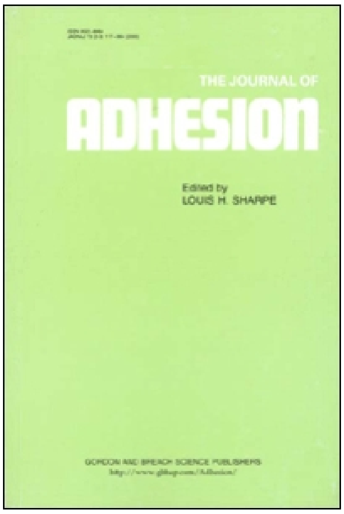

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The Wetting of Calcite Surfaces

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The Wetting of Calcite Surfaces*

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Three established methods for deriving the surface energetic parameters for calcite were studied. These are based on the contact angle in air using various wetting liquids, and submerged systems in water and in alkanes. Two variations of these methods that require less elaborate experimental procedures were also explored. Although the results of these methods were not entirely in agreement, several interesting observations emerged. The contact angles of water on the heated and alkylketene-dimer-(AKD)-treated calcite samples were higher than the untreated sample, and were observed to decrease with time. These results strongly suggest that these treatments alter the calcite surface to reduce its stability toward water. The work of adhesion determined in alkanes and water suggests that water interacts so strongly with calcite that it cannot be displaced by alkanes. This conclusion is reinforced by the results obtained using the more recent theory of adhesion of van Oss and Good which emphasizes the acid-base contribution of the surface and interacting liquid adhesion. These energy parameters were also determined for the calcite-water system.

Keywords: Calcite; calcium carbonate; contact angle; surface energetics; wetting; work of adhesion; acid-base interactions; alkylketene dimer

INTRODUCTION

A significant component of printing paper is now mineral filler. In recent years calcium carbonate has become the filler of choice. In view of this trend, the surface properties of calcium carbonates are currently

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being investigated in our laboratories by inverse gas chromatography (IGC) [1]. To complement these studies we have undertaken the examination of the wetting behavior of calcium carbonates and their modification so that the surface energetics by contact angle may be compared with and contrasted to those determined by IGC. These results may be further related to cellulose and its modifications [2,3] to give insight into the nature of the strength and surface interactive properties of paper.

Closely associated with the increased use of calcium carbonate in alkaline papermaking has been the extensive use of cellulose reactive sizes for the modification of the paper's surface properties. One such example of this type of size is alkylketene dimer (AKD) which is widely used at the present. When AKD is applied to papers that contain calcium carbonates, especially in the precipitated form, undesirable responses may occur, such as loss of sizing effectiveness with time, known as "sizing reversion" or increased sizing demand. An understanding of the interaction of AKD with calcium carbonate, the resulting surface chemistry, and time dependence of these properties is of considerable interest in the field of paper science. In this study, calcite was used as a model mineral surface to explore the fundamentals of the AKD – calcium carbonate system.

The contact angle technique used to study surface energetics requires a "smooth" surface. Compacting calcium carbonate powders to form a smooth surface for wetting analysis has been used, but the validity of results is questionable. Recently the "wicking" method was introduced to obtain the surface energetics of powders [4] and this technique may prove advantageous in future studies. However, we have chosen to use cleaved calcite crystals for determining the surface energetics by contact angle measurements.

Previous wetting [5–8] and non-wetting studies [9] with calcium carbonate indicate that its surface is considered to be in the high energy range. This suggests that contact angle measurements in air by themselves are of limited use since the surface tension values of most liquids are less than 72 $\mathrm{mJm^{-2}}$. Thus, the solid would be wetted by most liquids. To overcome this limitation Schultz *et al.* [10], based on the work of Tamai [11], developed a method that uses two liquid phases to determine the surface energetics of high energy surfaces. This technique has been used extensively for metals [11] mica [10] marble [5–8] and quartz [12]. It has also been applied to polymers including cellulose [13].

The objective of this investigation was to determine the surface energetics of different calcite surfaces, including freshly-cleaved, after heating at 105°C and 150°C and following treatment with alkylketene dimer (AKD). Wetting experiments based on the contact angle measurement of various liquids on the surfaces provided the data necessary to characterize the interfacial energies. Results were expressed as the surface energy and the work of adhesion.

Two Liquid Method

Experimentally, the two liquid method consists of measuring the contact angle of a water drop when the surface is immersed in an homologous series of hydrocarbons. By applying Fowkes' [14] formulation at the two interfaces and substituting into Young's equation at this interface and remembering that the surface free energy of *n*-alkanes consists only of the London dispersion term, Eq. (1) is obtained.

$$\gamma_W - \gamma_H + \gamma_{WH}\cos\theta_{SW/H} = 2(\gamma_S^d)^{1/2}[(\gamma_W^d)^{1/2} - (\gamma_H^d)^{1/2}] + W_{SW}^{AB} \quad (1)$$

where γ is the interfacial tension and the subscripts *S*, *L*, *W*, and *H* identify the material as the solid, liquid, water or hydrocarbon, respectively. Contact angle θ, with subscript *SW*/*H*, indicates measurement of a water drop on the solid in a hydrocarbon medium. The superscript *d* identifies the dispersive (London) component of the surface free energy. The residual, W_{SW}^{AB}, is the acid-base component of the work of adhesion. This can be considered equivalent [15] to the total non-dispersive interaction, I_{sw}^n, by the relationship

$$W_{SW}^{AB} = I_{SW}^n = 2(\gamma_S^p \gamma_W^p)^{1/2} \quad (2a)$$

$$W_{SW}^d = I_{SW}^d = 2(\gamma_S^d \gamma_W^d)^{1/2} \quad (2b)$$

from which the "polar" interaction, γ_s^p, may be calculated [10]. A plot of $(\gamma_w - \gamma_H + \gamma_{wH}\cos\theta)$ *versus* $[(\gamma_w^d)^{1/2} - (\gamma_H^d)^{1/2}]$ will yield the parameters γ_s^d and W_{SW}^{AB} as the slope and intercept, respectively. For this relationship to be valid, W_{SW}^{AB} must be greater than $2[(\gamma_s^d)^{1/2} - (\gamma_H^d)^{1/2}]$

$[(\gamma_H^d)^{1/2}-(\gamma_w^d)^{1/2}]$ indicating that water is capable of displacing the *n*-alkanes. It should be noted, however, that this procedure has been criticized by Johnson and Dettre [16] because the existence of hysteresis was not addressed and the adsorption of the wetting liquid (water) at the solid/vapor interface was ignored.

