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Prediction of hydrophobicity/hydrophilicity of a mineral from its surface free energy components in aspect of its flotability

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Based on experimental values of contact angles and mineral surface free energy components, the thermodynamic condition for efficient flotability is investigated in model systems. The condition implies the replacement of solid/ liquid interface (mineral grain/water) by the solid/gas interface (the mineral grain/air bubble) has to be accompanied by a negative change in the free energy ΔF. This means that the work of water spreading on the mineral surface should be negative. This phenomenological thermodynamic condition was compared with flotation results for several minerals whose surfaces were bare (natural flotability) and precovered with a collector. For these model systems it was found that with proper kinetic conditions the flotation may be efficient if the work of spreading is at least -20 mJ/m^2, which may be due to an energy barrier present. Such a study may also be useful for testing the hydrophobic/hydrophilic characteristics of a solid surface in relation to kinetic conditions.

1. INTRODUCTION

Although hundreds of papers dealing with the flotation process of minerals have been published, many problems of mineral enrichment by this method are still open. Flotation may also be applied to solid surface hydrophobicity testing, especially in kinetic conditions, and more generally, wetting phenomena in the presence and absence of surfactants [1–7]. In this paper we are not going to discuss the flotation problems encountered in real systems, but only to test quantitatively fundamental thermodynamic conditions for efficient flotation in model systems.

The flotation act relies on the replacement of solid/liquid interface by solid/gas interface, which appears in the solid (mineral) grain attachment to the gas bubble. In constant temperature and pressure, this process is described by Dupre's equation [8]:

$$\text{Mineral/water} \Leftrightarrow \text{water/gas} \Rightarrow \text{mineral/gas}$$

$$\gamma_{sl} \quad + \quad \gamma_{lg} \quad \rightarrow \quad \gamma_{sg}$$

$$\Delta F = \gamma_{sg} - (\gamma_{lg} + \gamma_{sl}) \qquad \Delta F < 0 \tag{1}$$

where ΔF is the free energy accompanying the attachment process, γ_{sg} is the solid surface free energy, γ_{lg} is the liquid surface free energy (surface tension), and γ_{sl} is the solid/liquid interfacial free energy. For the process to be spontaneous, the free energy change ΔF, has to be negative. The interfacial solid/liquid free energy is defined as [8]:

$$\gamma_{sl} = \gamma_s + \gamma_l - W_a \tag{2}$$

where W_a is the work of adhesion of the liquid to the solid surface. For simplicity the subscript g has been omitted at the free energy symbol γ of the solid and liquid. Inserting Eq. (2) into Eq. (1) one obtains:

$$\Delta F = \gamma_s - \gamma_l - \gamma_{sl} = \gamma_s - \gamma_l - \gamma_s - \gamma_l + W_a \tag{3}$$

$$\Delta F = W_a - W_c = W_s \tag{4}$$

where $W_c = 2\gamma_l$ is the work of cohesion and W_s is the work of spreading of the liquid. From Eq. (4) it is clearly seen that the adhesion of a gas bubble to a solid grain is possible if the work of liquid (water) cohesion is higher than the work of adhesion to the solid surface, or in other words, the work of water spreading on the mineral surface must be negative. In these model systems, as a good approximation, the work of cohesion of pure water can be considered. In real flotation systems the surface tension of the water can be reduced because of the presence of collector and frother. This may affect the work of spreading [4, 7]. To determine the energy change ΔF, the work of adhesion has to be known. The simplest way of determining W_a is to measure the contact angle θ of a water droplet on a smooth surface of the mineral. Then using the Young – Dupre equation the result is:

$$\gamma_s = \gamma_l \cos\theta + \gamma_{sl} = \gamma_l \cos\theta + \gamma_s + \gamma_l - W_a \tag{5}$$

$$W_a = \gamma_l (1 + \cos\theta) \tag{6}$$

The work of adhesion results from interfacial interactions. At present the formulation of van Oss, Good and Chaudhurry [9–11] of the surface and interfacial free energy is commonly accepted, although the determined values are relative ones. According to this approach surface free energy of phase i can be expressed in the following way:

