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SURFACE ENERGETICS OF CALCIUM CARBONATE POWDERS BY INVERSE GAS CHROMATOGRAPHY (IGC) AND CLEAVED CRYSTALS BY CONTACT ANGLE MEASUREMENT

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ABSTRACT

Inverse gas chromatography (IGC) and sessile drop contact angle measurement were used to study the surface energetics of calcium carbonates from different sources and the effects of surface conditioning. A compilation of the results using these two methods to determine the apolar and polar nature of the surface is given. The results of the two analytical methods are summarized individually. IGC analysis provided a sensitive tool for detecting differences in surface energy attributed to variation in surface water, or by contamination with other chemisorbed species. Basic probes were used to characterize surface acidic sites. Acidic probes, however, were found too reactive with the calcium carbonate to enable a quantification of the surface basicity. Strong adsorption of acidic probes indicates the presence of a strong basic component at the surface. The susceptibility of the IGC method to misinterpretation retention data obtained from chemisorbed probes was also identified. Contact angle experiments were conducted on cleaved calcite samples using multiple wetting liquids and two techniques to separate the polar and apolar contributions of surface energy. The results demonstrate a strong interaction of water with the calcite surface and the reduction of total surface energy when the surface is treated with alkylketene dimer. A comparison of results from both methods is provided. Differences in the application of the results of the two methods to access the surface energetics are addressed. The importance of distinguishing between the thermodynamics of gas/condensed and condensed/condensed phase interactions when comparing the results from IGC and wetting experiments is also discussed. For calcium carbonate, the trends observed by the two approaches are consistent, although a defining link between the two was not established.

INTRODUCTION

Calcium carbonate from a variety of sources, including precipitated, ground limestone and marble and chalk, is used as filler for paper or as a pigment in coating for its superior optical and physical properties and relative cost effectiveness. However, additional demands have been placed on the papermaker to improve the quality of papers surfaces to meet the specifications of highly specialized imaging technologies while maintaining print runnability. In addition to the wide variety of physical forms that have been used to improve the performance of calcium carbonates in paper and coatings, the surface chemistry is also of critical importance. The characterization of the surface properties and especially the surface energetics of such materials is recognized as the key to the understanding of the wetting and strength properties of papers. This information provides essential insight into the mechanisms of such interactions as the liquid wetting and adhesive properties of inks and toners, or the internal strength as related to bonding in the fiber/additive/filler system.

The classical approach used to determine the interfacial energies of materials, and thereby enabled the prediction of the works of adhesion, has been through wetting experiments. One widely used method is contact angle measurement where an estimate is made of the angle, θ, formed between a solid surface and a line tangent to a sessile drop profile where the drop intersects the surface. The thermodynamic work of adhesion, W_A, is obtain from the Young's equation in the form:

$$W_A = \gamma_{LV}(1+\cos\theta) + \pi_e \tag{1}$$

where γ_{LV} is the surface tension of the wetting liquid and π_e is spreading pressure resulting from the vapor adsorbed on the solid surface. For low energy surfaces, π_e is considered small or negligible. The analysis of high energy surfaces, e.g. calcium carbonates, by wetting methods is complicated by an appreciable spreading pressure, and the tendency of the wetting liquids to readily wet the surface.

Several methods have been reported which have improved the value of contact angle for the determination of surface energies of high-energy surfaces (1-8). Furthermore, the results from contact angle measurement using selected groups of wetting liquids may be combined to separate determination of the polar and apolar contributions to the total surface energy of the solid surface. From this information, the adhesive behavior of the surface with other materials may be predicted. Two methods based on comparing the behavior of different wetting liquids have been used in the analysis of cleaved calcite surfaces, which acts as a model for calcium carbonate fillers. The surface properties of the calcite

were examined under different conditions including heating, or reaction with alkylketene dimer (AKD), as compared with the freshly cleaved state.

Conventional contact angle measurement is unreliable and impractical for determining the surface energetics of fine powders such as fillers, pigments and fibers. Alternate methods have therefore been used to study calcium carbonates particles including immersion calorimetry (9-11), capillary wicking (12), and spectroscopic methods (13). Static gas adsorption isotherms have also been utilized for the characterization of the surface properties of calcium carbonates (14-18) although these methods may be tedious and time consuming.

Inverse gas chromatography (IGC) is a method that was developed to determine the surface energetics of fine powders and liquids by measuring the dynamic adsorption characteristics of probe gases. The convenience of experimentation and control of test conditions has inspired the recent interest in applying IGC for the analysis of a various papermaking materials including wood meal (19), mechanical pulps (20,21), cellulose and paper (21-24), lignin (25) and filler/pigments including calcium carbonate (26-32). The effects of treatment of fibers and calcium carbonates with alkylketene dimer has also been examined (23,29,30). An estimate of the dispersive (London) component of the surface free energy, γ_S^d, may be determined by measuring the interaction of linear alkane probe gases with the surface. Polar gaseous probes are used to determine the specific interaction parameters from which the relative acidity and basicity of the surface can be established (19,29,33-35).

