Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Critical Surface Tension of Wetting and Flotation Separation of Hydrophobic Solids

S. Kelebek[a]; G. W. Smith[a]; J. A. Finch[a]; S. Yörük[b]
[a] DEPARTMENT OF MINING AND METALLURGICAL ENGINEERING, MCGILL UNIVERSITY MONTREAL, QUEBEC, CANADA [b] DEPARTMENT OF CHEMICAL ENGINEERING, FIRAT UNIVERSITY, ELAZIG, TURKEY

To cite this Article Kelebek, S. , Smith, G. W. , Finch, J. A. and Yörük, S.(1987) 'Critical Surface Tension of Wetting and Flotation Separation of Hydrophobic Solids', Separation Science and Technology, 22: 6, 1527 — 1546
To link to this Article: DOI: 10.1080/01496398708058416
URL: http://dx.doi.org/10.1080/01496398708058416

SEPARATION SCIENCE AND TECHNOLOGY, **22(6)**, pp. 1527-1546, 1987

Critical Surface Tension of Wetting and Flotation Separation of Hydrophobic Solids

---

S. KELEBEK, G. W. SMITH, and J. A. FINCH

DEPARTMENT OF MINING AND METALLURGICAL ENGINEERING
MCGILL UNIVERSITY
MONTREAL, QUEBEC H3A 2A7, CANADA

S. YÖRÜK

DEPARTMENT OF CHEMICAL ENGINEERING
FIRAT UNIVERSITY
ELAZIĞ, TURKEY

Abstract

Wetting characteristics of a number of minerals including layer-type hydrophobic minerals as well as common sulfides were investigated. For the majority of the minerals, the critical surface tension of wetting, γ_c, determined using Zisman's technique was in the range of 40 to 45 mN/m. Surface pressures of water, Π_e, on molybdenite and coal samples were determined from adsorption isotherms. The dispersion component of the surface-free energy, γ_s^d, for molybdenite was estimated to be 113 ± 3 mJ/m^2 as compared to the γ_s^d value for graphite, 109 mJ/m^2. The wettability data of aqueous methanol solutions, presented in the form of adhesion tension diagrams, yielded significantly lower γ_c values. Flotation behavior of common sulfides, which was similar to that of inherently hydrophobic polymers and minerals, was attributed to elemental sulfur formation. The relevance of critical surface tension of wetting to selective flotation and separation of hydrophobic solids is discussed.

INTRODUCTION

The relationship between wettability of a solid and the surface tension of a wetting liquid dates back many decades. As early as 1926, Freundlich (*1*) qualitatively expressed this relationship as follows: "... liquids in general wet the better the lower their surface tension." Bartell and his coworkers (*2, 3*) studied the wetting of various solids such as carbon black, paraffin wax, and talc using liquids of different surface tensions but apparently did not seek an empirical correlation between these two relevant properties. Zisman and his coworkers (*4, 5*), working with a variety of polymers in the 1950s, were able to establish a linear relationship between the cosine of a slowly advancing contact angle, θ, and the liquid surface tension, γ_{lv}. They defined a new term, "the critical surface tension of wetting, γ_c," as that value of surface tension below which liquid wets the surface completely. In addition to various polymeric solids, different ranks of coals and minerals coated with a variety of heteropolar surfactants generally exhibit a linear relationship between cos θ and γ_{lv} (*6, 7*).

The Zisman relationship is described by

$$\cos \theta = 1 - b(\gamma_{lv} - \gamma_c)$$

where b is the slope of the line.

Both γ_c and b values have been utilized to characterize the relative hydrophobicities of solids. For example, Shafrin and Zisman used γ_c as a criterion to classify highly nonpolar polymers with respect to their atomic constitution (*8*), and b has been related to the coal rank (*6*).

Critical surface tension has been used in flotation studies (*9–12*). In the present study, critical surface tension of wetting of a number of minerals that show natural floatability (e.g., talc, molybdenite) or that are claimed to show natural floatability (e.g., various sulfides) is reported. Wettability data obtained using aqueous methanol solutions are compared to those obtained using pure liquids and in turn are compared to flotation behavior.

EXPERIMENTAL MATERIALS AND PROCEDURES

Solid Samples

With the exception of talc and coal, the mineral samples were obtained from Ward's Natural Science Establishment, Rochester, New York. The talc sample was from Quebec. Acid leaching and ignition loss tests showed a high purity form of talc sample. The coal specimen tested was a bituminous coal from Sydney, Nova Scotia, and contained 2.5% ash. A list of the minerals with their original location and purity level is shown in Table 1. The purity of the samples was determined by atomic absorption spectrophotometry.

TABLE 1
Mineral Samples Studied

Sample	Source	Purity (%)
Molybdenite	Ontario	99.4
Talc	Quebec	—
Stibnite	Borneo	80.2
Graphite	Sri Lanka	—
Chalcocite	Butte, Montana	99.2
Chalcopyrite	Rouyn, Quebec	97.4
Pyrite	—	97.0
Galena	Kansas	99.6
Orpiment	Geltchell, Nevada	85.3
Realgar	Manhattan, Nevada	—

The following polymeric solids were included in the floatability tests: polyethylene, PE (Union Carbide); polystyrene, PS (Shell Chemical Co.); polyvinyl chloride, PVC (B.F. Goodrich Co.); and nylon (polyamide) 6, PA6 (Badische Canada Ltd., BASF). These are typical low-surface-energy solids with γ_c values ranging from about 31 to 45 mN/m (*5*).

Reagents

The reference liquids used for the determination of the critical surface tension of wetting were water (γ_{lv} = 72.6 mN/m), glycerol (γ_{lv} = 63.4 mN/m), formamide (γ_{lv} = 58.2 mN/m), methylene iodide (γ_{lv} = 50.8 mN/m), and 1-bromonaphthalene (γ_{lv} = 44.6 mN/m).

Methanol was used to prepare aqueous solutions with surface tensions ranging from about 23 to 70 mN/m. These solutions were used in contact angle measurements as well as in flotation tests.

Sample Preparation

For contact angle measurements, the samples were prepared either by cleaving (e.g., molybdenite) or by successive grinding and polishing (e.g., galena). The cleavage was done using a razor-sharp thin metal plate or wooden plate, and forceps which had been throughly cleaned before use. The cleavage was most easily accomplished for molybdenite. Talc and graphite did not yield smooth cleavage planes. When necessary, they were polished after cleaving. The specimens (with sides ranging from 0.3

to 1.5 cm) were handled with clean surgical latex rubber gloves and/or clean crucible tongs at all times. Grinding was done on graded clean emery paper with a variable speed wheel. Alumina powder used for making up the polishing slurry had been heated in a porcelain crucible to a red heat (700°C) for an hour to remove any possible organic contaminant. All the glassware used for temporary storage of the specimens under distilled water was previously cleaned with fresh chromic-sulfuric acid mixture and later with distilled water.