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB} \tag{7}$$

where γ_i is the total surface free energy of the phase i, γ_i^{LW} is its apolar Lifshitz-van der Waals component, and γ_i^{AB} is acid-base (Lewis) component, which in many systems is due to hydrogen bonding interactions. This component consists of two parameters, electron donor γ_i^- and electron acceptor γ_i^+. They are related to each other by a geometric mean:

$$\gamma_i^{AB} = 2(\gamma_i^- \gamma_i^+)^{1/2} \tag{8}$$

In the case of a solid/liquid system, using the above approach, the work of adhesion for liquid is expressed as [9–11]:

$$W_a = 2(\gamma_s^{LW}\gamma_l^{LW})^{1/2} + 2(\gamma_s^- \gamma_l^+)^{1/2} + 2(\gamma_s^+ \gamma_l^-)^{1/2} \tag{9}$$

It is shown that the work of adhesion of a liquid to the solid (mineral) surface can be calculated from its surface free energy components. This method of determining W_a, instead of direct measurement of contact angle, must be used when a smooth surface of the investigated solid (mineral) cannot be obtained because the solid is dispersed in a rock or appears as a powder. Although in such cases the compressed pellets of the separated solid powder can be used for the contact angle measurements, it should be kept in mind that the pellets are always porous to some extent, and this may affect the measured contact angles. Therefore, by applying "thin layer wicking" or "thin column wicking" techniques [12–16], the solid surface free energy components can be determined and then work of adhesion calculated. This relies on applying a modified version of Washburn's equation to describe the wicked distance (x) vs. time (t) relationship:

$$x^2 = \frac{Rt}{2\eta}\Delta G \tag{10}$$

where R is an effective radius of interparticle pores in the thin porous layer deposited on a glass slide (or packed in a thin glass tube), η is the penetrating liquid viscosity, and ΔG is the specific free energy accompanying the wicking process. Resulting from Eq. (10) for a particular liquid the $x^2 = f(t)$ dependence should be a straight line with a slope of ΔG. The value of ΔG depends on the nature of the probe liquid used as well as whether the investigated solid surface is bare (non-equilibrated) or precontacted (equilibrated) with the liquid vapor before the wicking experiment [13–15]. In this notation a positive ΔG means the process is spontaneous. The theoretical background and details of the experimental procedure were described elsewhere [13–15]. For this purpose, in wicking experiments, three liquids must be used (of which at least two are polar), where the surface tension components are known. N-alkane, water and formamide are often applied as probe liquids.

Having determined the mineral surface free energy components, the free energy change accompanying the flotation process ΔF can be calculated. One may then draw conclusions about the hydrophobic/hydrophilic character of the mineral surface as well its flotability. In the flotation process, collectors (surfactants) are used to selectively change the hydrophilic characteristics of the mineral surface into a hydrophobic one. Usually, the adsorbed collector decreases the polar interactions while the apolar Lifshitz-van der Waals component of the mineral is only slightly changed.

In this paper, the hydrophilic/hydrophobic characteristics of a mineral surface will be investigated studying the relationship between mineral surface free energy components, changes in the free energy ΔF, and flotability of the mineral. Detailed results will be presented for a barite/collector – water system. Some results from literature for other minerals will be reviewed also.

2. EXPERIMENTAL

The barite used in these experiments originated from the Stanisławów (Poland) deposit. The grains of mineralogical specimens were ground and sieved. A fraction of 0.12–0.3 mm was used for flotation tests and 0.06–0.12 mm for compressed pellets preparation and thin column wicking [12–16].