To study the surface in an aqueous environment, the contact angle of the hydrocarbon on the solid surface immersed in water can be determined from the expression

$$\gamma_H-\gamma_W+\gamma_{HW}\cos\theta_{SH/W}=2(\gamma_S^d)^{1/2}[(\gamma_H^d)^{1/2}-(\gamma_W^d)^{1/2}]-W_{SW}^{AB} \quad (3)$$

Once again, plotting $[\gamma_H-\gamma_W+\gamma_{HW}\cos\theta]$ *vs.* $[(\gamma_H^d)^{1/2}-(\gamma_W^d)^{1/2}]$ permits the γ_s^d and W_{SW}^{AB} values to be obtained from the slope and intercept, respectively. This method has been applied to hydrated polymers [17,18]. For both methods, the polar component of the surface free energy, γ_s^p, may be calculated by solving Eq. (2a) using W_{SW}^{AB} determined graphically. The dispersive component of the work of adhesion, W_{SW}^d, was determined using Eq. (2b).

Abridged Two-Liquid Method

While the two-liquid methods described in the previous section are time consuming and experimentally cumbersome, an abridged method has been used [2,19–21] to determine the surface energetics of solids. The method takes advantage of the fact that octane and water have the same value for the dispersive component, γ_s^d, at 20°C, and that the polar component, γ_s^p, of octane is zero. Two approaches have been taken to characterize surface free energies by this method. In the first, contact angle values of air or octane with the surface when it is immersed in water are determined. This is identified as the "water immersed method". The second involves the measurement of contact angles of water on the surface in air, or immersed in octane, and is identified as the "dry method". These will be discussed separately.

For the water immersed method, Jho [20] and Andrade [21] have shown that the γ_s^d and γ_s^p values can be obtained by using contact angle measurements of air bubbles in water and octane droplets in water in contact with the solid surface. Such determinations in an aqueous environment have been used extensively, especially for hydrophobic polymer surfaces. Equations (4) and (5) give the relationships used to determine the dispersive and polar components from the two contact angles.

$$\gamma_s^d = \left[\frac{\gamma_O + \gamma_{WO}\cos\theta_{SO/W} - \gamma_W\cos\theta_{SA/W}}{2(\gamma_O^d)^{1/2}}\right]^2 \tag{4}$$

$$\gamma_s^p = \left[\frac{\gamma_W - \gamma_O - \gamma_{WO}\cos\theta_{SO/W}}{2(\gamma_W^p)^{1/2}}\right]^2 \tag{5}$$

The subscript O refers to octane. The value for the interfacial tension of octane and water, γ_{WO}, was taken from Andrade *et al.* [21] as 50.5 mJ/m^2. Also recall that the surface free energy of octane consists only of the dispersive component, *i.e.* $\gamma_O^d = \gamma_O$.

The dry method was used by Toussaint and Luner [2] to examine cellulose films. If the contact angle of water in air is combined with the contact angle of water in octane, the γ_s^d and γ_s^p in the "dry" environment may be determined by using the relationship

$$\gamma_s^d = \left[\frac{\gamma_O + \gamma_W\cos\theta_{SW/A} - \gamma_{WO}\cos\theta_{SW/O}}{2(\gamma_O^d)^{1/2}}\right]^2 \tag{6}$$

$$\gamma_s^p = \left[\frac{\gamma_W - \gamma_O + \gamma_{WO}\cos\theta_{SW/O}}{2(\gamma_W^p)^{1/2}}\right]^2 \tag{7}$$

The dispersive and polar components of the work of adhesion were determined by applying the appropriate components of surface free energy to Eqs. (2a) and (2b).

Acid-Base Method

According to Fowkes [22] the work of adhesion between a liquid and a surface was proposed to be given by

$$W_A = W_A^d + W_A^p + W_A^{AB} \tag{8}$$

where W_A^d, W_A^p and W_A^{AB} are the works of adhesion arising from dispersive, polar and acid-base interactions, respectively. Assuming that the geometric mean combining rule holds for dispersive forces, and that the polar interactions, W_A^p, are negligible, Eq. (8) may be written as [23]:

$$W_A = 2(\gamma_w^d \gamma_s^d)^{1/2} + W_{sw}^{AB} \tag{9}$$

where W_{SW}^{AB} includes the work of adhesion from acid-base (AB) interactions. More recently, [24,25] van Oss *et al.* have identified the γ_s^d terms with the Lifshitz-van der Waals interaction, or the apolar component, γ_s^{LW}. This term includes the London, Debye and Keesom forces. The W^{AB} component in Eq. (8) arises from the electron-acceptor (Lewis acid) and electron-donor (Lewis base) intermolecular interactions. Thus, for the AB component of a surface one writes

$$\gamma^{AB} = 2(\gamma^+ \gamma^-)^{1/2} \tag{10}$$

where γ^+ and γ^- are the contributions from the electron-acceptor and electron donor interactions. Therefore,

$$W_{SW}^{AB} = 2(\gamma_s^+ \gamma_L^-)^{1/2} + 2(\gamma_s^- \gamma_L^+)^{1/2} \tag{11}$$

The surface free energy components are related to the contact angle by combining Eqs. (9) and (11) to form

$$\gamma_L(\cos\theta + 1) = 2(\gamma_S^{LW} \gamma_L^{LW})^{1/2} + 2(\gamma_S^+ \gamma_L^-)^{1/2} + 2(\gamma_S^- \gamma_L^+)^{1/2} \tag{12}$$

The values of γ_s^{LW}, γ_s^+ and γ_s^- may be determined for a surface by measuring the contact angles with three liquids: water, a polar liquid, *e.g.* formamide and a non-polar liquid, *e.g.* methylene iodide. Results are obtained by solving the system of equations using Eq. (12).