In this paper, an examination of the surface energetics of calcium carbonate using inverse gas chromatography (IGC) at infinite dilution and surface wetting by contact angle is conducted. Characterization of the apolar and polar nature of the surfaces by measuring the interactions of n-alkanes and polar probes were performed using both methods. Results will be presented from experiments using IGC and contact angle measurements to analyze calcium carbonate samples differing in origin or subjected to surface conditioning. Surface energetics determined from both methods will be compared and the limitations of such comparisons will be demonstrated.

INVERSE GAS CHROMATOGRAPHY

IGC involves the determination of the dynamic sorption interaction of gaseous polar or non-polar probes on a stationary phase test material at various fixed temperatures. The measurements are performed as the probe gases elute through a column packed with the material under examination, in this case fine particles. The thermodynamic basis for determining the surface energetics is well established (36). IGC may be divided into two experimental techniques that differ in the concentrations of adsorbate applied to the column. The first is *infinite dilution* or *zero coverage*, in which the gas phase is sufficiently dilute so that intermolecular interaction between probe molecules is considered negligible. The second involves the application of much higher concentrations of probe so that a complete adsorption isotherm may be obtained. The former technique was used in this investigation.

The surface free energy, γ_S, is a material specific parameter which, when known for two materials, can be used to estimate the wettability and work of adhesion. Total surface free energy may be further separated into the Lifshitz - van der Waals or *apolar* component, γ_S^{LW}, and the Acid-Base or polar component, γ_S^{AB}, in the form:

$$\gamma_S = \gamma_S^{LW} + \gamma_S^{AB} \tag{2}$$

IGC methods for determining both components of the surface free energy will be considered separately.

Theory

Calculation of the thermodynamics of adsorption from IGC analysis is based on the determination of the specific retention volume, V^o, of a known adsorbate probe as it passes through a chromatographic column containing the adsorbent under examination. The specific retention volume represents the volume of carrier gas required to completely elute the adsorbate, less the dead volume of the column, per unit mass or surface area of adsorbent. Many of the earlier studies in IGC, especially with polymers, involved the analysis across the gas/liquid interface where it was useful to express the specific retention volume in terms of adsorbent mass, V_g^o. However, for the analysis of solid surfaces, as in the present study, expression in terms of specific surface area, V_S^o, is more appropriate.

The mass and area specific retention volumes are related to the retention time, t, of injected probes and the specific surface area, A_{sp}, by the relationship (21)

$$V_S^o = \frac{V_g^o}{A_{sp}} = \frac{j F_{col}(t_p - t_m)}{A_{sp} w} \tag{3}$$

The subscripts p and m identify the retention times of the probe and a non-interacting marker, respectively. The parameter w is the weight of adsorbent in the column, j represents the James-Martin correction for compressibility, and F_{col}, is the flow rate of carrier gas within the column that has been corrected for column temperature. A more detailed discussion of experimental parameters is given elsewhere (29-31).

The partition coefficient or Henry's law constant, K_S, may be expressed as (36):

$$K_S = \lim_{c \to 0} \left(\frac{\partial \Gamma}{\partial c} \right)_{A,T} \tag{4}$$

where c is the molar concentration of the adsorbate in the gas phase and Γ is the molar concentration per unit surface area of the adsorbent, assuming constant surface area, A, and temperature, T. For analysis at *infinite dilution*, (or *zero coverage*), Eq.(4) becomes the simple ratio of Γ/c and may take the form:

$$V_S^o = \frac{V_g^o}{A_{sp}} = \frac{K_S}{RT_C} \tag{5}$$

where R is the gas constant and T_C is the column temperature.

The differential enthalpy of adsorption, ΔH_A^o, may be determined by measuring values for V_S^o at different column temperatures and applying the relationship:

$$\Delta H_A^o = -R \frac{d(\ln V_S^o)}{d(T_C^{-1})} \tag{6}$$

ΔH_A^o is obtained graphically from the slope of the plot of $-R\ln V_S^o$ vs. $1/T_C$.

The standard molar free energy of adsorption, ΔG_A^o, of the probe on the adsorbent is related to the Henry's law constant by the relationship

$$\Delta G_A^o = -RT\ln\left(\frac{K_S p_{sg}}{\pi_s}\right) = -RT\ln V_S^o + C \tag{7}$$

Here a standard reference gas pressure, p_{sg}, and the spreading pressure, π_s, are defined by the chosen reference state. The integration constant, C, is a function of these parameters and may be assumed constant for a given adsorbent and a homologous series of probes.

Experimental

The experimental procedures for Inverse Gas Chromatography at infinite dilution involved packing a chromatographic column with the powdered calcium carbonate as the stationary phase. While the column was held at a fixed temperature within a conventional gas chromatograph elution times of various probe gases were recorded. Specific details of the IGC experiments were discussed elsewhere (29, 30). The origin of the calcium carbonate samples and additional characterization of the pore structure, specific surface area, and chemical composition are also provided in those references.