The barite samples (10 g) were also equilibrated (48 h) with 10^{-4} M and 10^{-3} M aqueous solution (100 cm^3) of sodium dodecyl sulfate (SDS) (from Koch-light Laboratories Ltd, England, p.a.) and the resulting adsorption was determined spectrophotometrically (Specol, Karl Zeiss, Germany). Methylene blue was used to obtain a color complex with SDS, which was next extracted into chloroform and analyzed at $\lambda = 645$ nm [17]. First, straight-line dependence for the light intensity versus SDS concentration was found.

The liquid penetration was measured using the thin column wicking method [16] and surface free energy components were calculated from van Oss et. al.'s approach [9-11]. The contact angles were also measured directly, on the barite pellets with preadsorbed SDS (hydrophobized sample) using a goniometer–telescope system with 25x magnification.

The probe liquids used for the wicking and contact angle methods and their surface tension components are listed in Table 1. Water used for the experiments was of Mili-Q Plus quality. The probe liquids (except for the n-alkanes) were of analytical grade and were used as received. The n-alkanes were pure (Reachim, Russia), and no polar impurities were detected by gas-chromatography test.

Table 1. Surface tension γ_l and its components: Lifshitz-van der Waals γ_l^{LW}, electron acceptor γ_l^+, and electron donor γ_l^- of probe liquids, in mN/m

Liquids	γ_l	γ_l^{LW}	γ_l^+	γ_l^-
n-Octane	21.8	21.8	0	0
n-Nonane	22.9	22.9	0	0
n-Decane	23.9	23.9	0	0
Diiodomethane (D)	50.8	50.8	≈0	0
	50.8	50.8	0.72	0
α-Bromonaphthalene (B)	44.4	44.4	≈0	≈0
	44.4	43.6	0.4	0.4
Water (W)	72.8	21.8	25.5	25.5
Formamide (F)	58.0	39.0	2.28	39.6
Glycerol (G)	64.0	34.0	3.92	57.4

The flotation tests were performed earlier and are published elsewhere [18, 19]. A single-bubble Hallimond tube was used. The 1.5 g barite samples (bare and with preadsorbed SDS or tetradecylammonium chloride, TDACl) were floated with 100 cm^3 of N_2 (carbon dioxide free) for 5 min, or if the sample had floated completely, the nitrogen volume at which it occurred was recorded. In the case of partial flotation of the sample, the floated amount of barite was found by weighing the recoveries.

3. RESULTS AND DISCUSSION

Some examples of wicking results of the barite grains in the thin column are presented in Figures 1 and 2. Shown here, the relationships are linear as required by Eq. (10). The results are an average of 3–4 wicking experiments both for a non-contacted (bare) and the liquid vapor equilibrated (precontacted) samples [13–16]. Figure 1 presents wicking results for three n-alkanes used, octane, nonane and decane. From these results it was possible to determine the effective *R* value (see Eq. (10)) (precontacted samples) as well as the apolar Lifshitz-van der Waals component γ_s^{LW} (bare samples) [13–16]. In Figure 2 wicking results are shown for water, formamide, and diiodomethane, also on bare and precontacted samples. These results allow calculation of acid-base parameters, electron donor γ_s^-, and electron acceptor γ_s^+, as well as verification of γ_s^{LW} component from diiodomethane wicking results [13–16].

Table 2. Contact angles and their standard deviations (degrees) of the probe liquids on barite pellets

Liquids	Bare surface	a = 0.47 μmol/g SDS	a = 5.44 μmol/g SDS
	Contact angles, θ		
Diiodomethane (D)	20.8 ± 0.6	28.0 ± 4.1	35.5 ± 5.9
α-Bromonaphthalene (B)	–	13.3 ± 1.4	17.3 ± 1.3
Water (W)	12.0 ± 1.5	19.7 ± 2.8	68.9 ± 3.1
Formamide (F)	17.1 ± 1.1	4.0 ± 0.6	46.0 ± 2.5
Glycerol (G)	32.0 ± 1.5	29.3 ± 1.9	66.5 ± 2.2

The measured contact angles on the barite pellets are listed in Table 2. It can be seen from this table that for the surface with preadsorbed SDS the standard deviations are higher than for a bare surface, especially for a 5.44 μmole SDS/g sample. This suggests that the surface coverage is non-uniform [7].