EXPERIMENTAL

Wetting Liquids

The liquids used for the contact angle measurements were obtained from Aldrich Chemical Co. and were either anhydrous or spectrophotometric grade. They were stored under N_2 and used without further purification. The water used was doubly distilled. The liquids used and their surface tensions [3] are listed in Table I.

Preparation of Calcite Samples

The calcite sample originated from Chihuahua, Mexico and was obtained from Ward's Natural Science Establishment, Inc. The calcite was cleaved with a razor blade in air, to yield 2 cm x 2 cm x 5 mm samples. Samples with no further treatment were tested immediately after cleavage and designated as *freshly cleaved.* For immersion experiments, the freshly-cleaved sample was dropped immediately into either an alkane or water to prevent contamination. The calcite identified as *heated* was done so in an oven at 105°C or 150°C for 2 hours and then cooled in a desiccator. Figure 1 shows an SEM of a typical cleaved calcite surface.

The sample designated as *AKD treated* was prepared by reacting the surface of a freshly-cleaved sample with alkylketene dimer (AKD). The AKD was supplied by Hercules Inc. as Aquapel 364® prepared from a mixture of stearic acid (55%) and palmitic acid (45%). It was recrystallized with acetone before use. The recrystallized AKD dissolved in methylene chloride was deposited on the freshly-cleaved calcite [2,3]. The methylene chloride was removed by evaporation and the samples were then heated overnight in an oven at 150°C to induce the reaction between the AKD and the calcite. Unreacted AKD was removed by Soxhlet extraction with tetrahydrofuran (THF) for 8 hours.

TABLE I Surface tensions (mJm^{-2}) and contact angles of liquids on calcite samples in air

		Contact Angle, $\theta°$, at 0.5 min		
	$\gamma_{L\dagger}$	*Freshly Cleaved*	*Heated (150°C)*	*AKD Treated*
Water	72.8	spreads	56.0 ± 4.0	84.0 ± 8.0
Glycerol	63.4	19.2 ± 1.3	66.0 ± 5.3	76.9 ± 6.2
Formamide	57.9	spreads	49.1 ± 4.6	66.0 ± 4.9
Methylene Iodine	50.8	29.7 ± 2.7	43.8 ± 3.6	40.8 ± 2.9
Ethylene Glycol	48.0	48.0 ± 2.8	51.7 ± 3.8	58.9 ± 5.4
1,3 Propanediol	45.6	45.6 ± 2.1	51.3 ± 2.7	54.2 ± 4.8
s-Tetrabromoethane	47.5	47.5 ± 2.0	30.3 ± 2.8	32.2 ± 3.6
1-Bromonaphthalene	44.6	44.6 ± 3.8	29.2 ± 2.1	18.2 ± 2.3
1-Chloronaphthalene	41.8	41.8 ± 2.1	27.1 ± 5.3	19.4 ± 3.6

†from [3] measured using a Du Nouy ring-type tensiometer.

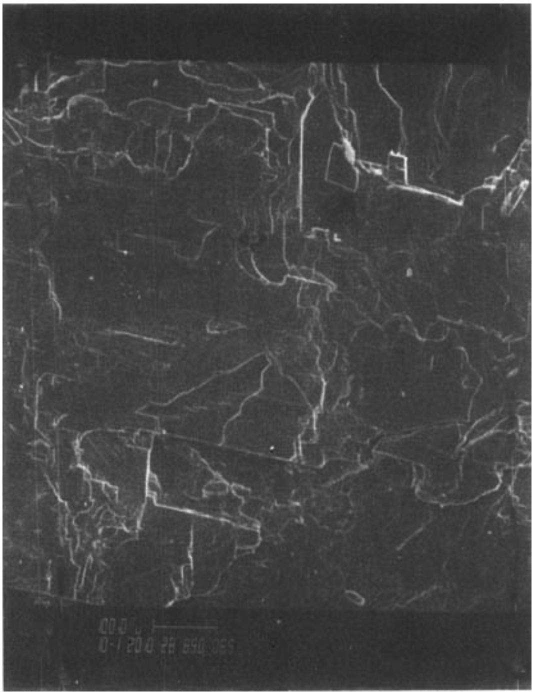

FIGURE 1 SEM micrograph of the cleaved surface of calcite.

Additional AKD deposition followed by extraction showed on further change in the surface properties and, as a result, it was assumed that the reactive sites on the calcite surface were saturated.

Contact Angle Measurements

All contact angle measurements were made using a Ramé-Hart contact angle goniometer at 23°C. In some instances an environmental chamber was used. Contact angles in air were directly measured by estimating the location of a tangent line to the profile of the sessile drop at the location where the sessile drop profile intersected the solid surface. The liquid was supplied by a Gilmont microliter syringe with a stainless steel needle. The syringe was adjusted to deliver a drop volume of 3 ml. The contact angles were measured on both sides of the drop. Results reflect the average of at least ten drops that were measured for each sample test.