Two approaches were taken to determine the thermodynamics of adsorption of probes on the sample surfaces. The first, identified as *preconditioned analysis,* may be considered the conventional approach to IGC experiments (19,26-29,31) where the sample was conditioned by outgassing at an elevated temperature, e.g. 100, 150, 200°C, for 24 hours prior to testing the retention time if different probes. The second procedure was introduced by Keller and Luner (30) as *sequential isothermal analysis* which involved monitoring the changes in retention time of probe gases as the sample is held at a constant temperature, e.g. 60, 100, 140°C, under a continual sweep of dry nitrogen gas. The results of the earlier study (30) demonstrate that the sample underwent a weight loss during the experiment that was associated with dehydration, which significantly influenced the surface properties. Columns were packed with fresh sample prior to each experiment, which lasted for up to 150 hours.

Apolar Contributions

When non-polar molecules, such as n-alkanes are used as probe gases in IGC, the energetics of adsorption are considered non-coulombic and result entirely from Lifshitz -van der Waals (LW) interactions. The LW contributions to the surface free energy, γ_S^{LW}, en-

compasses the electromagnetic interactions including the dispersive (London), γ_S^d, induction (Debye), γ_S^i, and orientation (Keesom), γ_S^μ, components so that:

$$\gamma_S^{LW} = \gamma_S^d + \gamma_S^i + \gamma_S^\mu \tag{8}$$

In the case of IGC experiments conducted at *infinite dilution* of the gaseous probe, the pairwise-addition approximation (37) provides a means to interpret the significance each separate component to the overall LW interaction. The assumption in this case is that intermolecular distances between probe molecules are large and the Debye and Keesom components are not suppressed by neighboring molecules as in condensed phase-condensed phase interactions, eg. liquid/solid or solid/solid. The impact of this perspective on existing theory for the determination of γ_S^d by IGC, and experimental evidence for the significant effect that surface polarity has on the apolar interactions that occur in IGC are given in this section.

A method for estimating the London-dispersive component of surface free energy, γ_S^d, from IGC data was proposed Dorris and Gray (21). Their approach involved the use of Fowkes (38) equation for the work of adhesion of a non-polar liquid and a surface in terms of the incremental change in free energy per methylene group, $\Delta G_A^{CH_2}$. Values for $\Delta G_A^{CH_2}$ are accessed from the difference in ΔG_A^o for adjacent members of a homologous series of linear alkanes from the relationship:

$$\Delta G_A^{CH_2} = -RT\ln\left(\frac{K_S^{n+1}}{K_S^n}\right) = -RT\ln\left(\frac{V_S^{n+1}}{V_S^n}\right) \tag{9}$$

$\Delta G_A^{CH_2}$ values are determined graphically as the slope of a plot of V_S^o vs. the number of carbons in the alkane, n. The equation that Dorris and Gray derived (21) may be rearranged to solve for γ_S^d so that

$$\gamma_S^d = \frac{1}{4\gamma_{CH_2}}\left(\frac{\Delta G_A^{CH_2}}{4Na}\right)^2 \tag{10}$$

where N is Avogadro's number, a is the cross sectional area of the methylene group (6Å) and γ_{CH_2} is the surface energy of a solid consisting of only -CH_2- groups, i.e. polyethylene.

Since the interactions of the alkanes with the surface will involve all of Lifshitz-van der Waals interactions, the solution to Eq.(10) is more appropriately given as γ_S^{LW} (30,39). Furthermore, since the probes are in the dilute gaseous state, the Debye induction interactions, γ_S^{I}, that result from dipoles induced in the alkane molecules by the electric fields at the adsorbent surface may be considerable (37), especially for high energy materials such as mineral fillers (40). It is evident that Dorris and Gray considered the significance of the induction forces even for the low energy cellulosic surfaces that they studied (21). This aspect, however, has been overlooked in many subsequent investigations where γ_S^{d} derived from IGC experiments have been reported for both low and high-energy materials. Assumption that the interaction of gaseous alkanes with low energy surfaces, absent of appreciable electric fields, are dominated by dispersive (London) interactions may be valid. It should be noted that for the alkane/solid system, the Keesom orientation term, γ_S^{μ}, is zero since n-alkane probe gases do not possess a permanent dipole.

Results

The results from the IGC analysis (determined at 100°C) of various $CaCO_3$ samples expressed as the apolar component of surface free energy, γ_S^{LW} vs. the temperature at which the column was conditioned, T_P, are shown in Figure 1. For the ground marble and the precipitated calcium carbonate (PCC), γ_S^{LW} increases exponentially with T_P. Also shown in Figure 1. are the results Lundqvist *et al.* (32), Ahsan *et al.* (41) and Schmitt *et al.* (27), who also studied PCC using IGC. Close agreement between the results of the various investigations and those of the present study is apparent. The results for the marble at T_P = 100°C where γ_S^{LW} = 57 mJ/m^2 compared favorably with the results from Janczuk *et al.* (42) who studied cleaved calcite by wetting and found γ_S^{LW} = 64 mJ/m^2. The two chalk samples had relatively high γ_S^{LW} values as compared with the other $CaCO_3$ samples and showed minimal change as a function of conditioning temperature. Chalk I was commercially milled, and chalk II was hand ground from the nugget form just prior to IGC analysis.