Flotation tests with polymer samples (excluding PE) were conducted using the 48-150 mesh fraction. The flotation feed sample of PE was obtained by cutting pieces (1-2 mm in size) from a sheet of PE. Immediately prior to flotation tests, some sulfide minerals were pretreated to remove oxidation products that may have formed at the particle surface. Treatment of the surface of orpiment was performed by leaching in hot 0.1 *N* sodium hydroxide solution for 5 min, washing with hot distilled water and dilute hydrochloric acid solution (2-4%), and finally rinsing thoroughly with distilled water. This treatment was used to dissolve the oxides such as As_2O_3 from the surfaces (*13a*). Chalcocite was pretreated by leaching in ammonia solutions to remove oxides of copper from the surface followed by a washing operation similar to the above (*13b*). Treatment of galena surfaces was carried out using ammonium chloride solutions (*14*). Preliminary observations proved these pretreatments to be effective in increasing the floatability of these samples. However, for some minerals such as talc, graphite, and chalcopyrite, no pretreatment was necessary. The flotation feed for the layer type minerals was 80-150 mesh and for the rest of the mineral samples 100-200 mesh.

In addition to low-surface energy polymers, a high-surface-energy solid, acid purified silica sand (80-150 mesh) was included in the flotation tests.

Procedure

For determination of γ_c using reference liquids, the samples were stored after preparation for 24 h under oxygen-free nitrogen gas in desiccators and studied two at a time. The contact angles were measured using the sessile drop method of Fox and Zisman (*4*) at room temperature of 23 ± 2°C. The procedure was similar to that followed by Parekh and Aplan (*6*) for coals. The contact angles were found to be reproducible within ±3° for different specimens of the same mineral. A test was made to check for any organic contamination by comparing the contact angles of water on galena, pyrite, and chalcopyrite before and after ether washing. In all cases the angles before and after the washing were similar (i.e., ±2°). For each sample, four to six pairs of contact angles were measured and averaged. The deviation from the mean was ±2°.

All flotation tests as well as the captive bubble contact angle measurements were carried out at natural pH of methanol solutions (pH = 5.7–6.2) using the apparatus and following the general procedure described elsewhere (*12*).

RESULTS

Critical Surface Tension of Wetting

For clarity, the Zisman plots for the minerals studied are given in two figures; Fig. 1a gives the results of talc, orpiment, graphite, cinnabar, stibnite, and molybdenite; and Fig. 1b gives the results for galena, realgar, chalcopyrite, pyrite, and chalcocite. For most samples the data points are quite scattered. However, as in the case of coals (*6*), a linear trend between cosine θ and γ_{lv} is apparent. The Zisman parameters (i.e., γ_c and b values) are collectively given in Table 2. With the exception of galena with a γ_c value of 31 mN/m, all the samples studies have γ_c values ranging from 40 to 50 mN/m. In contrast, b varied significantly. In Table 2, b values are shown in the order of increasing values from 0.6×10^{-2} for talc to 4.7×10^{-2} for molybdenite.

The wettability data obtained using aqueous methanol solutions are presented in the form of an adhesion tension diagram. Figure 2 illustrates the results for a polished coal sample, a cleavage plane of graphite, and includes the wettability data for polyethylene studied by Bernett and Zisman (*15*) using ethyl and *n*-butyl alcohol solutions. The slope of the adhesion tension lines β and γ_c values for these samples are shown in Table 3, which also includes the β and γ_c values obtained for two samples of molybdenite and sulfur (*12*). The samples listed exhibit a wide variation of γ_c (from 41.7 to 26.9 mN/m) and β values (from +0.3 to −0.5).

Floatability Tests

The results of flotation tests with polymers are shown in Fig. 3. The recoveries change from 100% to close to 0% over a certain range of surface tension. The lower limit of this critical range, γ_{clf}, is nearly the same (30 mN/m) for PS, PVC, and PA6 while it is between 20 and 25 mN/m for PE.

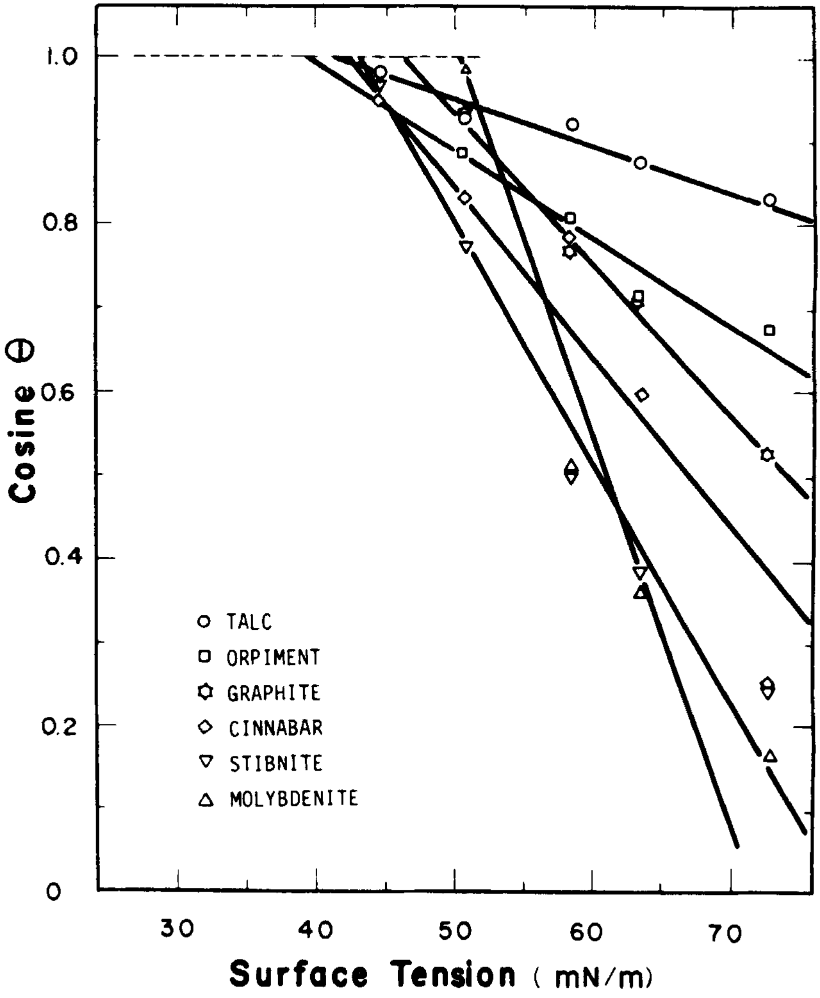

FIG. 1a. Zisman plots of various minerals.