Contact angle measurements in hydrocarbons were made using the two-liquid method with the goniometer using an environmental chamber. Doubly-distilled water and the alkanes were equilibrated with each other prior to use. The calcite samples were immersed in the hydrocarbon for at least 24 hours before measurement. The sample was placed in the chamber filled with the hydrocarbon. A sessile droplet of water was delivered on the sample surface in the hydrocarbon by means of the microliter syringe.

Contact angles measurements in water were made by placing the sample on two glass blocks in the chamber filled with the hydrocarbon saturated water. The measurements were made after 24 hours of immersion. An air bubble or sessile droplet of hydrocarbon was delivered to the sample surface with an inverted needle.

RESULTS AND DISCUSSION

Two-Liquid Method - Water in Alkanes

Four pre-treatment procedures for the calcite were studied: i) freshly cleaved, ii) heated at 105°C (2 hr), iii) heated at 150°C (2 hr) and iv) reacted with alkylketene dimer (AKD). Figure 2 shows the change in contact angle with time for the *freshly cleaved* and *heated* samples (150°C). All three calcite samples show contact angle variations with time, with the *freshly-cleaved* sample showing much less variation. The *freshly-cleaved* sample had equilibrium (20 min) contact angles ranging from 30° to 60° while the *heated* sample had higher contact angles, reaching equilibrium contact angles in the 60° range. The higher contact angles in the *heated* samples suggest fewer higher energy sites to interact with water. This is further implied by the fact that water readily spreads on *freshly-cleaved* calcite but not on an "aged" sample that was exposed to airborne contaminants. The strong decay observed with the *heated* sample suggests an interaction between the water drop and the surface and that the surface structure is unstable until after approximately 10^3 seconds.

The literature regarding the variation of contact angle with time in systems such as calcite is mixed. In the original study by Tamai *et al.* [11] who examined perfectly smooth metal surfaces, *e.g.* copper, iron, chromium, and cadmium, only contact angles which achieved stability

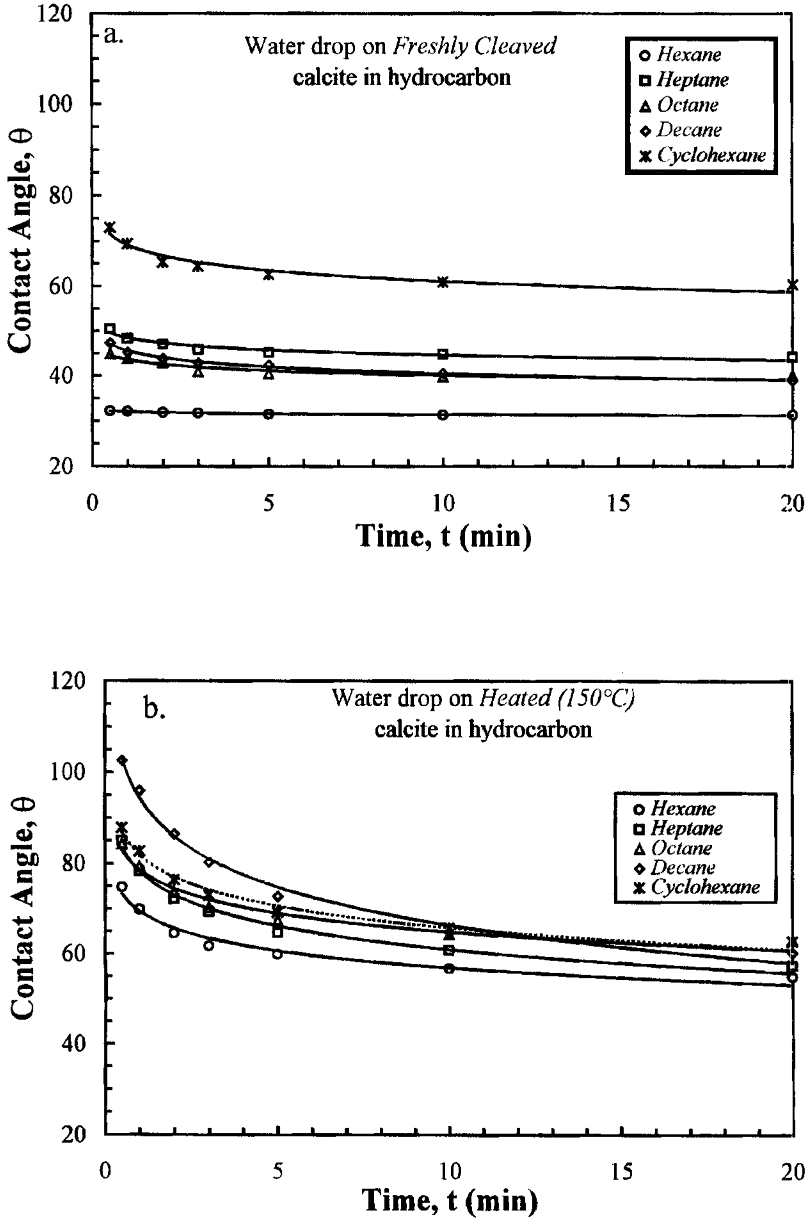

FIGURE 2 The contact angles of water sessile droplets on calcite samples immersed in various alkanes as a function of time: a) freshly cleaved; b) heated at 150°C for 2 hours.

were reported. The time to achieve stability varied from a few minutes to nearly one hour. Schultz *et al.* [10] mention that the contact angles in their work with polymers showed no time dependence. For the present study, perhaps a clue to the behavior in Figure 2 may be found in the higher than normal standard deviations found in this system. Figure 1 shows that the cleaved calcite crystals have a very irregular surface with many planes of fracture. These irregularities may result in unstable drops if placed on the edges of these planes. It is also possible that these edges are energetically different from the smooth surface. Consequently, these irregularities may contribute to the time dependence of the contact angle and scatter. The contact angles of water in the alkanes on the AKD-treated sample (not illustrated) fell between 125° and 140° and were practically invariant with time. The surface was rendered hydrophobic by the alkyl chain in the AKD sample, as expected.