The barite free energy components for an untreated surface, as calculated from contact angles, are shown in Table 3. The values were calculated from two triads of probe liquids, namely; diiodomethane–water–formamide, and diiodomethane–water–glycerol. Moreover, two cases were considered. In the first, diiodomethane was treated as a completely apolar liquid, and in the second as a liquid possessing small $\gamma_l^+ = 0.72$ mJ/m^2 (see Table 1). As is seen, the results fit each other much better, and with smaller standard deviation, when the γ_l^+ parameter of diiodomethane was taken into account. It is worth of notice that the γ_s^{LW} component is essentially smaller (ca. 10 mJ/m^2) if the γ_l^+ of diodomethane was taken for the calculations. Also γ_s^+ value of the barite is relatively much higher (Table 3). The components obtained from thin column wicking are given in Table 4. There are two sets of component values, as calculated from the n-alkanes–water–fromamide and diiodomethane–water– formamide, and they are comparable.

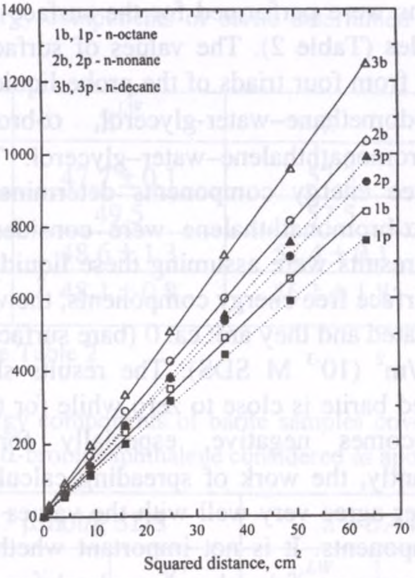

Figure 1. Penetration time of n-alkanes into barite thin column packing for bare (b) and precontacted (equilibrated with the alkane vapor) (p) surface vs. squared distances

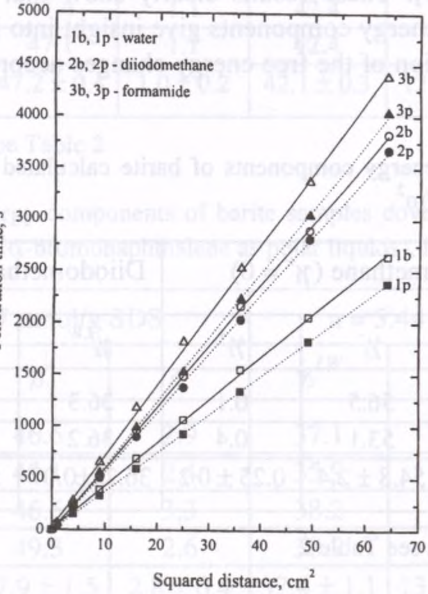

Figure 2. Penetration time of water (1), diiodomethane (2) and formamide (3) into thin column packing of barite bare (b) and precontacted (p) surfaces vs. squared distances

Similar calculations were performed for the surface with preadsorbed SDS from the contact angles (Table 2). The values of surface free energy components were calculated from four triads of the probe liquids; diiodomethane–water–formamide, diiodomethane–water-glycerol, α-bromonaththalene–water–formamide and α-bromonaththalene–water–glycerol. Table 5 presents the results of surface free energy components determined for the case when diiodomethane and α-bromonaththalene were considered as apolar liquids, while in Table 6 the results were assuming these liquids as weakly polar (see Table 1).

