite [24–30]. In the case of chemical adsorption, an insoluble layer of the salt is formed as a result of surface exchange reaction between the mineral surface and the collector cation [24]

$$BaSO_4 + 2RNH_3^+ = Ba^{2+} + (RNH_3)_2SO_4 \quad (12)$$

This reaction is only possible if the solubility product of $[RNH_3^+]^2 \times [SO_4^{2-}]$ is less than that of barite. When physical adsorption takes place, the collector molecules are bonded by hydrogen bonding. Also multilayer adsorption of the molecular form of the amine may occur due to hydrolysis of TDACl [31].

Fig. 2 shows the changes in zeta potential for barite in water as a function of TDACl coverage up to three statistical monomolecular layers. The negative zeta potential decreases with increasing coverage of the surface. Initially positively charged RNH_3^+ ions are probably chemically adsorbed. In this figure there are also shown values of zeta potential obtained after treatment of the precovered barite surface in the ultrasonic bath. As can be seen, zeta potentials remain almost the same. Hence it can be concluded that the interaction of the collector molecules with the barite surface is strong. Moreover, the data indicate that the surface coverage is not uniform (cluster formation), because even at two calculated monolayers of TDACl, the zeta potential is still negative (Fig. 2), dropping to zero only at three monolayers. If the coverage were uniform, the potential should be positive or close to zero at one monolayer coverage. The conclusion that the coverage is not uniform is also in agreement with the flotation results (Fig. 1). High flotation recovery (~ 80%) occurs only when the barite surface precoverage is three or more statistical monolayers.

To learn about possible desorption of the collector from the surface during the flotation tests the post-flotation waters were analysed for TDACl. The results of the determinations are presented in Fig. 3. Only about 0.4 monolayer of the collector is desorbed in the most extreme case. This agrees with the hypothesis of strong $BaSO_4$–TDACl interactions.

To test quantitatively the relationship between the flotability of the samples and their surface free energy, we applied van Oss *et al.*'s [1–10] approach to the surface free-energy components. For the bare surface of barite from the adsorption isotherms (obtained by the gas chromatographic method), Wójcik and Biliński [32] determined dispersion and polar components of the surface free energy to be 77.2 and 68.5 mJ m^{-2}, respectively. They used Owens and Wendt's [33] approach (Equation 1) which, in the light of van Oss *et al.*'s [1–10] and Fowkes *et al.'s* [34] findings, is not correct as for the non-dispersion component.

In order to find the apolar γ_s^{LW} and polar γ_s^{AB} (γ_s^+ and γ_s^-) components, we used three different liquids for which the particular components are known. Thus, to determine the γ_s^{LW} component, *n*-hexane was used. This liquid possesses the γ_l^{LW} component (18.49 mJ m^{-2}), i.e. dispersion (London) interaction. To determine the γ_s^+ component of the barite surface, we used *n*-hexanol, which is a monopolar liquid (γ_l^-) [3, 4], and glycerol or water, for which γ_l^+ and γ_l^- components are known [6–10]. The γ_s^{LW} component was determined from the zeta potentials measured in the system barite/*n*-hexane film–water. The known

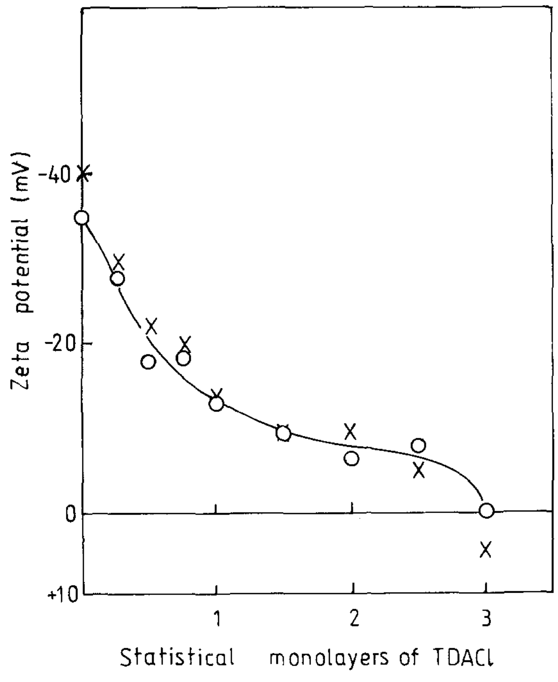

Figure 2 Zeta potential of barite in doubly distilled water as a function of TDACl monolayers deposited on the surface. (×) After treatment of the precovered samples in an ultrasonic bath.