Figure 3 shows a plot of Eq. (1) using contact angles after 20 minutes for the four calcite samples. The γ_s^d values were determined graphically from the slope of a least-squares fit of each data set. W_{SW}^{AB} values were obtained from the y-intercept of the same line (centerline of the plot). Results are given in Table II. The γ_s^d values appear high when compared with mica, ~40 mJm^{-2} [10], but close to the values

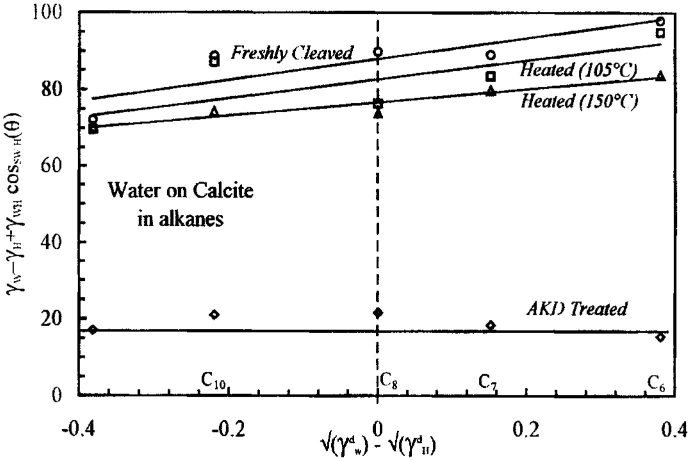

FIGURE 3 A plot of the terms in Eq. (1) used to determine the wetting parameters of the calcite samples from the two-liquid method for the water-in-alkane systems. The slope represents $2(\gamma_s^d)^{1/2}$ and the intercept is W_{SW}^{AB}.

TABLE II Wetting parameters derived from two-liquid method (mJm^{-2})

	Water immersed in Alkanes			Alkanes immersed in Water		
	W_{SW}^{AB}	γ_s^d	γ_s^p	W_{SW}^{AB}	γ_s^d	γ_s^p
Freshly Cleaved	88	185	38	96	21	46
Heated (105°C)	83	149	33	97	19	46
Heated (150°C)	77	73	29	96	29	45
AKD Treated	20	1.6	1.9	90	4.9	39

of dry clay, ~ 140 mJm^{-2} [25], and silica, ~ 105 mJm^{-2} [26] determined by the same method. Tamai [11] found γ_s^d values of ~400 mJm^{-2} for polished metals. The two-liquid method was also used by Andebrant and Pugh [12] to determine the energetics of quartz and several silicate materials. They did not report values for γ_s^d since they observed that small errors in contact angle resulted in large errors in γ_s^d. Therefore, they [12] used the W_{SW}^{AB} values and an alternate method to determine γ_s^d. For the present study, it is evident in Figure 3 that a significant scatter about the line exists. The origin of this variability may be the heterogeneity of the cleaved calcite surface. In view of this, several alternate methods for determining the surface energetics were also explored.

Two-Liquid Method – Alkanes in Water

The reverse of the previous method involves measuring the contact angles of alkane droplets on calcite immersed in water. For the calcite samples that were *freshly cleaved* and *heated* at 105°C and 150°C, the contact angles ranged from 158° to 148° and were invariant with time (not shown). The range of the contact angle values approached the standard deviations (± 7°). This behavior is interpreted as the complete wetting of the calcite surface by water. The alkane droplets cannot displace the water interphase due to the strong calcite-water interaction. This leads to a screening of the calcite from the alkanes and suggests changes in the calcite surface imparted by the continuous phase. One can conclude from these results that the two-liquid method in water or alkane is more applicable to low energy surfaces such as polymers than to the present system, since surface modification by the polar solvents, *e.g.* water, will be less likely.

Figure 4 shows the change in contact angle of alkane drops on the *AKD-treated* sample immersed in water as a function of time. The contact angles were lower than for the *freshly-cleaved* (untreated) surface. This is consistent with surface hydrophobicity. The wetting increased with a decrease in molecular weight of the alkane. One explanation may be the greater mobility of the shorter chain alkanes permitted them to interpenetrate the AKD chains and expel water. Figure 5 plots the contact angles after 20 minutes according to Eq. (3). The values for γ_s^d and W_{SW}^{AB} derived from Eq. (3) are presented in Table II. The γ_s^d values are nearly one order of magnitude lower than that obtained with the water in the hydrocarbon system. The W_{SW}^{AB} values are similar in both systems with the exception of the *AKD-treated* sample. When the calcite samples are immersed in water, their polar components uniformly approach that of water, *i.e.* 51 mJm^{-2} and suggests the interaction of the alkanes with calcite is substantially modified by an immobile layer of water.

Abridged Two-Liquid Method

Both approaches to the abridged two-liquid method were used to test the calcite samples. Table III provides the wetting parameters, including the

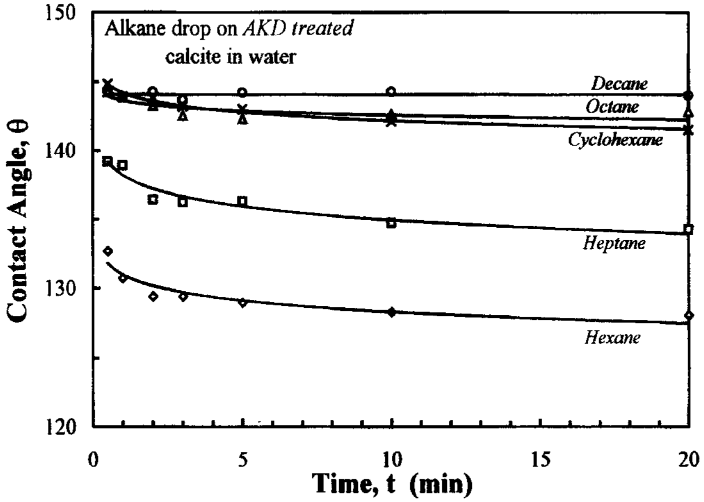

FIGURE 4 The contact Angles of various alkane sessile droplets on calcite samples immersed in water as a function of time.