The results from sequential isothermal analysis of the different $CaCO_3$ samples are shown in Figure 2. In those experiments, the column temperature was maintained at 100 °C. The specific retention volumes V_S^o of various alkanes (heptane is shown) were recorded as a function of exposure to a dry nitrogen sweep at the elevated temperature. The results indicate that V_S^o, i.e. the ΔG_A^o of the alkanes on the surface for the PCC and the ground marble, had similar behavior and increased substantially during the course of the experiment, i.e. 100 hours. Although the relative increase in V_S^o for the chalk samples was much less, the initial values were much greater than the other samples, cf. Figure 2. The response of different $CaCO_3$ surfaces in these experiments suggested that the surfaces

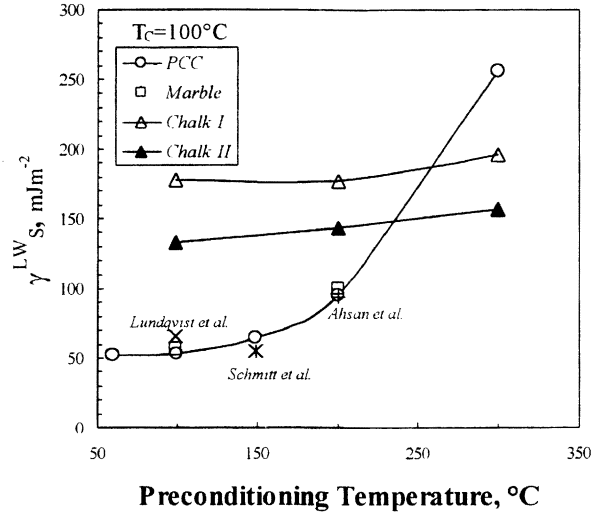

Figure 1: The apolar component of the surface free energy of the $CaCO_3$ samples plotted as a function of preconditioning temperature (30). T_C = 100°C.

continually underwent physical and/or chemical changes, even beyond 100 hours. This casts uncertainty on the generally accepted assumption that a state of equilibrium is attained after a preconditioning period of 24 hours (27,33). The Sequential isothermal method also provided insight into the initial state of the surfaces, prior to dehydration, through the extrapolation of the sequenced data back to low time values. The behavior of surfaces at near ambient conditions may have more practical applicability to systems of interest in paper science as compared to the more rigorously modified surface following conditioning at elevated temperatures in conventional IGC experiments.

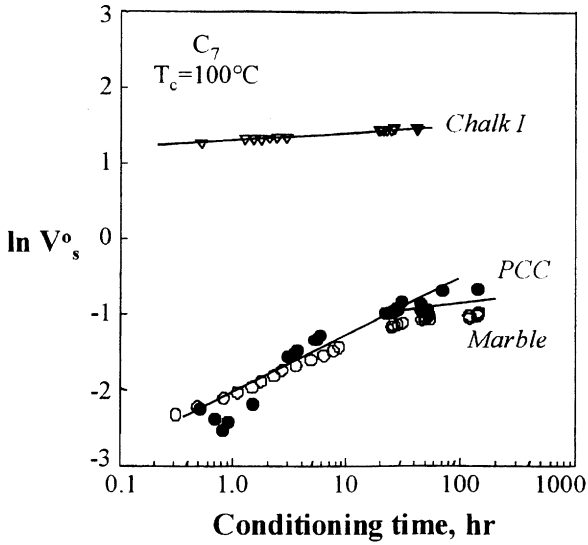

Figure 2: Sequential isothermal analysis of various $CaCO_3$ samples at T_C = 100°C. Specific retention volume of heptane adsorbed on the $CaCO_3$ samples plotted as a function of exposure time (30).

Discussion

The results of the two methods of IGC analysis demonstrated that the apolar nature of the $CaCO_3$ surfaces changed as a result of preconditioning by heating under a dry, inert gas sweep. Investigation of possible sources of the observed changes in these surfaces involved the additional examination of the surface area, pore structure, and weight changes that occurred on preconditioning. The details of this work are given elsewhere (30).

The evolution of water from the $CaCO_3$ samples by desorption of the physisorbed water or by dehydroxylation of residual $Ca(OH)_2$ was expected to occur under the conditions of IGC experiments (17). Conducting sequential isothermal analysis on columns that were first exposed to heat and nitrogen sweep for 100 hours and then purged with saturated water

vapor for 24 hours demonstrated this. Following the water vapor purge, the material appeared to revert to its original state. Sequential isothermal analysis of the regenerated column replicated the original results.

Decomposition of the $CaCO_3$ to CaO by the evolution of CO_2 was considered a remote contributor to the changes observed on the surface. This conclusion was based the results of regeneration experiments using CO_2 in place of water vapor that were conducted in the original study (30), and the supported extensively in the literature that the $CaCO_3$ decomposes very slowly at temperatures below 300 °C.