The upper limits, γ_{cmf}, are approximately 27, 40, 45, and 60 mN/m for PE, PS, PVC, and PA6, respectively. The flotation behavior of these polymers can be contrasted with that of silica. The recoveries of silica, included in Fig. 3, are very low (less than 5%) regardless of the surface tension.

The recoveries obtained using pretreated sulfide minerals are shown in Fig. 4. The flotation curves resemble those obtained with polymer samples in that the recoveries decrease sharply with decreasing γ_{lv} values. For the samples of galena and chalcopyrite, γ_{cmf} is 39 and 47.5 mN/m,

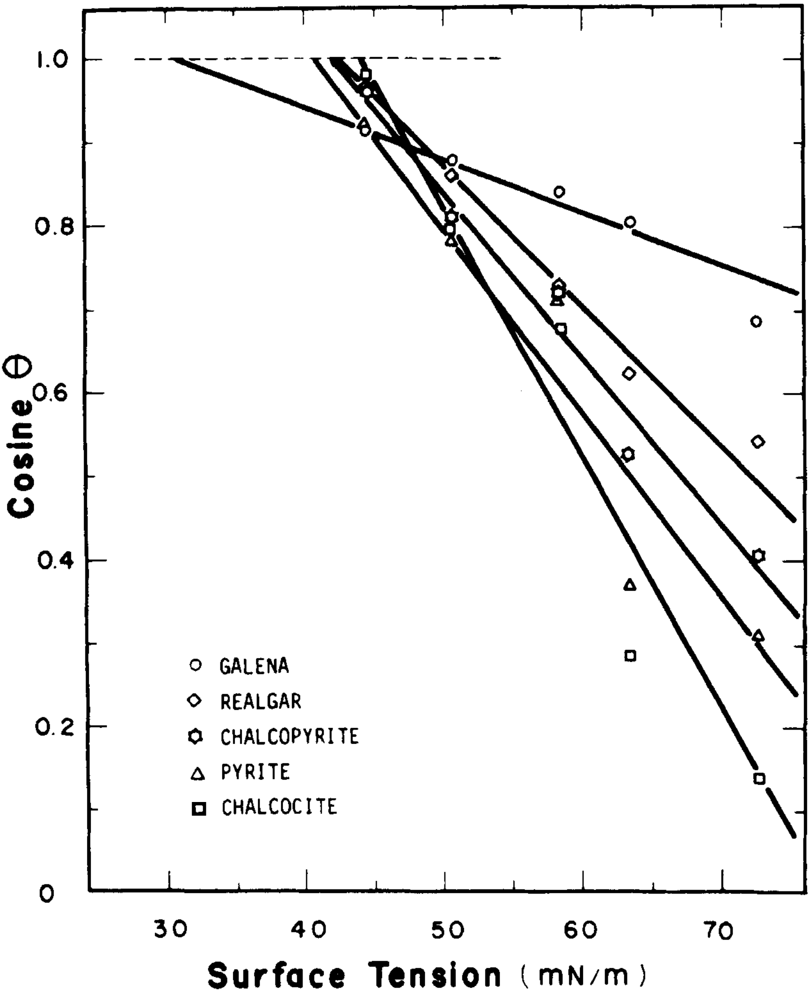

FIG. 1b. Zisman plots of various sulfide minerals.

respectively, and γ_{clf} is about 30 mN/m, the same as that observed for PS, PVC, and PA6. For realgar, orpiment, and chalcocite, the recoveries are represented practically by the same curve (γ_{clf} = 33 mN/m, γ_{cmf} = 47.5 mN/m).

Reproducibility of the flotation tests is illustrated for a sulfide and nonsulfide mineral (chalcopyrite and talc) in Table 5. Note that the standard deviation for chalcopyrite is higher than for talc, and that

TABLE 2
Values of the Zisman Parameters of Various Mineral Samples

Mineral	γ_c (mN/m)	b ($\times 10^2$)
Talc	41.5	0.57
Galena	31.0	0.63
Orpiment	39.5	1.12
Realgar	42.5	1.68
Graphite	46.5	1.83
Chalcopyrite	42.0	2.00
Pyrite	41.0	2.22
Stibnite	43.0	2.86
Chalcocite	44.0	3.00
Molybdenite	50.0	4.65

TABLE 3
Values of γ_c and β Obtained Using Aqueous Methanol Solutions

Sample	γ_c (mN/m)	β	Ref.
Molybdenite (disk)	41.7	0.34	12
Coal	35.5	0.31	This work
Sulfur (disk)	33.3	0.05	12
Molybdenite (face)	29.2	−0.43	12
Graphite	33.4	−0.47	This work
Sulfur (face)	26.9	−0.48	12
Polyethylene[a]	26.6	−0.67	15

[a] Using aqueous ethanol and butanol solutions.

standard deviation within the critical surface tension range is considerably higher than above it.

DISCUSSION

Wetting Characteristics of Minerals; Zisman Parameters

The γ_c and b values obtained for graphite are 46.5 mN/m and 1.83×10^{-2}, respectively (Table 2). These values are in good agreement with 47.5 mN/m (γ_c) and 2.01×10^{-2} (b) reported for graphite by Parekh and Aplan (*6*). The γ_c value of 41.5 mN/m for the polished specimen of talc is also in agreement with the value of 41.0 mN/m for a talc sample studied (origin and preparation technique not specified) by Parekh (*16*). However, the