Using the barite surface free energy components, the values of work of water spreading were calculated and they are: ca. 0 (bare surface), –4.1 mJ/m^2 (10^{-4} M SDS), and –44.6 mJ/m^2 (10^{-3} M SDS). The results show that the work of spreading for untreated barite is close to zero while for the surface with preadsorbed SDS it becomes negative, especially for the adsorption of 5.44 μmol/g. Importantly, the work of spreading calculated directly from the contact angles of water agree very well with the values calculated via the surface free energy components. It is not important whether diiodomethane and α-bromonaphthalene were considered as completely apolar liquids or as possessing small electron acceptor interaction γ_l^+, the calculated W_s are practically the same because the components are mutually dependent when determined experimentally [9–11]. These results clearly show that determination of the mineral surface free energy components give insight into interfacial interactions and allow determination of the free energy changes accompanying the flotation process.

Table 3. Surface free energy components of barite calculated from measured contact angles on pellets, in mJ/m^2.

Liquids	Diiodomethane ($\gamma_l^+ = 0$)			Diiodomethane ($\gamma_l^+ = 0.72$ mN/m)		
	γ_s^{LW}	γ_s^-	γ_s^+	γ_s^{LW}	γ_s^-	γ_s^+
DWF*	47.5	56.5	0.1	36.3	55.3	1.6
DWG*	47.5	53.1	0.4	36.2	55.9	1.5
Av.	47.5 ± 0	54.8 ± 2.4	0.25 ± 0.2	36.25±0.07	55.6 ± 0.4	1.55 ± 0.07

* – for the abbreviations see Table 2

Table 4. Surface free energy components of barite determined from wicking experiments, mJ/m^2

System	γ_s^{LW}	γ_s^-	γ_s^+
AWF* (A – alkanes)	47.7 ± 0.1	57.3	0.1
DWF*	49.5	57.5	0.04
Av.	48.6 ± 1.3	57.4 ± 0.1	0.07 ± 0.04
Av. of two methods	48.1 ± 0.8	56.1 ± 1.8	0.2 ± 0.1

* – for the abbreviations see Table 2

Table 5. Surface free energy components of barite samples covered with anionic collector (diiodomethane and α-bromonaphthalene considered as apolar liquids), in mJ/m^2

System	a = 0.47 μmol/g SDS			a = 5.44 μmol/g SDS		
	γ_s^{LW}	γ_s^-	γ_s^+	γ_s^{LW}	γ_s^-	γ_s^+
DWF*	45.0	47.5	0.8	41.8	10.2	0.4
DWG*	45.0	46.7	0.9	41.8	15.3	0.01
BWF*	43.2	47.4	1.1	42.4	10.3	0.3
BWG*	43.2	47.1	1.1	42.4	15.3	0.02
Av.	44.1 ± 1.0	47.2 ± 0.4	1.0 ± 0.2	42.1 ± 0.3	12.8 ± 2.9	0.2 ± 0.2

* – for the abbreviations see Table 2

Table 6. Surface free energy components of barite samples covered with anionic collector (diiodomethane and α-bromonaphthalene as polar liquids), in mJ/m^2

System	a = 0.47 μmol/g SDS			a = 5.44 μmol/g SDS		
	γ_s^{LW}	γ_s^-	γ_s^+	γ_s^{LW}	γ_s^-	γ_s^+
DWF*	34.9	46.6	2.9	37.1	10.0	1.0
DWG*	34.7	49.1	2.4	35.9	16.1	0.1
BWF*	33.7	46.5	3.3	38.2	10.1	0.8
BWG*	33.7	49.3	2.6	38.2	15.8	0.01
Av.	34.3 ± 0.7	47.9 ± 1.5	2.8 ± 0.4	37.4 ± 1.1	13.0 ± 3.0	0.5 ± 0.5