The effects of chemisorbed water on the surface energetics of mineral oxides were investigated by Suda *et al.* (40,43). They found that the electrostatic field strength of the materials was inversely proportional to the surface hydroxyl concentration. Figure 3. Shows a plot of γ_S^{LW} vs. the estimated monolayer coverage of water for the three $CaCO_3$ samples. Monolayer water coverage was calculated using the total weight loss during conditioning and a molecular area of water of 10.4 Å (44). The estimation assumes that the weight loss is entirely due to water from the surface and that the water is completely desorbed at 300 °C. The difference between the different forms of $CaCO_3$ is apparent. The results from Chassin *et al.* in their investigation of Ca-montmorillonite using contact angle measurements are also included in Figure 3. (45). Note the similarity in the curves as γ_S^{LW} decreases with the adsorbed water concentration. Dorris and Gray observed a similar trend with water on silica (46).

The effect of water on decreasing the interactions of gaseous alkanes with $CaCO_3$ surfaces has been reported by several investigators (15,47). The water acts to present a low energy surface to the non-polar molecules (18,48) and interacts mostly due to dispersion (London) forces. In IGC this is manifested as shorter observed retention times. When the water layer is desorbed by dry heating, highly polar sites are exposed which increases the magnitude of the dispersion (London) and induction (Debye) forces substantially (40). Figure 4. illustrates a model of the surface that accounts for the change in γ_S^{LW} that accompanies the desorption of water from the $CaCO_3$ surface. Trace amounts of contaminants at the surface, e.g. silica or iron, may contribute to the increased surface energies of the chalk samples. Although important differences in the surface energetics of the three $CaCO_3$ samples exist, identification of the origin of such differences is still under investigation.

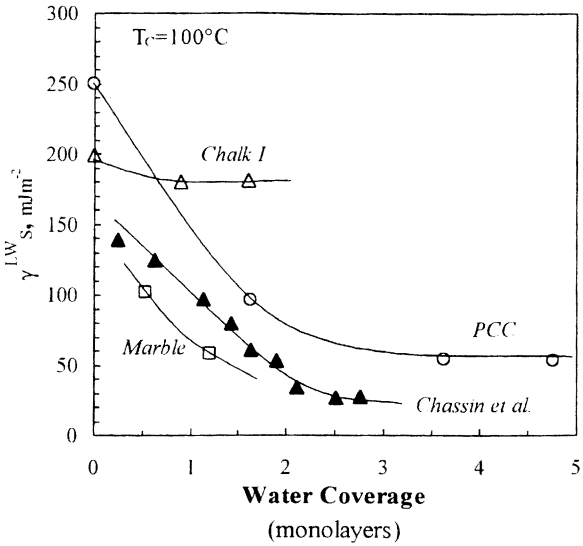

Figure 3: The apolar component of the surface free energy plotted as a function of the apparent monolayer water coverage of $CaCO_3$ samples (30).

Polar Contributions

By comparison with the apolar or Lifshitz interaction forces, the polar or acid/base forces are generally considered stronger and of greater importance to adhesion and wetting in practical systems. For this reason, considerable priority has been given to the development of methods that utilize IGC for characterizing the polar nature of surfaces (26,29,31).

The acid/base component of the surface free energy, γ_S^{AB}, may be considered the sum of separate Lewis-acid, $\gamma_S^{\oplus}$, and Lewis-base $\gamma_S^{\ominus}$ components. Although wetting experiments have been employed to quantify these separate components on solids by contact angle

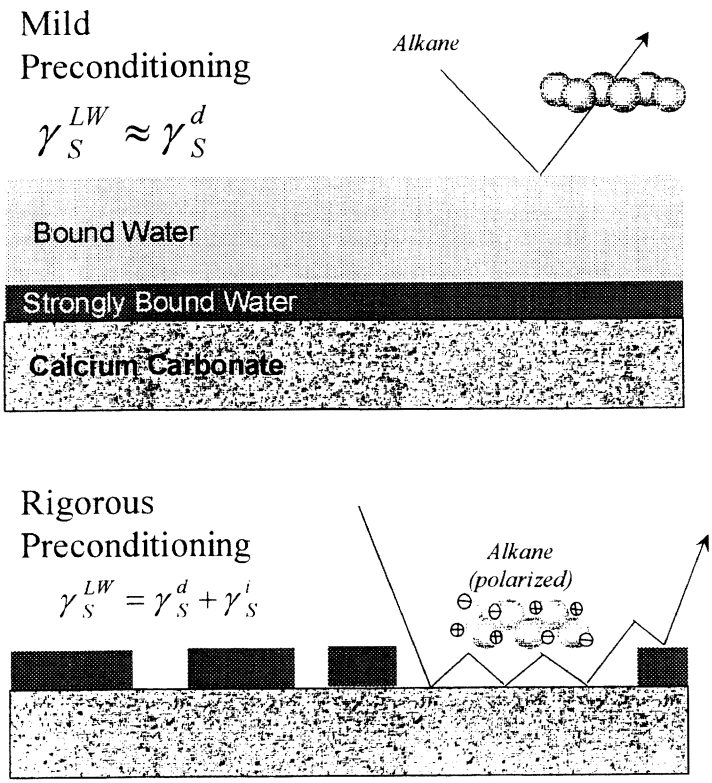

Figure 4: Proposed mechanism for the increase in the apolar component of surface free energy with thermal pretreatment and dry sweep dehydration. With mild preconditioning, bound water is retained at the calcium carbonate surface and tends to shield the electric field. The induced (Debye) component is negligible. As the heat and dry gas sweep of rigorous preconditioning remove water, the electric field of the crystal surface is exposed inducing a dipole in the dilute alkane molecules. The induced (Debye) component is by the increased interaction between the permanent dipole of the $CaCO_3$ crystal and the induced dipoles in the alkane molecules.

measurement, methods based on IGC are not yet widely used. Alternate systems have been applied to IGC data, such as that based on the Gutmann (49) acceptor (AN) and donor (DN) to give acidity, C, and basicity, C*, indexes for surfaces (19,29) or the system of Drago that uses electrostatic (E) and covalent (C) parameters for acid and base sites.