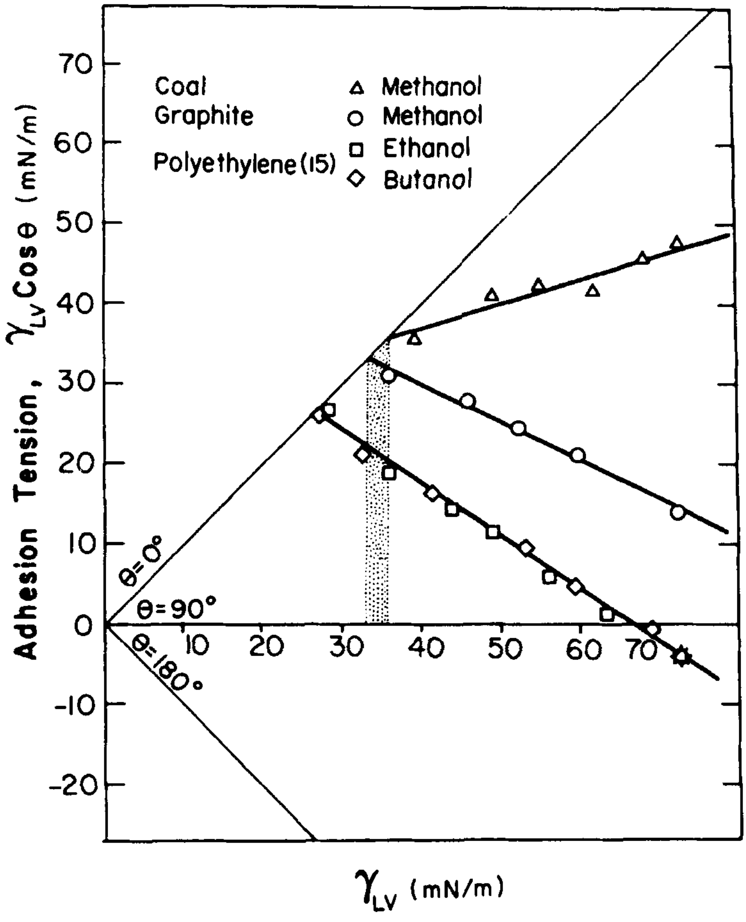

FIG. 2. Adhesion tension diagram for coal, graphite, and polyethylene in aqueous alcohol solutions.

contact angle data by Bartell and Zuidema (*3*) indicate that for a well-cleaved talc sample, γ_c is about 35.5 mN/m. For galena, the γ_c value of 31 mN/m is nearly the same as that of sulfur, 30 mN/m (*17*). This may suggest the presence of elemental sulfur on the galena specimen. The sulfur extraction tests on flotation feeds of several sulfides such as galena, chalcopyrite, and realgar have indeed shown elemental sulfur in the range 40 to 190 ppm (about 2 to 8 equivalent monolayers) depending on the mineral and its preparation technique (*18*). The rest of the mineral samples have γ_c values similar to those of various coals (*6*). In contrast to

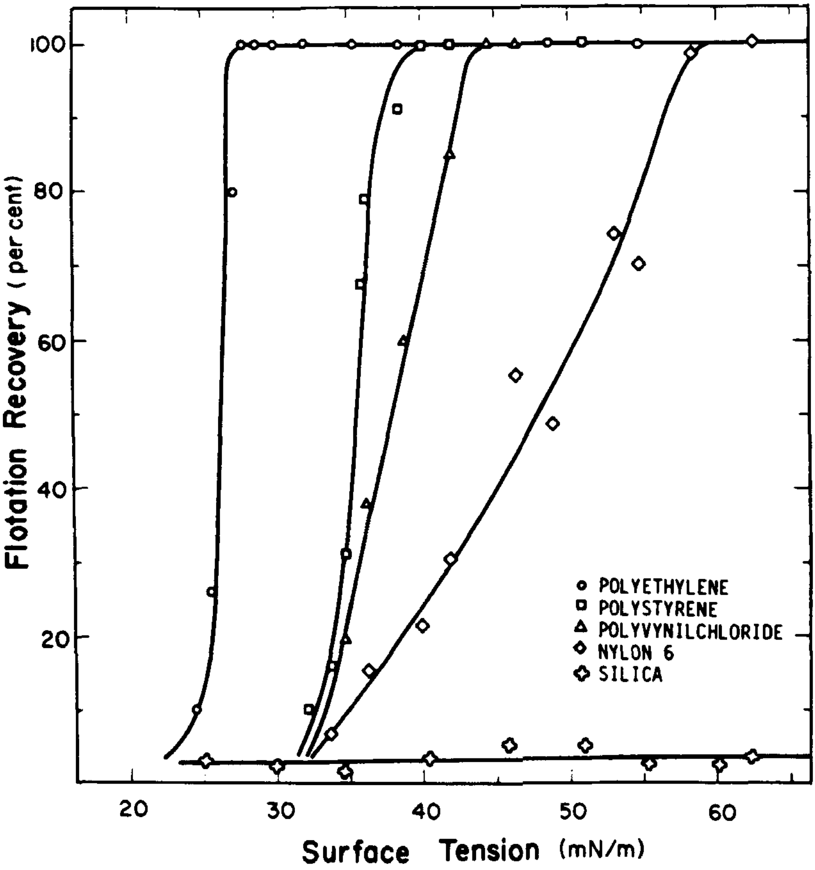

FIG. 3. Floatability of various polymers and silica in aqueous methanol solutions of various surface tension.

TABLE 4
Surface Pressure of Water Vapor on Inherently Hydrophobic Minerals

Sample	Π_e (mJ/m^2)	T (°C)	A_s (m^2/g)^a	Ref.
Graphite [1]	19	25	4.18	27
Graphite [2]	19	25	6.2	27
Graphite [3]	58	25	27.6	27
Molybdenite [1]	14	20	9.1	28
Molybdenite [2]	97	30	12.0	29
Coal (subbituminous)	143	20	200.0	30

[a] A_s: Specific surface area.