– for the abbreviations see Table 2

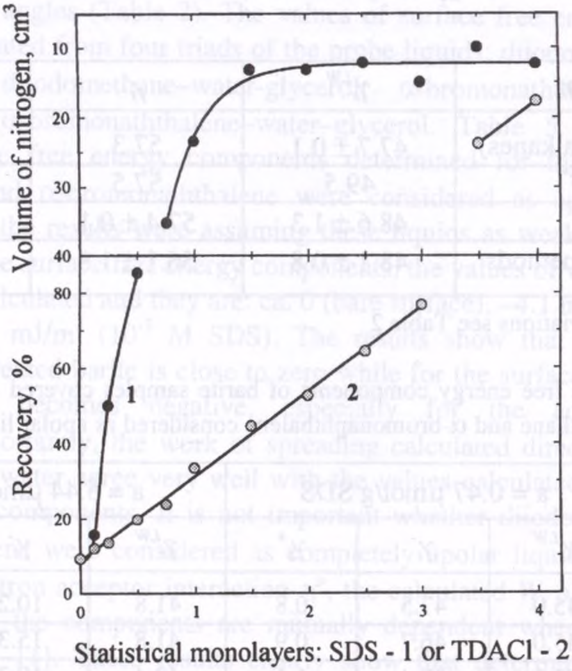

Figure 3. Flotation of barite in doubly distilled water as a function of the number of statistical monolayers of sodium dodecyl sulfate (curve 1) and tetradecylamine chloride (curve 2) deposited on the barite surface

Based on the results from Table 4 it may be expected that natural flotability of barite is low and covering its surface with SDS should increase the flotation activity drastically. The flotation tests for barite with preadsorbed SDS as well as tetradecyloammonium chloride (TDACl) were conducted earlier and published elsewhere [18,19]. Figure 3 shows flotation results for barite samples with preadsorbed SDS and TDACl as a function of calculated monolayers of the collector, which was deposited on the surface by evaporation of the solvent (here methanol) [18, 19]. The flotation tests were then conducted in doubly distilled water. It is seen from Figure 3 that SDS is much more active, where 1 statistical monolayer deposited caused complete flotation of the sample. For the same coverage with TDACl the flotation was only ca. 20%, and it needed as much as 3.5 statistical monolayers of this collector to completely float the sample. This points out that the adsorption is patch-like, as was found for other minerals [7, 20, 21–24]. To verify the thermodynamic condition of mineral flotation, the recoveries of barite precovered with SDS or TDACl were plotted against work of spreading W_s, shown in Figure 4. From these results it can be concluded that for the flotation to be efficient in kinetic conditions the work of water spreading ($W_s = \Delta F$) should be at least –20 mJ/m^2. Small negative values of W_s are not sufficient to obtain high recoveries. This may be due to the energy barrier, which can be determined from advancing and receding contact angles [22, 24, 25].

To get a more general picture about the discussed condition for efficient flotation, Figure 5 presents results, similar to those in Figure 4, for other minerals. However, in this figure the results originate from papers published earlier [2, 18, 19, 26–34], when Owens and Wendt's [35] formulation of the surface and interfacial free energy was applied, which later appeared to be an unappropriate one. From this approach the work of liquid adhesion to the solid surface reads:

$$W_a = 2(\gamma_s^d \gamma_l^d)^{1/2} + 2(\gamma_s^n \gamma_l^n)^{1/2} \tag{11}$$

where γ_i^d is the dispersion component of the solid (s) or liquid (l) surface free energy, and it is practically equal to the Lifshitz-van der Waals component from van Oss et al's [9–11] approach, while γ_i^n is so called nondispersion component [35], which involves all nondispersion interactions, and it may somehow correspond to the acid-base interaction [9–11]. Nevertheless the discrepancies of this approach, the relative changes also reflect the free energy changes, ΔF, accompanying the flotation process (Figure 5) and clearly show that the phenomenological thermodynamic condition is necessary to be fulfilled for an efficient flotation process of a mineral. On the other hand determination of the condition together with the flotation test is a useful tool for hydrophobicity testing of model systems in dynamic conditions. However, it should be kept in mind that real flotation systems are much more complicated and both collector and frother are also introduced. The discussed condition for efficient flotation is described by phenomenological thermodynamic, and as such, says nothing about kinetic of the process. An energy barrier may appear that can hinder sufficiently the kinetics of the process. Any reader interested in this problem is referenced to the papers published by Laskowski et al. [4, 25] and Drelich et al. [22]. On the other hand, as was mentioned above, determination of the surface free energy components is also useful in studying all interfacial processes in which the interactions play a role, like wetting, adhesion, adsorption, etc.