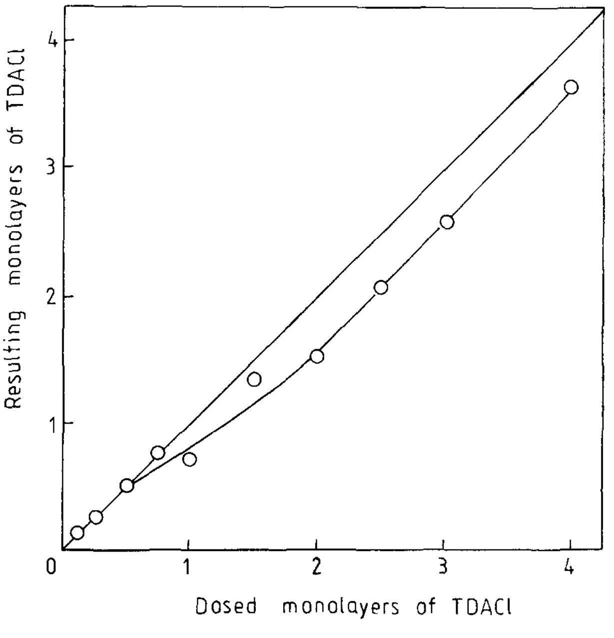

Figure 3 Relationship between the initially deposited concentration and that resulting after the flotation tests of TDACl on barite in units of the calculated monolayers.

volumes of hexane film were deposited on the surface. Then, from the experimental relationship (zeta potential–specific film volume) the *n*-hexane film pressure were determined by graphical integration of Equation 11, using a computer program for this purpose.

Zeta-potential changes as a function of the specific volume of the *n*-hexane film are shown in Figs 4 and 5 for barite samples precovered with 0.25 and 1.0 statistical monolayer of TDACl. They are typical in nature to those obtained previously in other systems [14, 15, 19, 35]. Standard deviations of the particular values (10–15 readings) are shown on the curves by bars. An explanation of the zeta-potential changes based on the classical theory of an electrochemical double layer is rather difficult. We postulated that they may be due to preferential orientation of water dipoles [13, 16, 17]. From the theoretical work and computer simulations it results that at a solid–liquid interface, oscillations in the liquid (film) density may occur [36]. They are due to the geometric effect of the crystal wall and may extend up to several molecular diameters resulting in structuring and oscillations in density. Moreover, Israelachvili [36] found experimentally an oscillatory character of the solvation forces in a mica–liquid–mica system. We believe that the changes of the solvation forces may also appear in the oscillatory changes of zeta potential.

Using the results from Figs 4 and 5, and Equation 11, the *n*-hexane and *n*-hexanol film pressures were determined. Because of oscillatory changes of the zeta potential, the determination of the film pressure actually relies on a summation procedure of the graphically determined integrals for zeta potentials ranged between subsequent extremes, starting from ζ_0 (Equation 11). It was assumed here that no desorption of the film molecules took place from the barite surface into the water phase, at low coverages at least, say up to three to four statistical monolayers. Thus calculated values of the film pressure are shown in Figs 6 and 7, respectively, as a function of statistical monolayers of hexane or hexanol, for both precoverages (0.25 and 1.0 monolayer) of the surface with TDACl. An area of 0.318 nm^2 was assumed for *n*-hexane (horizontal position) [37] and 0.22 nm^2 for *n*-hexanol (vertical position) [38].

As can be observed, there are bends on the π versus surface coverage curves between the second and fourth monolayers. Based on the literature data for insoluble films on liquid surfaces [39, 40] as well as solid ones [41, 42], we somewhat arbitrarily assumed that the bends were probably connected with completion of the spreading wetting process [14, 15, 20, 22, 43]. It is accepted [22] that in the adsorption process of a vapour, the maximum pressure of the film reaches the value equal to the spreading wetting work. However, it seems to be not always true. In some systems [44, 45], the film pressure may correspond even to the work of adhesion if determined from the adsorption isotherm.