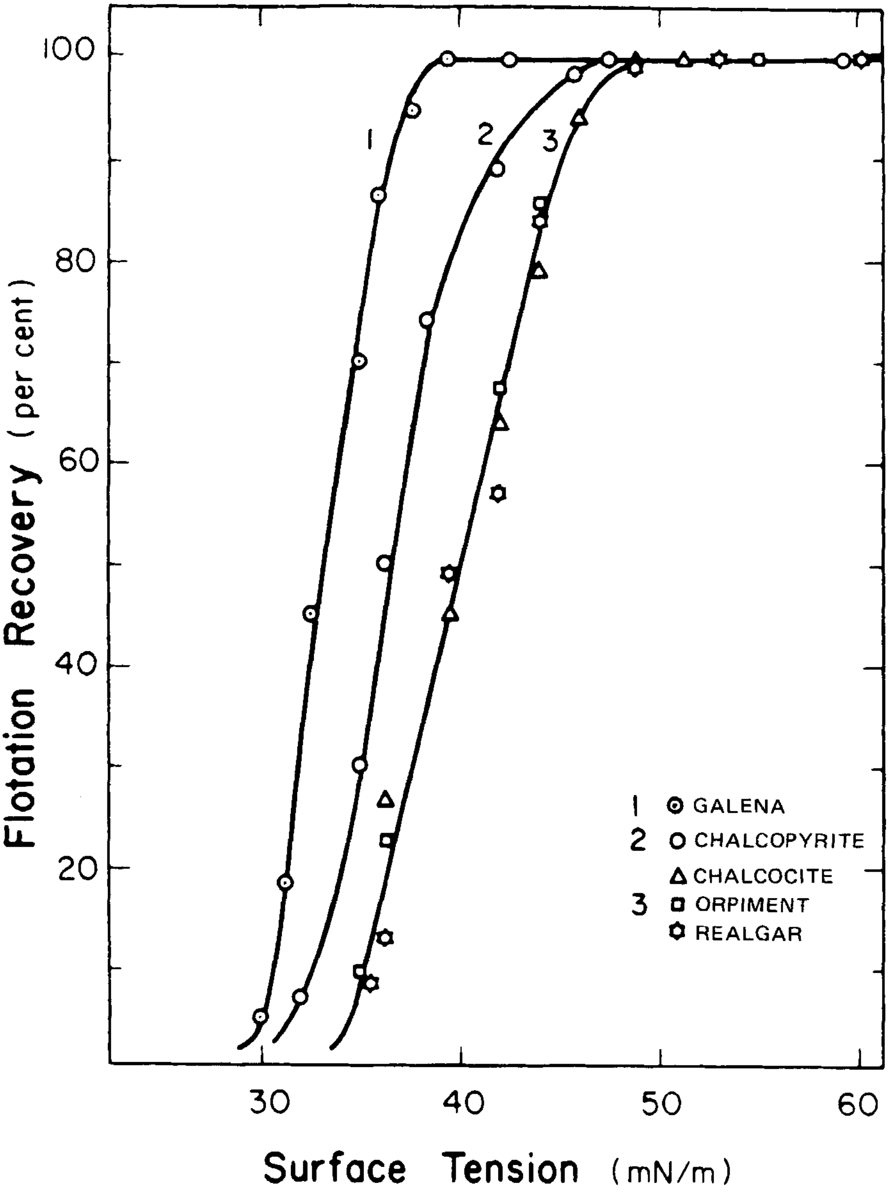

FIG. 4. Floatability of pretreated sulfide minerals in aqueous methanol solutions of various surface tension.

the nearly constant γ_c values, the slopes (*b*) exhibit great variation (Table 2). As suggested by Gray (*19*), a higher *b* value indicates that a hydrophobic solid surface will be difficult to wet by high surface tension liquids but easily wetted by low surface tension liquids.

The γ_c range for the minerals investigated would place these minerals as low surface energy solids near the nitrated hydrocarbons in the "wettability spectrum" proposed by Shafrin and Zisman (*8*). This might imply support for the hydrophobic character of common sulfides. However, this range of γ_c values can hardly be regarded as evidence of their inherent hydrophobicity. In defining low- and high-energy surfaces, Zisman (*5*) refers to the hardness of the solids and cites metal sulfides as being among the high-surface-energy solids. Indeed, an indication of the relative surface tension of solids may be judged from their relative hardness. The well-known softness of talc, sulfur, and graphite is basicly in agreement with their inherently hydrophobic (i.e., low surface energy) character. As noted by Bartell and Zuidema (*3*) in these solids, the elementary units are apart from each other, and hence forces of attraction are weak. Thus, the work of cohesion and the surface tension of soft minerals should be relatively small. The hardness of common sulfides is several times that of talc. On the Moh scale the hardness of 1 is for talc as compared to 2.5, 3.5, and 6.0 for galena, chalcopyrite, and pyrite, respectively (*20*). Therefore, it seems unrealistic to expect similar surface-free energies, and hence γ_c values, for talc and these common sulfides.

The reason why most sulfide mineral samples have similar γ_c values is not clearly understood. The liberation of elemental sulfur on sulfides does occur. The presence of sulfur can play a role in the establishment of similar γ_c values for sulfides, but this alone does not account for the observed γ_c values (about 40–45 mN/m); γ_c for various allotropic forms of sulfur is in the range of 30 to 31.5 mN/m.

At this point the effect of water vapor adsorption on surfaces should also be mentioned. This may have played a more decisive role in the observed γ_c values for sulfides. Zisman and coworkers discovered that adsorption of water as a monolayer or thicker layer on the surface of high energy solids considerably lowered their surface energies. For a number of metals and an oxide (Fe_2O_3), γ_c value was found to be 45 mN/m when the surfaces were covered by even a fraction of a monolayer of adsorbed water. It was concluded that γ_c as well as γ_s (surface free energy of the solid in vacuum) of clean high energy solids after exposure to a humid atmosphere was dependent upon the surface concentration of water adsorbed on the surface, but that it was independent of the chemical nature of the underlying solid (*21*).

Surface Pressure of Water on Hydrophobic Minerals

The surface pressure of an absorbed film, Π_e, is defined by

$$\Pi_e = \gamma_s - \gamma_{sv}$$

where γ_s and γ_{sv} are the surface free energy of the solid in vacuum and in the presence of the saturated vapor of the liquid, respectively. Fox and Zisman regard Π_e as being negligible for low-surface energy polymers. Good (*22*), as a result of a theoretical analysis, concluded that Π_e should be negligible on a smooth and homogeneous surface of a low-energy solid such as Teflon. Recently, it has been proven by Fowkes et al. (*23*) that Π_e is zero for water on Teflon. Inherently floatable minerals and coals are by no means as homogeneous or as hydrophobic as Teflon. Kiselev (*24*) notes that the amount of water vapor adsorption is low on hydrophobic solids which, according to him, includes the metal sulfides. Π_e may be determined by the following relation (*25*):

$$\Pi_e = RT\int_0^{P^\circ} \Gamma d \ln P$$

where Γ is the amount of water adsorbed per unit area at vapor pressure P. P° is the saturated vapor pressure of water. Using the graphical method described by Gregg (*26*), the values of Π_e for two samples of molybdenite and a coal sample were determined from the available adsorption isotherm for water vapor. These are given in Table 4, which includes the Π_e values determined by Harkins (*27*) for various graphite samples. Because of the absence of adsorption data in the vicinity of P°, the Π_e values for molybdenite and coal listed in the table are only approximate (±10%). The values of Π_e are high and dependent on the nature of the sample. The samples of Graphite [1], [2], and [3] were reported to contain the ash contents of 0.004, 0.46, and 10%, respectively. Molybdenite [1] was reported to have an assay of 99% MoS_2. Before being used in the adsorption tests, the powdered MoS_2 sample was sulfidized under a dry H_2S atmosphere for 12 h (*28*). This treatment should have minimized the extent of oxidized regions which can take up most of the water vapor. Molybdenite [2], treated with HF to reduce the silica content to <0.02%, was dried in a stream of air (*29*). Coal was a subbituminous type containing 6.8% ash (*30*). These values indicate the extent of high-energy impurities and artificial oxidation of the samples. As expected, the value of Π_e for air-dried molybdenite is much greater than that for the H_2S-treated-molybdenite due to the presence of a greater number of hydro-