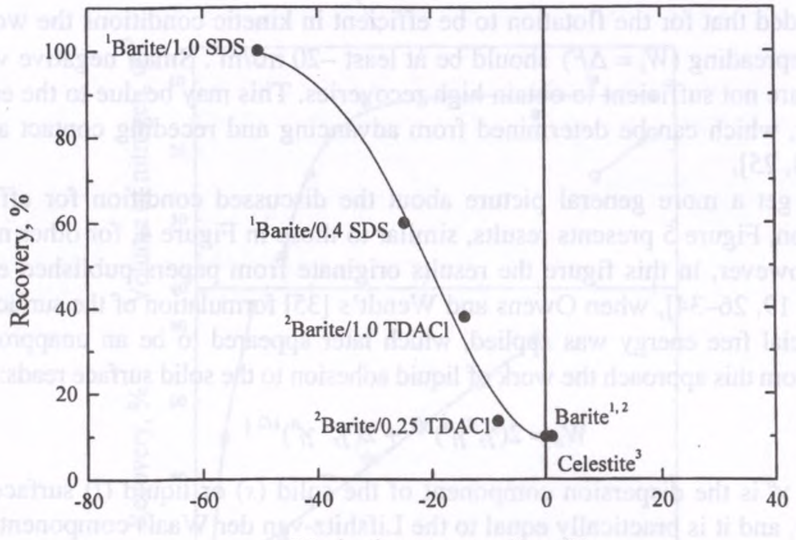

Figure 4. Flotation recovery of barite samples with preadsorbed SDS or TDACl collector vs. work of spreading of water (using van Oss et al's approach). For comparison natural flotability of celestite is also shown. Key: 1 – ref. 18; 2 – ref. 19; 3 – ref. 26