Recalling the transitions in the insoluble organic monolayers on water [39, 40] some similarity can be

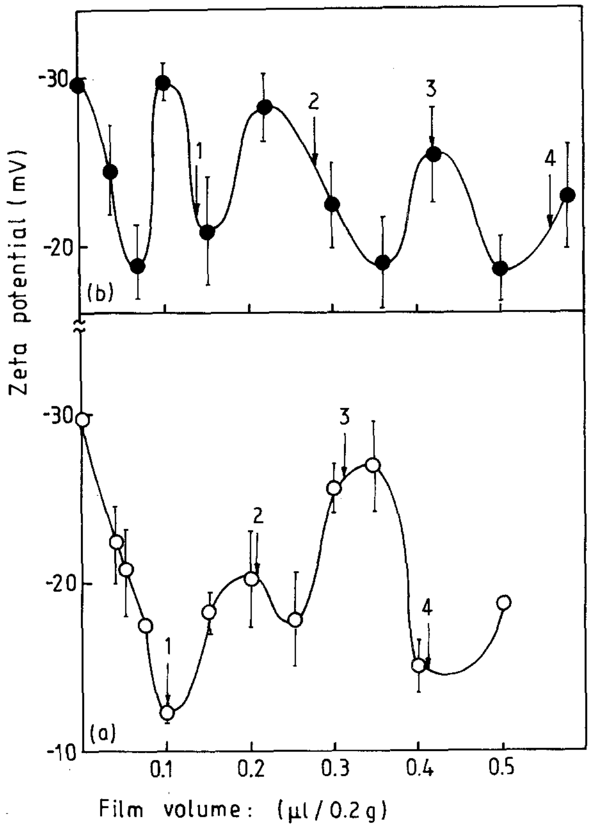

Figure 4 Zeta potentials of 0.25 TDACl monolayer-precovered barite samples in doubly distilled water as a function of (a) *n*-hexane and (b) *n*-hexanol film volumes. The bars on the curves show standard deviation, and the arrows show statistical monolayers.

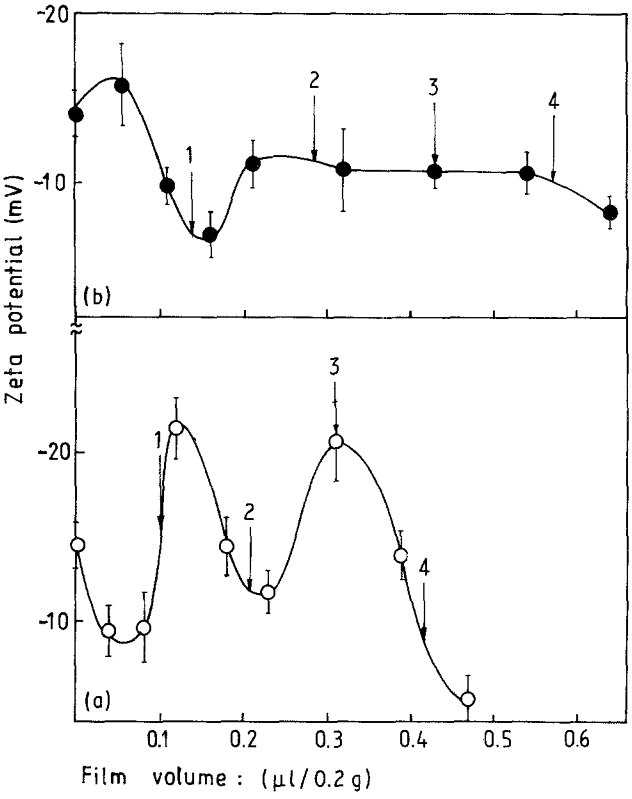

Figure 5 Zeta potentials of 1.0 TDACl monolayer-precovered barite samples in doubly distilled water as a function of (a) *n*-hexane and (b) *n*-hexanol film volumes. The bars on the curves show standard deviation, and the arrows show statistical monolayers.