Characterization of polar forces by IGC methods involves the determination of those interactions present for polar probes that are in excess of those measured for an alkane probe with presumably comparable apolar interaction energy. Selection of an appropriate method to separate the respective contributions of the apolar and polar forces must then be addressed. Saint-Flour and Papirer proposed a semi-empirical method (33). By plotting $RT\ln(V_S^o)$, which is a direct function of ΔG_A^o, cf. Eq.(9), vs. the logarithm of the vapor pressure, P_O, of the probes, a linear relationship is obtained for n-alkanes. Assuming that the Lifshitz - van der Waals and acid-base (polar) components are additive, cf. Eq.(2), the difference in ordinates between the alkane straight line and the point corresponding to the polar probe (having the same P_O as a real or hypothetical alkane) is defined as the specific interaction parameter, I_{SP}. The relationship is represented as:

$$I_{SP} = RT\ln\left(\frac{V_g^{polar}}{V_g^{alkane}}\right) \tag{11}$$

I_{SP} may also be considered equivalent to the acid-base component of the work of adhesion, W^{AB}, between the probe and the surface (50). The specific interaction capacity, indicative of the polar nature of the solid surface, is comprised of the acid-base interactions (26). Several different approaches have been used to arrive at I_{SP} values, but these approaches do not seem to offer any new insights (51,52).

The complications introduced by recognizing the significance of induction (Debye), γ_S^{μ}, component in the total surface free energy may preclude the use of several of the previous approaches to characterization of the acid-base properties of surfaces using IGC, depending on whether the surface is low or high energy. Since the interactions of the homologous series of linear alkanes cannot be attributed solely to non-specific or dispersive (London) interactions, its use as a reference may not be appropriate for all surface conditions, especially those that exhibit high energy (polarity) such as minerals. As indicated in the previous section, induction effects may be minimal for a surface shielded with multiple layers of surface water, but may become increasingly significant as water is removed and appreciable electric field is exposed (40,43). Furthermore, the use of polar probes intro-

duces the potential for increased significance of the orientation (Keesom) contributions. Good *et al.* (53), however, discussed the difficulty in separating the γ_S^{μ} component from the acid-base, γ_S^{AB} component of the surface free energy. Solution to this deficiency in the theory remains a fundamental problem in surface science.

As a refinement of the general approach for the quantification of polar interactions by IGC, Sidqi *et al.* (54, 55) employed a comparison of ΔG_A^o values of n-alkanes with 1-alkenes. This allowed the measurement of the effects of the Lewis donor (basic) properties of the π electrons in the double bond and interactions with acceptor (acid) sites on the adsorbent surface. The defined new thermodynamic parameters to quantify this interaction including the specific interaction parameter, ΔG_π^o

$$\Delta G_\pi^o = \Delta G_{alkane}^o - \Delta G_{alkene}^o \tag{12}$$

which is simply Eq.(11) rewritten in terms of ΔG_A^o, cf. Eq.(9), using 1-alkenes as the polar probe. This approach makes use of the similarity of properties including the molecular dimensions, i.e. cross sectional area, vapor pressures, etc., to simplify separation of the apolar and polar interactions.

Results: Polar Probes

Specific interaction parameters, I_{SP}, were determined for the adsorption of a group of polar probes on the surfaces of a PCC sample, and on one that was treated to the equivalent of one monolayer of alkylketene dimer (29). Figure 5 and Figure 6 show the plots of $RT\ln\left(V_g^o\right)$ vs. log P_O for the untreated and AKD treated PCC samples, respectively.

The results for the series of n-alkanes formed a linear relationship in both cases. The slope of the line was used to determine values of γ_S^{LW} which for the untreated PCC was 50 mJ/m^2. This agreed with the results from a previous study discussed above, cf. Figure 1. The value of γ_S^{LW} for the AKD treated sample was 36 mJ/m^2, which may indicate the attachment of AKD molecules to the exposed polar sites at the surface. It may also represent steric coverage of the surface sites. In either case, the long chain alkyl group on the AKD molecule interacts with the probe gases, rather than the polar site. This was previously attributed to a reduction in the dispersive (London) component. However, in view of the results of the apolar section discussed above, coverage of polar sites may be attributed to a reduction in the (Debye) induced interactions, which also reduce γ_S^{LW} values.