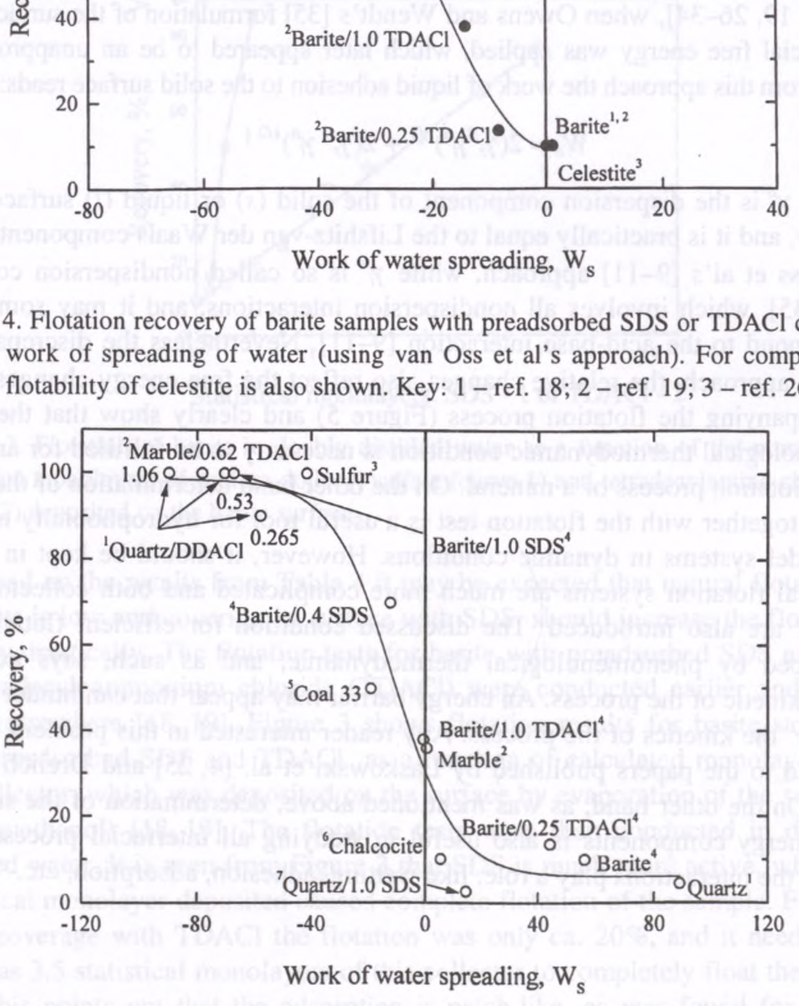

Figure 5. Flotation recovery of some minerals (natural and with preadsorbed collectors) vs. work of spreading of water (Owens and Wendt approach). Key: 1– ref. 27; 2 – ref. 29; 3 – ref. 3, 30; 4 – ref. 31; 5 – ref. 32; 6 – ref. 33; 7 – ref. 28

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CURRICULA VITAE

Prof. Emil Julian Chibowski. Born in Poland in 1943. He studied Chemistry (1962–1967) at Maria Curie-Skłodowska University (Lublin, Poland) and was graduated in 1967 receiving M.Sc. Then, he was employed at the Department of Physical Chemistry, Institute of Chemistry UMCS where he received Ph.D in 1973, D.Sc in 1981 (habilitation) and in 1989 title of the professor of chemistry. In 1987–1989 he was v-director of the Institute of Chemistry UMCS and at present he is head of the Chair of Physical Chemistry, Faculty of Chemistry UMCS. He is also co-chairman of the Scientific Council of the Institute of Agrophysics, Polish Academy of Sciences (Lublin) and a member of the Editorial Advisory Board of the Journal of Adhesion Science and Technology, Polish Chemical Society, European Colloid and Interface Society and Adhesion Science Society. In 1989–1990 he was visiting research professor at the Department of Chemistry, Baylor University (Waco, Texas) and in 1991–1992 on sabbatical at the Department of Applied Physics, Faculty of Science, Granada University (Granada, Spain). He also visited for a short term University of Groningen (The Netherlands), University of Jaen and Badajoz (Spain) and University of Minho (Braga, Portugal). He published over 120 papers in professional journals and books. He was also a member of the International Advisory Committee of *9th* and *10th International Symposium on Surfactants in Solution* (1992, Varna, Bulgaria, and 1994, Caracas, Venezuela), and *1st International Congress on Adhesion Science and Technology* (1995, Amsterdam, The Netherlands). His fields of interest are: interfacial phenomena at solid-liquid, solid-gas, and liquid-liquid interfaces, electrochemical phenomena, surface and interfacial free energy, its components and their experimental determination, suspensions, emulsions, stability of the dispersed systems, effects of the external fields (high frequency electric and magnetic) on the properties of the dispersed systems, adhesion, wetting, flotation, stability. He received several awards of the Rector of Maria Curie-Skłodowska University.

Dr Lucyna Hołysz. Born in Poland in 1952. Education: M.S. Maria Curie-Skłodowska University, 1975: Physical Chemistry. Ph. D.: "The investigation of the surface energetic changes of some minerals and their flotability", Maria Curie-Składowska University, 1985: physical chemistry. Professional: since October, 1985 – doctor and university teacher in physical chemistry in the Department of Interfacial Phenomena, Faculty of Chemistry, Maria Curie-Skłodowska University. Teaching of graduate and undergraduate students in physical chemistry and physicochemistry of interfaces. Fields of interest: the adsorption layers and the electrochemical properties of solid-liquid interface; the energetic properties of the interfacial films; physicochemical of flotation process; surface free energy of solids and its determination; surface properties of solids due to exposure to radiofrequency electric field (zeta potential and surface free energy components).