TABLE 5
Reproducibility of Flotation Tests in the Critical Surface Tension Range of Floatability and Above for Talc and Chalcopyrite Samples[a]

γ_{lv} (mN/m)	R (wt%)[b]	SD[c]	CI[d]	n[e]
30.0	9.4	1.50	9.4 ± 2.4	4
	—	—	—	—
32.0	38.8	2.25	38.8 ± 3.6	4
	6.8	2.45	6.8 ± 3.9	4
35.0	85.2	2.14	85.2 ± 3.4	4
	—	—	—	—
38.5	—	—	—	—
	74.1	5.20	74.1 ± 8.3	4
42.1	—	—	—	—
	85.5	5.72	85.5 ± 9.1	4
45.7	99.8	0.21	99.8 ± 0.3	4
	98.6	0.73	98.6 ± 1.2	4
72.5	96.0	0.78	96.0 ± 1.2	4
	95.6	0.87	95.6 ± 1.4	4

[a] For each γ_{lv} value, the figures on the first line refer to talc, those on the second one to chalcopyrite.

[b] R (wt%) = recovery on a weight percent basis, mean value.

[c] SD = standard deviation.

[d] CI = the 95% confidence interval.

[e] n = number of tests.

philic sites at its surface. Coal, a weakly hydrophobic and heterogeneous material, has the greatest Π_e value. It should be emphasized that these Π_e values represent the surface pressures on the powdered samples. On smooth surfaces used for contact angle measurements, the amount of water vapor adsorption is expected to be smaller (*31*). However, it is very unlikely that Π_e is negligibly small as recently assumed for coals (*32*). Assuming the validity of the Π_e value of 14 mJ/m^2 for molybdenite, one can calculate the dispersion component of its surface-free energy, γ_s^d, from the following expression by Fowkes (*33*):

$$\cos\theta = -1 + 2[\gamma_l^d\gamma_s^d]^{1/2}/\gamma_{lv} - \Pi_e/\gamma_{lv}$$

For water at 20°C on a molybdenite cleavage plane, $\theta = 80°$ (*12*), $\gamma_l^d = 21.8$ mJ/m^2, and $\gamma_{lv} = 72.8$ mJ/m^2. By using these values in the above equation, a γ_s^d value of 113 ± 3 mJ/m^2 is obtained for molybdenite. Fowkes determined γ_s^d for graphite to be 109 mJ/m^2. Recently, Janczuk and Chibowski (*34*), using a different equation (assuming Π_e is negligible), reported γ_s^d values of 124.1 and 121.7 mJ/m^2 for sulfur and graphite, respectively.

Adhesion Tension Behavior

The γ_c values established in aqueous solution are significantly lower than those γ_c values obtained using single reference liquids. For example, for graphite the former is 33.4 mN/m (Table 3) as compared to the latter, 47 mN/m (Table 2). This difference is apparently brought about by the adsorption of solute at interfaces. Critical surface tension of wetting values determined using aqueous solutions are more relevant to froth flotation than those using pure liquids. An interesting feature of the adhesion tension diagram is that it can provide a relation between slope and the adsorption densities of the solute at the three interfaces (*35*).

$$\gamma_{lv} \cos \theta = \beta \gamma_{lv} + (1 - \beta)\gamma_c$$

$$\beta = (d\gamma_{lv} \cos \theta)/d\gamma_{lv} = (\Gamma_{sv} - \Gamma_{sl})/\Gamma_{lv}$$

It has been previously noted (*10, 12*) that β represents the extent of the polar nature of the hydrophobic surface. The greater the slope, the less hydrophobic are the samples listed in Table 3. In a more recent study (*36*), β was found to be linearly related to the fractional area occupied by hydrophilic sites at the hydrophobic mineral surfaces. The adhesion tension diagram is convenient to characterize and compare the wettabilities of hydrophobic solids. In aqueous methanol solutions, graphite has a γ_c value of 33.4 mN/m as compared to 35.5 mN/m for coal. In solutions for which 33.4 mN/m $< \gamma_{lv} <$ 35.5 mN/m, coal can be completely wetted while graphite will only be partially wetted. Therefore, this narrow range of solution surface tension constitutes a selective wetting region between the graphite and coal samples. In the case of polyethylene and graphite, the selective wetting region in aqueous alcohol solutions is relatively greater. In general, the larger the selective wetting region, the more readily will the solids be separated by selective flotation.

Flotation Behavior

Flotation behavior of plastics and the minerals studied (excluding silica) show characteristic similarities (Figs. 3 and 4). Galena pretreated with xanthates as well as bulk lead alkyl xanthates also show this type of flotation behavior (*37*). As the concentration of methanol is increased and γ_{lv} is decreased, high recoveries are maintained up to a certain point beyond which a sharp decrease occurs. These floatable/nonfloatable transitions should be attributable to the formation of stable wetting films which cause the induction periods to increase and eventually to become larger than the bubble–particle contact times. From the reproducibility of flotation tests, it is notable that confidence intervals are larger within the critical range (Table 5). This is not surprising, because, within the critical range, partial wettabilities are such that the wettabilities are most sensitive to small changes in other variables besides surface tension. This is reflected as fluctuations in the recoveries. Above the critical range, the particles are relatively nonwettable by the flotation medium so that the effect of other variables causing fluctuations is overcome by this nonwettable condition of surface. In general, the variables affecting the recoveries include changes in particle size, slimes, prewashing the flotation feed prior to tests, and weathering of samples. Oxidation is especially important for sulfides. For example, if the sulfide mineral surface is oxidized so that elemental sulfur is liberated, then γ_c may be changed to a lower value. Ultimately, the surface may assume a γ_c value close to that of sulfur. However, if oxidation proceeds to a further stage, then γ_c may be changed to a higher value. Then the surface may be converted to an oxide-like surface with a flotation response similar to that of silica (Fig. 3).