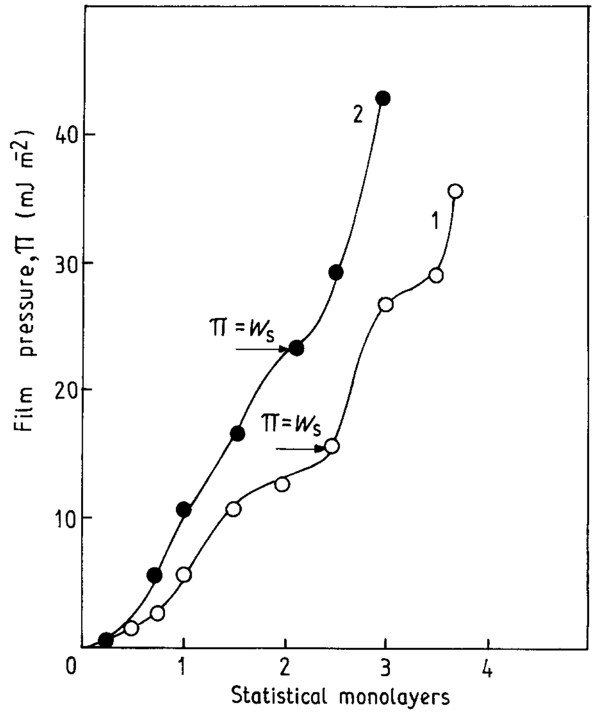

Figure 6 Film pressure, π, of *n*-hexane (curve 1) and *n*-hexanol (curve 2) on the barite surface precovered with a 0.25 statistical monolayer of TDACl.

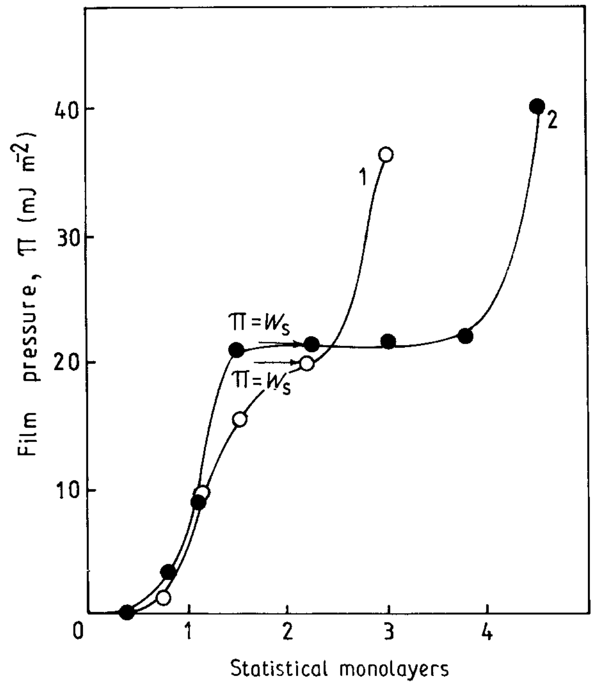

Figure 7 Film pressure, π, of *n*-hexane (curve 1) and *n*-hexanol (curve 2) on the barite surface precovered with a 1.0 statistical monolayer of TDACl.

found. Below one close-packed monolayer of these organic molecules on the water surface, six different states (thus different energies) can be distinguished. It starts from a gaseous state to reach a solid-like one. The states are reflected by inflections on the pressure–area isotherm curve. Moreover, Malcolm [39], for example, has found five transitions (inflections) on the pressure–area isotherms for polypeptides at 20 °C. It was supposed [39] that the transitions arose from the consecutive formation of five layers of the molecules. Most of the monolayers must have a high degree of order [39]. This was supported by a diffraction diagram of crystalline type.

Data concerning the film structure on solids are rather scarce [41–43]. Transitions in *n*-octadecanol monolayers on silica gel were found during heating the system by measuring the retention volume of *n*-octane (inverse gas chromatography), differential thermal analysis and contact-angle measurements. The solid compact–liquid expanded transition was postulated for the *n*-octadecanol film exceeding one monolayer [41, 42]. For helium films on graphite at several degrees Kelvin, the heat capacity peaks appeared between two and three monolayers. They disappeared between three and six to appear again above six to ten monolayers. The peaks were due to structural transitions (melting) in the film.

The above data show that the observed inflections on the film pressure–surface coverage curves in Figs 6 and 7 may result from more or less abrupt transitions in the film structure. Fowkes [37] calculated that up to ten water monolayers can be adsorbed on the quartz surface. However, using his calculations it can be easily shown that already the fourth water monolayer possesses the dispersion interaction, γ^{LW}, proper for bulk water surface [44]. Based on these data [37], we postulated [44, 45] that the inflection on the curves in the range of two to four statistical monolayers results from the spreading wetting process [46]. This assumption allowed us to calculate the long-range component γ_s^{LW} from the *n*-hexane film pressure curve, and the γ_s^+ component from the *n*-hexanol film pressure curve.