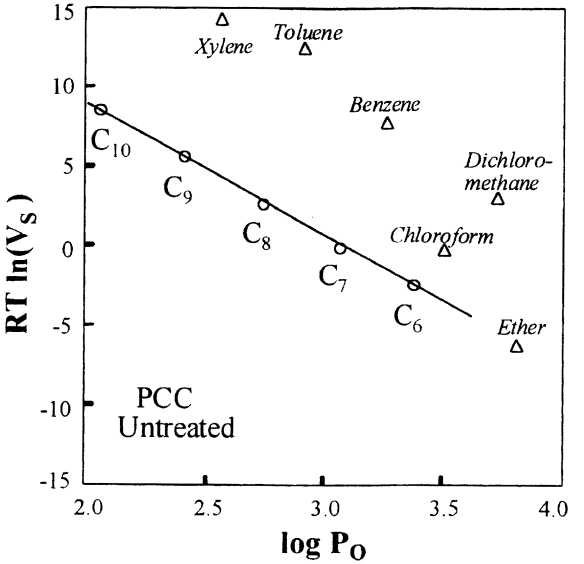

Figure 5: The standard free energy of adsorption between gaseous probes and the untreated precipitated calcium carbonate (PCC) surfaces plotted as a function of the saturated vapor pressure of the probe (29). T_C = 100°C.

Figure 5 and Figure 6 also show the results for the polar probes used to test the acid-base nature of the sample surfaces. All of the probes gave greater interaction energies than the alkanes for a give vapor pressure. The difference between the values for the polar probes, and the line formed by the alkanes at the same vapor pressure is the specific interaction parameter, I_{SP}, the results of which are provided in Table 1. The I_{SP} values decreased after modification with AKD, except for the cases of chloroform and ether, which suggests that the treated and untreated $CaCO_3$ surfaces contain more basic than acidic sites: for I_{SP} values, $CHCl_3$ is greater than ether.

No desorption peaks were observed for tetrahydrofuran when adsorbed on either of the $CaCO_3$ samples. When acetone was used as the test probe, desorption was only observed for the AKD-treated sample. The absence of peaks may indicate that the probe reacted with the surface to form a stable bond, e.g. strong ionic bonding. It may also indicate that the interaction is of sufficient strength, or desorption slow enough that it was below the detection capabilities of the IGC method.

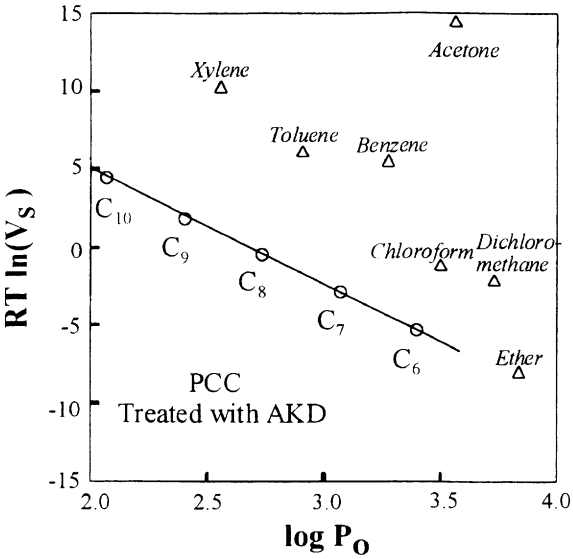

Figure 6: The standard free energy of adsorption between gaseous probes and the surface of PCC treated with one monolayer of alkylketene dimer, plotted as a function of the saturated vapor pressure of the probe (29). T_C = 100°C.

	I_{SP}, kJ/mole	
Adsorbate	Untreated	AKD Treated
Ether	-	0.2
Chloroform	3.4	4.8
Dichloromethane	8.4	5.3
Benzene	9.5	9.5
Toluene	11.0	7.9
Xylene	9.8	9.4
Acetone	-	20.6
Tetrahydrofuran	-	-

Table 1: Specific interaction parameters, I_{SP}, of polar probes on PCC and PCC/AKD (29).

It is important to recognize that these experiments were conducted with close consideration of the concentrations of probe injected into the column, and for the history of injections into the column. It was found that if a "non-desorbing" probe was injected in excess, or if multiple injections of that probe were made, it was possible that saturation of the surface sites could occur. This could result in the detection of an elution peak that reflected the interaction of the probe molecules with the adsorbed species, rather than with the surface. Such results could confound an effort to characterize the true polarity of the sample surface. The interaction of non-desorbing probes may be similar to that of sorbed surface water, where IGC retention times measure the interaction of the probe with the surface contaminated with an adlayer that varies in thickness, rather of the $CaCO_3$ surface.

Results: Linear Alkenes (Lewis-Base)

Experiments were conducted to investigate the adsorption energetics of 1-alkenes of various chain lengths on PCC and chalk samples (56). Figure 7. shows a plot of the first term of the standard free energy of adsorption, ΔG_A^o, cf. Eq.(7), vs. the number of carbon atoms in the hydrocarbon chain for PCC. The origin of $\Delta G_{CH_2}^o$ values from the slope of the line formed by the data from a series of hydrocarbon is demonstrated in this figure. Notice that the values of $\Delta G_{CH_2}^o$ for the alkenes and alkanes are comparable. The standard free energy attributed to the interactions of the π electrons in the alkene with acid sites on the PCC surface, ΔG_π^o, is also shown in is figure. Values for ΔG_π^o are determined from the energetic differences of the 1-alkenes and n-alkanes from Eq.(12). For the chalk sample (not shown), the separation between the 1-alkene and n-alkane, hence ΔG_π^o, were similar to the results for PCC. However, the slopes of the lines were much steeper for both probe series, indicating larger values of $\Delta G_{CH_2}^o$.