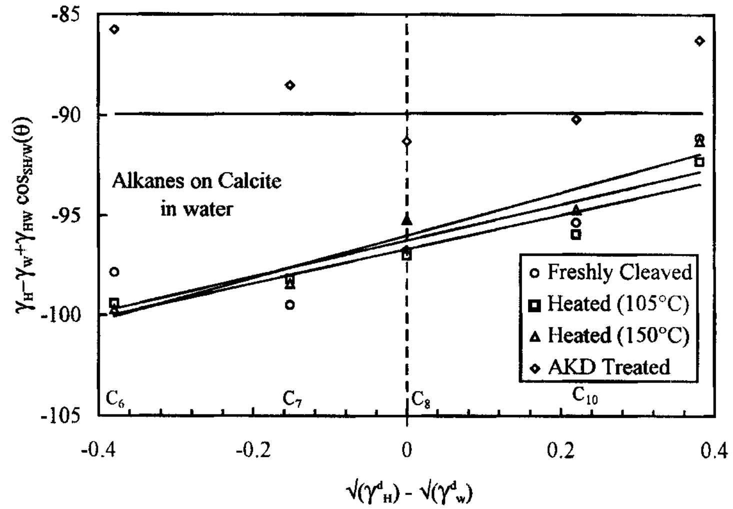

FIGURE 5 A plot of the terms in Eq. (2) used to determine the wetting parameters of the calcite samples from the two-liquid method for the alkane-in-water systems measured after 20 minutes. The slope represents $2(\gamma_s^d)^{1/2}$ and the intercept is $-W_{SW}^{AB}$.

TABLE III Wetting parameters of calcite samples derived from the abridged two-liquid methods

	Dry method				Water immersed method			
	$\theta_{SA/O}$	$\theta_{SW/O}$	γ_s^d	γ_s^p	$\theta_{SA/W}$	$\theta_{SO/W}$	γ_s^d	γ_s^p
Freshly Cleaved	spreads	45 ± 6	–	37	155 ± 4	157 ± 3	20	47
Heated (105°C)	53 ± 6	78 ± 13	34	19	158 ± 3	158 ± 2	21	47
Heated (150°C)	56 ± 7	84 ± 8	38	15	157 ± 3	152 ± 5	22	45
AKD Treated	84 ± 5	132 ± 6	46	1.5	147 ± 8	144 ± 7	20	41

contact angles and the calculated dispersive and polar components for the dry (water in air and in octane), and the water-immersed (octane or air in water) experiments. For the dry method, the polar components correlate well with those of the complete two-liquid method that tests water on calcite as immersed in the various alkanes, *cf.* Table II. The dispersive components, however, have no such correspondence. For the water-immersed state, rather good agreement between the abridged and complete methods is observed for both surface energetic components. An exception is the dispersive component, γ_s^d, for the AKD-treated sample.

Wetting in Air: Application of the Acid-Base Method

The contact angles on the three calcite samples were determined with the liquids listed in Table I. Zisman plots were made in the anticipation of deriving some meaningful information. However, no consistent picture emerged in examination of the critical surface tension of wetting, γ_c, that were determined. Therefore, values are not reported.

Figure 6a through 6c show time dependence of contact angles for several liquids on calcite measured in air. It is clear that *heated* and *AKD-treated* samples gave increased contact angle values. Furthermore, the water contact angle decreases significantly with time on both the *heated* and *AKD-treated* sample. This suggests that the presence of water modifies the surface while the other probes are less intrusive. From the rapid decrease, complete wetting may be expected. For the *AKD-treated* sample, (Fig 6c), complete coverage is apparently not achieved although the contact angle is higher than for the *heated* sample. The behavior may also be explained by the rehydration of the calcite surface and expansion of the interphase which results in weaker AKD anchoring. Supporting evidence for this interpretation is found in the work of Bottorff who showed by NMR that reaction between AKD and calcium carbonate occurs, but in a complicated pattern [28].

According to van Oss and Good [24], upon selection of a suitable set of liquids (*i.e.*, probes) and after measuring the contact angle on a solid surface, one may determine γ_s^{LW} as well as the electron donor γ_s^- and acceptor γ_s^+ components of the surface free energy. This was done for our systems by using Eq. (9) and the necessary surface free energy components for the probe liquids used in this study as given in Table IV. The γ_s^{LW} of a surface may be determined by using:

$$\gamma_s^{LW} \approx \gamma_s^d = \frac{\gamma_L}{4}(1 + \cos\theta)^2 \tag{10}$$

where γ_L is the surface tension of the liquid with only dispersion forces, *e.g.* methylene iodide, and θ is the corresponding contact angle of this liquid on the surface as measured in air. Table V shows the experimental contact angles observed for methylene iodide as well as water, formamide and glycerol. The values of γ_s^{LW} determined from