Thus, in Figs 6 and 7 arrows mark the π values of *n*-hexane (curves 1) and *n*-hexanol (curves 2) films which were considered to be equal to the spreading wetting work, which is simply equal to ΔG from Equation 9. In the case of hexane film pressure, Equation 9 reduces to the first two terms on its right side with only γ_s^{LW} unknown. However, in the case of *n*-hexanol film, the first three terms have to be taken into account as this liquid interacts by γ_a^{LW} and γ_a^- components [3, 4].

Because we could not find data of γ_a^- for *n*-hexanol in the literature, it was determined by measuring the interfacial tension water/hexanol. Van Oss *et al.* [3, 4] stated that alcohols are strongly monopolar, electron-donor liquids with γ_a^- component. This component does not contribute to the surface tension of alcohols, but it interacts with γ^+ component of other contacted phases. Unfortunately, data for γ_l^+, and γ_l^- for various liquids are still scarce. We chose water, for which $\gamma_w^+ = 25.5\ \mathrm{mJ\,m^{-2}}$ and $\gamma_w^- = 25.5\ \mathrm{mJ\,m^{-2}}$ had been assumed by van Oss *et al.* as the reference values [6–10]. It should be stressed that *n*-hexanol dissolves a little in water (0.59 g/100 g H_2O at 20 °C), which can somewhat interfere in the results.

So, we measured for water–hexanol interfacial tension a value equal to $6.75\ \mathrm{mJ\,m^{-2}}$, and a value of $25.32\ \mathrm{mJ\,m^{-2}}$ for the surface tension of *n*-hexanol. Taking for water $\gamma_w^{\mathrm{TOT}} = 72.8\ \mathrm{mJ\,m^{-2}}$, $\gamma_w^{\mathrm{LW}} = 21.8$

TABLE I Surface free-energy components, work of water spreading $\Delta G = W_s$, and flotation recovery of barite samples precovered with TDACl

Barite sample, TDACl coverage	γ_s^{LW} (mJ m^{-2})	γ_s^{+} (mJ m^{-2})	γ_s^{-} (mJ m^{-2})	$\Delta G = W_{spr}$ (mJ m^{-2})	Flotation recovery
Bare[a]	26.2	1.50	118.9^{+3}_{-3} 63.7	$24.6^{+1.4}_{-1.5}$ -4.9	10.0
0.25	37.5	1.89	$41.6^{+5.6}_{-5.8}$[b] $43.8^{+3.0}_{-3.2}$[c]	$-9.4^{+4.3}_{-5.4}$ $-7.6^{+2.2}_{-2.6}$	13.6
1.0	44.1	0.42	$36.8^{+6.8}_{-6.6}$ $40.6^{+1.8}_{-1.8}$	$-15.8^{+5.4}_{-5.7}$ $-12.7^{+1.4}_{-1.5}$	38.0

[a] [47].

[b] Calculated from the contact angle of glycerol.

[c] Calculated from the contact angle of water.

mJ m^{-2}, and γ_w^+, γ_w^- as above, from Equation 14 the value of $\gamma_a^- = 19.7$ mJ m^{-2} for *n*-hexanol was calculated

$$\gamma_{aw}^{TOT} = \gamma_a^{TOT} + \gamma_w^{TOT} - 2(\gamma_w^{LW}\gamma_a^{LW})^{1/2} - 2(\gamma_w^+\gamma_a^-)^{1/2} \tag{13}$$

This value seems to be a reasonable one. Van Oss *et al.* [4] reported a value of 25 mJ m^{-2} of γ_a^- of ethanol, which may be expected to be higher than that for hexanol, and this is indeed the case. Having determined γ_a^- of hexanol, it was possible to calculate from Equation 9 the electron acceptor interaction γ_s^+ for the barite samples.