The fact that the γ_c values as obtained by the Zisman approach are comparable with those of plastics, and the similarity displayed by the floatability curves of both polymers (Fig. 3) and mineral samples (Fig. 4) may lead one to conclude that sulfide minerals are inherently floatable. This is an old, controversial topic that has undergone a detailed reexamination recently (*38–40*). However, sulfur extraction tests with galena, chalcopyrite, and realgar showed the presence of elemental sulfur on these minerals (*18*). It is likely, therefore, that the observed flotation behavior of common sulfides is due to the liberated sulfur, not necessarily due to the original surface chemistry of the sulfides.

Separation of Hydrophobic Solids

Selective wettability as determined by using the critical surface tension of wetting approach may be exploited for the separation of hydrophobic solids. The separation of native floatable minerals from their artificial binary mixtures has recently been shown (*12*). Another application area of considerable interest is in processing of plastic wastes. In industrialized countries, parallel to the increase in production, the amount of plastic wastes has increased drastically. In Japan alone, one-third of 35 million tons of plastics produced between 1971 and 1976 ended up as wastes which were incinerated and/or subjected to land filling for disposal. Selective flotation as a process for sorting out plastics from wastes for the purpose of reutilization is already under investigation (*41,* 42). Unlike major components of natural ores, plastics have a fixed chemistry. It appears that virtually no attention has been given to the concept of critical surface tension of wetting for the selective recovery of plastics. There are enormous data available in the literature regarding the surface chemistry and wetting characteristics of plastics (*5*), which could be directly or indirectly helpful.

The following expression represents the "selective wetting" at a solution surface tension of γ_{lv} between two hydrophobic solids, S1 and S2:

$$\gamma_c^{S1} < \gamma_{lv} < \gamma_c^{S2}$$

In accordance with the concept of critical surface tension of wetting, S2 at γ_{lv} will be completely wetted whereas S1 will only be partially wetted. Analogously, the expression shown below represents the "selective flotation" for the same solids:

$$\gamma_{cf}^{S1} < \gamma_{lv} < \gamma_{cf}^{S2}$$

As emphasized by Hornsby and Leja (*10*), these two expressions are not necessarily equivalent due to the dynamic nature of the flotation process. Considering the surface tension of floatability curves of plastic samples (Fig. 3), it is readily noted that PE can selectively be floated at a surface tension of, say, γ_{lv} = 30 mN/m, leaving the mixture of PS, PVC, and PA6 in the cell in a completely wetted (depressed) state. Similarly, PS may be separated from PA6 at an intervening γ_{lv} value, say γ_{lv} = 37 mN/m. The separation of PVC from PS will be relatively difficult due to the similar wettability and floatability of the samples used in this work. It has been noted that unlike the case in mineral flotation, very coarse pieces of plastic may be floated due to their low specific gravity. For the same reason, turbulence-free conditions (or nearly so) are essential for successful selective flotation.

CONCLUDING REMARKS

The present study has demonstrated that differences exist in the wettability and floatability of hydrophobic solids. These differences may conveniently be evaluated by such wetting parameters as γ_c and β as well as by small-scale flotation experiments. In the present work, as well as in that of others (*10, 11*), methanol has been used to create aqueous test solutions having a wide range of surface tension. It is obviously not suitable for actual processing. Surfactants with long hydrocarbon chain lengths should be tested. Since their surface activity is expected to be much greater than that of methanol, a low concentration range may be sufficient for the possible separation of hydrophobic solids. Mixtures of surfactants may also be tested. In order to select the most suitable reagents for flotation separations involving hydrophobic solids, the depressing action of various surfactants may be characterized and compared by using adhesion tension diagrams. This may help to classify these reagents according to the γ_c and β values obtained.

SYMBOLS

θ	contact angle (degrees)
γ_{lv}	the liquid/vapor interfacial tension (mN/m)
γ_c	critical surface tension of wetting (mN/m)
b	the slope of the Zisman relationship
β	the slope of the adhesion tension line
γ_{cf}	critical surface tension of floatability (mN/m)
γ_{clf}	critical surface tension of least floatability (mN/m)
γ_{cmf}	critical surface tension of maximum floatability (mN/m)
Π_e	equilibrium surface pressure of adsorbed vapor (mJ/m^2)
γ_s	surface free energy of solid in vacuum (mJ/m^2)
γ_{sv}	surface free energy of solid in the presence of the saturated vapor of liquid (mJ/m^2)
Γ	adsorption density of water vapor on solid at pressure P (moles/cm^2)
P^{o}	saturated vapor pressure of water (mmHg)
R	universal gas constant (mJ/K^{-1}mol^{-1})
T	absolute temperature (°K)
γ_l^d	the dispersion component of the surface free energy of liquid (mJ/m^2)
γ_s^d	the dispersion component of the surface free energy of solid (mJ/m^2)
Γ_{lv}	the adsorption density of solute at the liquid/vapor interface (moles/cm^2)
Γ_{sl}	the adsorption density of solute at the solid/liquid interface (moles/cm^2)
Γ_{sv}	the adsorption density of solute at the solid/vapor interface (moles/cm^2)

Acknowledgments

Financial assistance offered by the Faculty of Graduate Studies, McGill University in the form of a scholarship (S.K.) is gratefully acknowledged. Authors also wish to thank Mr. L. A. Marshall of Badische Canada Ltd., Dr. N. Orbey (formerly with Dept. Chem. Eng., McGill University), and Mrs. J. Kaylor of Redpath Museum (McGill University) for supplying the samples of nylon 6, polyethylene and polystyrene, and some mineral specimens, respectively.

REFERENCES

1. H. Freundlich, *Colloid and Capillary Chemistry,* Methuen, London, 1926, p. 158.

2. F. E. Bartell and H. J. Osterhof, *The Measurement of Adhesion Tension on Solid Against Liquid* (Colloids Symposium Monograph), The Chemical Catalog Co., 1928, p. 113.

3. F. E. Bartell and H. H. Zuidema, "Wetting Characteristics of Solids of Low Surface Tension such as Talc, Waxes and Resins," *J. Am. Chem. Soc., 58,* 1449 (1936).

4. H. W. Fox and W. A. Zisman, "The Spreading of Liquids on Low Energy Surfaces. I. Polytetrafluoroethylene," *J. Colloid Sci.,* 5(6), 514 (1950).

5. W. A. Zisman, "Relation of Equilibrium Contact Angle, Wettability, and Adhesion," *Adv. Chem. Ser., 43,* 1 (1964).

6. B. K. Parekh and F. F. Aplan, "The Critical Surface Tension of Wetting of Coal," *Recent Dev. Sep. Sci., 4,* 107 (1978).