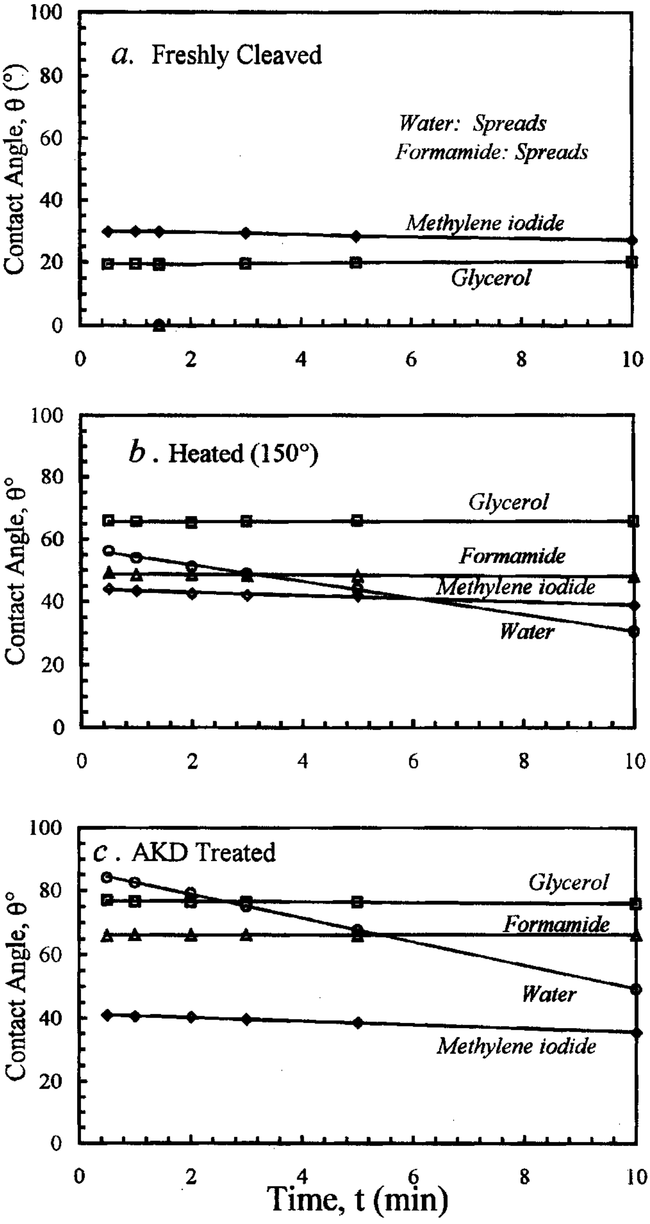

FIGURE 6 The contact angles of several liquids in air on the surface of calcite samples: a) freshly cleaved; b) heated at 150°C for 2 hours; and c) AKD treated. Results from these liquids were analyzed using the acid-base method.

Eq. (10) are given in Table VI and are similar to those determined by the abridged two-liquid methods for water in air and in octane, *cf.* Table III.

By using the van Oss *et al.* [24, 25] relationship given by Eq. (9) the electron-donor-acceptor components of the surface free energy were determined using water in conjunction with formamide or glycerol. Contact angles are given in Table V, while the calculated values are shown in Table VI. The spreading of water on the *freshly-cleaved* sample indicates a surface free energy in excess of 72 mJm^{-2}, making it impossible to calculate the acid-base components. For both the *heated* and *AKD-treated* samples the base components, γ_s^-, were significant. However, since values of the acid components were very small, these samples were found to be effectively monopolar. Treatment with AKD acted to give substantially lower values for the base component as compared with heat treatment alone.

TABLE IV Surface free energy components of wetting liquids from the acid-base method (mJm^{-2})

	γ_L	γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{AB}
Water	72.8	21.8	25.5	25.5	51.0
Glycerol	63.4	37.0	3.92	57.4	26.4
Formamide	57.9	39.6	2.28	39.6	19.0
Methylene Iodide	50.8	50.8	0.0	0.0	0.0

TABLE V Contact angles (°) of wetting liquids on calcite, measured in air, for the acid-base method

	water	*methylene iodide*	*formamide*	*glycerol*
Freshly Cleaved	spreads	30	spreads	19.3
Heated (150°C)	56	44	49	66.0
AKD Treated	84	41	66	77.0

TABLE VI Surface free energy components of calcite samples (acid-base method)

	formamide/water/methylene iodide				*glycerol/water/methylene iodide*			
	γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{AB}	γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{AB}
Freshly Cleaved	44	–	–	–	44	–	–	–
Heated (150°C)	38	0.04	28.8	2.15	38	~0	38.7	~0
AKD Treated	39	~0	6.7	~0	39	~0	7.9	~0

Works of Adhesion for Calcite-Water

Both the papermaking and printing process depend greatly on the adhesion properties of materials in paper, *i.e.* fibers, fillers, and toners. Calculation of the work of adhesion between calcite and liquids, especially water, therefore has significant interest. Values for the work of adhesion between different calcite samples and water, calculated from the contact angles determined by the different methods, including the two-liquid method, the abridged two-liquid method, and the acid-base method, are reported in Tables VII–IX, respectively.