The next task was determination of the γ_s^- component for the barite samples. Here the same problem arises with finding a suitable probe liquid. Another problem was to obtain a flat barite surface precovered with 0.25 and 1.0 monolayer of TDACl. For this purpose we used pellets obtained by pressing (150 kG cm^{-2}) the powder previously covered with TDACl between stainless steel plates. To determine the γ_s^- component, as the first approach we used diiodomethane as the probe liquid, but it penetrated instantly into the pellets, and no contact angle could be measured. Therefore, we then tried water and glycerol. It appeared that the more stable droplets were those of glycerol. For example, the contact angle, θ, of water on barite/0.25 TDACl was 26.5° with a standard deviation $\sigma_n = 4.2°$, for seven droplets, and for glycerol $\theta = 32.8°$, with $\sigma_n = 2.9°$ for eleven droplets. Using the measured contact angles and determined γ_s^{LW}, γ_s^+ values, the values of γ_s^- were determined from Equation 6 for the barite samples. All determined values of the barite samples surface free-energy components are listed in Table I together with the values obtained for a bare barite surface [47]. The same barite sample was used and the values were obtained by the same methods using the same probe liquids.

Analysing the results from Table I, first of all it can be found that the determined ΔG values, i.e. the free-energy change accompanied the process of replacement of the mineral/water by the mineral/gas interface, correlate with the changes of the flotation activity. This relationship means that the experimental values of the surface free-energy components are meaningful. It seems that small negative values of ΔG are not sufficient for fast and complete flotation of the sample. ΔG calculated with γ_s^- values determined from water contact angles are rather questionable for the reason mentioned above, the more so that a small negative value of ΔG was determined [47] even for a bare barite surface (Table I).

It is worth stressing that the values of the surface free-energy components are comprehensive, despite the fact they were determined using two different methods. The changes of the components throw some light on the "energetic mechanism" of the collector, TDACl, adsorption. Thus, the apolar component γ_s^{LW} increases from 26.2 mJ m^{-2} for a bare surface, to 44.1 mJ m^{-2} for the surface covered with one TDACl monolayer. Thus the bare surface is hydrated with probably two monolayers of physically adsorbed water [44, 45]. The adsorbing TDACl (or neutral TDA molecules) may partially remove water molecules from the barite surface. This leads to increased dispersion interactions. The higher TDACl coverage, the bigger is the γ_s^{LW} component. The changes also show that TDACl adsorption is not uniform, because otherwise the component should rather decrease to the value characteristic for the hydrocarbon chain, i.e. about 25 mJ m^{-2}, especially with a monolayer coverage.

The electron acceptor component γ_s^+ is rather meaningless but not zero. It is in agreement with van Oss *et al.*'s [4] observation that in most cases solids and liquids rather possess the electron donor, γ^-, interaction. TDACl adsorption with one monolayer coverage decreases it from 1.5 (bare surface) to 0.42 mJ m^{-2}. It is understandable, because the nitrogen atom in amine molecules is a weak electron donor, thus diminishing γ_s^+ of the barite surface.

The most interesting are the changes in the γ_s^- component of the barite surface. This component appears as a result of the electron donor properties of the surface (Lewis' base). In the case of barite they are due to the presence of oxygen atoms on the crystal cleavages. The γ_s^- component is responsible here for the hydrophilic properties of the barite surface (hydrogen bonding). These hydrophilic centres are blocked by the adsorbed ionic species of TDACl or its neutral molecules. However, it appears that even one statistical monolayer of TDACl does not screen the centres because the γ_s^- value is still sufficiently high $36.8\ \mathrm{mJ\,m^{-2}}$. Thus, it appears distinctly that TDACl molecules are not uniformly distributed over the barite surface, but form clusters. However, this decrease in γ_s^- from 118.9 (bare surface) to $36.8\ \mathrm{mJ\,m^{-2}}$ is enough to increase the flotation from 10% to 38%, but it is still insufficient to completely float the sample. In a subsequent paper we shall attempt to show that fast and complete flotation of the barite sample takes place when dodecylsulphate collector is used. At a monolayer coverage 25 ml nitrogen are needed to float the sample completely. It is accompanied by ΔG value as low as $-50\ \mathrm{mJ\,m^{-2}}$.

Summing up briefly, it can be stated that the approach of van Oss *et al.* [1–10] to express surface free-energy components in terms of apolar and polar interactions seems to be very useful and reliable. Using the experimentally determined values of the components, it has been shown that meaningful values of the free-energy changes taking place during the flotation process (replacement of solid/liquid by solid/gas) have been calculated.

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