7. B. K. Parekh and F. F. Aplan, "The Critical Surface Tension of Wetting of Minerals Coated with Collectors," in *XVth International Mineral Processing Congress,* Vol. 2, Societe de l'Industrie Minerale, Bureau de Recherches Geologiques et Minieres, Cannes, 1985, p. 3.

8. E. G. Shafrin and W. A. Zisman, "Constitutive Relations in the Wetting of Low Energy Surfaces and the Theory of the Retraction Method of Preparing Monolayers," *J. Phys. Chem., 64,* 519 (1960).

9. J. A. Finch and G. W. Smith, "Contact Angles with Wetting," in *Anionic Surfactants/ Physical Chemistry of Surfactant Action* (A. H. Lucassen-Reynders, ed.), Dekker, New York, 1981, p. 317.

10. T. D. Hornsby and J. Leja, "Critical Surface Tension of Floatability," *Colloids Surf.,* 7(4), 339 (1983).

11. B. Yarar and J. Kaoma, "Estimation of the Critical Surface Tension of Wetting of Hydrophobic Solids by Flotation," *Ibid., 11,* 429 (1984).

12. S. Kelebek and G. W. Smith, "Selective Flotation of Inherently Hydrophobic Minerals by Controlling the Air/Solution Interfacial Tension," *Int. J. Miner. Process., 14,* 275 (1985).

13. J. D. Bailar, H. J. Emeleus, R. Nyholm, and A. F. T. Dickenson (eds.), *Comprehensive Inorganic Chemistry,* Pergamon, Oxford, (*a*) Vol. 2, p. 607; (*b*) Vol. 3, p. 28 (1975).

14. A. M. Gaudin and W. D. Wilkinson, "Surface Actions of Some Sulphur-Bearing Organic Compounds on Some Finely Ground Sulfide Minerals," *J. Phys. Chem., 37,* 833 (1933).

15. M. K. Bernett and W. A. Zisman, "Relation of Wettability by Aqueous Solutions to the Surface Contitution of Low-Energy Solids," *Ibid., 63,* 1241 (1959).

16. B. K. Parekh, "Contact Angle Studies of Minerals Coated with Surfactants," MS Thesis, Pennsylvania State University, 1972.

17. D. A. Olsen, R. W. Moravec, and A. J. Osterhaas, "The Critical Surface Tension Values of Group VIA Elements," *J. Phys. Chem., 71,* 4464 (1967).

18. S. Kelebek and G. W. Smith, "Effect of Elemental Sulphur Formation on the Collectorless Flotation Rate of Chalcopyrite and Galena," Presented at the 115th AIME

Annual Meeting, New Orleans, and Submitted for Publication in *Minerals and Metallurgical Processing*.

19. V. R. Gray, "The Wettability of Wood," *For. Prod. J., 12,* 452 (1962).

20. N. L. Weiss (ed.), *SME Mineral Processing Handbook,* AIME New York, 1985, Properties of Minerals, Table 2.

21. W. A. Zisman, "Recent Advances in Wetting and Adhesion," *Adhesion Science Technology,* Vol. 9A (N. N. Lee, ed.), Plenum, New York, 1975, p. 55.

22. R. J. Good, "Spreading Pressure and Contact Angle," *J. Colloid Interface Sci., 52*(2), 308 (1975).

23. F. M. Fowkes, D. C. McCarthy, and M. A. Mostafa, "Contact Angles and the Equilibrium Spreading Pressures of Liquids on Hydrophobic Solids," *Ibid., 78*(1), 200 (1980).

24. A. V. Kiselev, "Adsorption Properties of Hydrophobic Surfaces," *Ibid., 28*(3/4), 430 (1968).

25. D. H. Bagham and R. I. Razouk, "Adsorption and the Wettability of Solid Surfaces," *Trans. Faraday Soc., 33,* 1459 (1937).

26. S. J. Gregg, *The Surface Chemistry of Solids,* Reinhold, New York, 1951.

27. W. D. Harkins, *The Physical Chemistry of Surface Films,* Reinhold, New York, 1952.

28. E. V. Ballou and S. Ross. "The Adsorption of Benzene and Water Vapor by Molybdenum Disulfide," *J. Phys. Chem., 57,* 653 (1953).

29. R. R. M. Johnston and A. J. W. Moore, "Water Adsorption on Molybdenum Disulfide Containing Surface Contaminants," *Ibid., 68,* 3399 (1964).

30. S. M. Senkan and E. L. Fuller Jr., "Effect of NaOH Treatment on Surface Properties of Coal," *Fuel, 10,* 729 (1979).

31. N. K. Adam and H. K. Livingston, "Contact Angles and Work of Adhesion," *Nature 182*(4628), 128 (1958).

32. J. A. Gutierrez-Rodriguez and F. F. Aplan, "Estimating the Hydrophobicity of Coal," *Colloids Surf., 12,* 1 (1984).

33. F. M. Fowkes, "Attractive Forces at Solid-Liquid Interfaces," in *Wetting,* S.C.I. Monograph 25, London, 1967, p. 3.

34. B. Janczuk and E. Chibowski, "Interpretation of Contact Angle in Solid Hydrocarbon-Water System," *J. Colloid Interface Sci., 95*(1), 268 (1983).

35. A. H. Lucassen-Reynders, "Contact Angles and Adsorption on Solids," *J. Phys. Chem., 67,* 969 (1963).

36. S. Kelebek, "Wetting Behaviour, Polar Characteristics and Flotation of Inherently Hydrophobic Minerals," *Trans. Inst. Min. Metall., Section C,* June 1987.

37. S. Kelebek, J. A. Finch, S. Yörük, and G. W. Smith, "Wettability and Floatability of Galena-Xanthate System as a Function of Surface Tension," *Colloids Surf., 20,* 89 (1986).

38. M. C. Fuerstenau and B. J. Sabacky, "On the Natural Floatability of Sulfides," *Int. J. Miner. Process., 8,* 79 (1981).

39. W. J. Trahar, "A Laboratory Study of the Influence of Sodium Sulphide and Oxygen on the Collectorless Flotation of Chalcopyrite," *Ibid., 11,* 57 (1983).

40. G. H. Luttrell and R. H. Yoon, "The Collectorless Flotation of Chalcopyrite Ores Using Sodium Sulphide," *Ibid., 13,* 271 (1984).

41. K. Saito, I. Nagano, and S. Izumi, "New Separation Techniques for Plastics," *Jpn. Plast. Age, 13*(3), 25 (1975).

42. V. Vogt and A. Bahr, "Flotation of Plastics," *Erzmetall, 36*(10), 479 (1983) (in German).

Received by editor August 5, 1986