The work of adhesion components for the water-calcite system were determined from Eqs. (1) to (3) and are given in Table VII. The

TABLE VII Work of adhesion between water and calcite samples from the two-liquid method (mJm^{-2})

	immersed in Alkane			*immersed in Water*		
	W^d_{SW}	W^{AB}_{SW}	W_{SW}	W^d_{SW}	W^{AB}_{SW}	W_{SW}
Freshly Cleaved	127	88	215	43	96	139
Heated (105°C)	114	83	197	40	97	137
Heated (150°C)	80	77	156	50	96	146
AKD Treated	13	20	33	21	90	110

TABLE VIII Work of adhesion between water and calcite samples from the abridged two-liquid method (mJm^{-2})

	Dry method			*Water immersed method*		
	W^d_{SW}	W^{AB}_{SW}	W_{SW}	W^d_{SW}	W^{AB}_{SW}	W_{SW}
Freshly Cleaved	–	87	–	42	98	139
Heated (105°C)	54	62	117	42	98	140
Heated (150°C)	58	55	113	44	95	139
AKD Treated	63	17	81	42	92	134

TABLE IX Work of adhesion between water and calcite samples from the acid/base method (mJm^{-2})

	formamide/water/methylene iodide			*glycerol/water/methylene iodide*		
	W^d_{SW}	W^{AB}_{SW}	W_{SW}	W^d_{SW}	W^{AB}_{SW}	W_{SW}
Freshly Cleaved	62	–	–	62	–	–
Heated (150°C)	57	56	113	57	63	120
AKD Treated	58	26	84	58	28	86

results for the water-in-alkane systems shows that the W_{SW} is greater than the work of cohesion for water, W_C, indicating a stronger interaction of the water with the surface than with itself. The greater part of W_{SW} originates from W^d_{SW}. This is illustrated as a bar graph in Figure 7. Heating the calcite samples decreases the W^d_{SW} component. This may result from relaxation of the surface free energy by structural rearrangement or contaminant adsorption. Both the dispersive and the acid-base components are affected.

For the two-liquid method with calcite immersed in water, the W_{SW} approximates the W_C for water. The W^d_{SW} and W^{AB}_{SW} are in the correct proportion for water. The AKD sample shows a lower W_{SW} due to the presence of alkyl chains and the values appear reasonable. It is apparent that we are observing a water-alkane system in the contact angle measurements. The calcite surface is effectively shielded by a strongly bound layer of water which agrees with the previous notion that there is a strong interaction between bare calcite and water.

Table VIII gives the works of adhesion, W_{SW}, and W^d_{SW}, W^{AB}_{SW}, determined using the abridged two-liquid method from Eqs. 2 and 4–7.

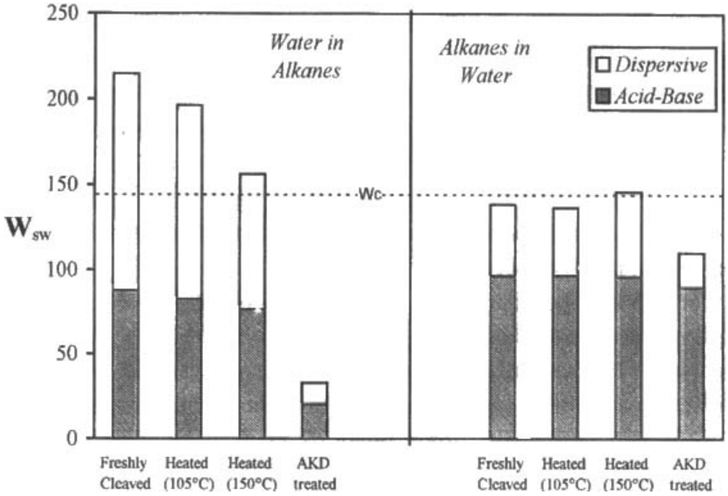

FIGURE 7 A plot of the work of adhesion, W_{SW}, and the dispersive, W^d_{SW}, and acid-base W^{AB}_{SW}, contributions for the calcite samples. Contact angles were measured after 30 sec, and data were analyzed using the two-liquid method. Results for both the alkanes in water and water in alkanes systems are presented.

Results from the water-immersed measurements were in good agreement with those from the complete two-liquid method, with the exception of the dispersive component for the *AKD-treated* sample. The values for the water-in-air and water-in-octane system are different when compared with the corresponding two-liquid method. The precise origin of this difference is unknown at present.

The work of adhesion between water and calcite derived from the van Oss *et al.* acid-base approach are given in Table IX. Since water wets the *freshly-cleaved* sample, no conclusions can be reached regarding its W_{SW}^{AB} and W_{SW} values. The relationship between the *heated* and *AKD-treated* samples compare favorably with the other two methods, given the limitations of the techniques. In view of this situation, the selection of the most accurate approach for the determination of the work of adhesion between the three methods examined in this study cannot be made from these results at present.

CONCLUSIONS

This investigation considered the wetting behavior of cleaved calcite subjected to various surface preparations. Three established methods for deriving surface energetic parameters and the work of adhesion between calcite and water were employed. The *freshly-cleaved* calcite samples had a high energy surface indicated by complete wetting by water and alkanes. Heating tended to reduce the surface free energy which was found to be largely monopolar basic from analysis using the acid-base method with the solid. In the presence of water, time-dependent changes occurred.

For the two-liquid method with immersion in alkanes, relatively high work of adhesion with water were observed for bare calcite samples. This was attributed to the apolar (dispersive) component. However, the abridged two-liquid method in air and in octane (dry), and the acid-base method gave much lower dispersive components in the range of 35–45 $\mathrm{mJm^{-2}}$ and, hence, lower overall works of adhesion between water and calcite.

Treatment with AKD tended to reduce the overall surface free energy and work of adhesion between water and calcite when determined by the two-liquid method in alkanes. The reduction appears to stem from both the dispersive and acid-base components. However, for the abridged and acid-base methods, energy reductions resulted largely from the acid-base components while the dispersive components remained stable.

When the calcite crystal was immersed in water, a quite different picture emerged from the contact angle measurements. The surface appeared similar for the bare calcite samples using both the two-liquid and abridged two-liquid methods. Both provided total works of adhesion, W_{SW}, that were slightly lower than the work of cohesion for water. This suggested that an immobilized layer of water existed at the calcite surface, and that the alkanes interacted with this interphase and not directly with the calcite. This was supported by the W_{SW} for the bare calcite surfaces which were higher than the cohesive energies, W_C, for water. Treatment with AKD gave a significant reduction in the work of adhesion between water and calcite.

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