Sequential Isothermal analysis (100°C) was performed on the PCC and chalk samples using 1-alkene and n-alkane as test probes. Results are illustrated in Figure 8. The surface adsorption interaction of the alkane probes continued to increase beyond 100 hours as water desorbed from the interphase at the PCC surface. The hexene exhibited greater interaction than the hexane for the entire duration. This may be attributed to the added interaction of the double bond electrons with the electric field proximate to the crystal surface. It is also apparent that the interaction of the 1-alkenes is more sensitive to the dehydration that occurs during conditioning as evidenced by the steeper slope of $\ln(V_s)$ with exposure time. This is likely due to additional interaction forces brought on by the

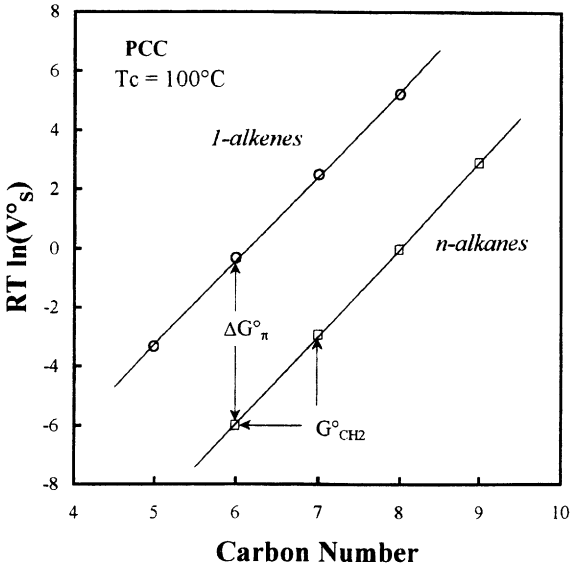

Figure 7: The standard free energy of adsorption of the n-alkanes and 1-alkenes on the PCC surface plotted as a function of carbon number chain length. Column was preconditioned at 100°C for 100 hours (56). T_C = 100°C.

polarity of these molecules. However, the possible intersection of the n-hexane and 1-hexene curves at very low exposure times implies that the two probes interact with the surface in a similar manner at the initial state, i.e. at ambient moisture. Under such conditions, water layers effectively dissipate the electric field from the crystal lattice, and a relatively low energy surface may be presented to the probe molecules. In such cases, there is little difference in adsorption interaction between the saturated and unsaturated probes. This was observed by other investigators studying low energy surfaces such as squalane (57), and carbon black (58,59).

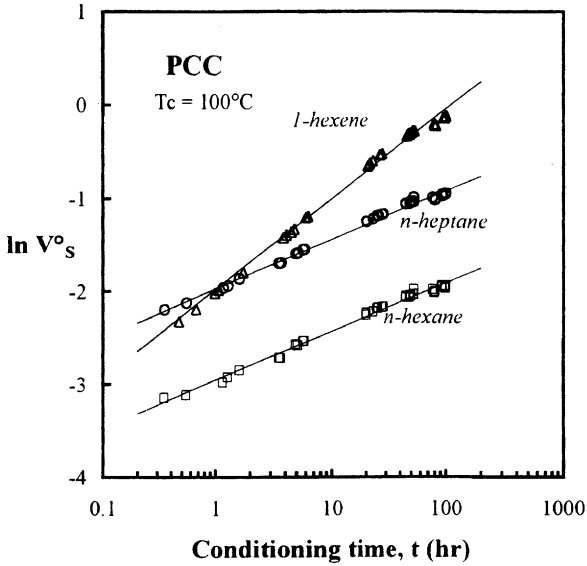

Figure 8: Sequential isothermal analysis of PCC at T_C = 100°C. Specific retention volume of n-heptane, n-hexane, and 1-hexene adsorbed on PCC plotted as a function of exposure time (56).

Figure 9. shows the variation of $\Delta G^o_{CH_2}$, i.e. sensitivity of adsorption interation to alkyl chain length, with the conditioning time of the PCC at 100 °C. The 1-alkenes have lower values of $\Delta G^o_{CH_2}$ as compared with the n-alkanes under the given conditions. This suggests that as the alkene chain length increases, the free energy of adsorption does not increase as rapidly as that of the alkanes. Since the alkenes exhibit additional interaction due to molecular polarity, cf. Figure 7., the decreasing differential between alkenes and alkanes suggests that chain lengthening reduces the π bond interaction. This may be due to steric interference of the alkyl chain, although this has not been confirmed. It should be noted that the chalk sample was tested in a similar manner (results not shown) $\Delta G^o_{CH_2}$ values for the 1-alkenes were ~5.0 kJ/mole and for n-alkanes ~5.4 kJ/mole. Little variation was observed for both probe series for conditioning at 100°C for extended periods of time.

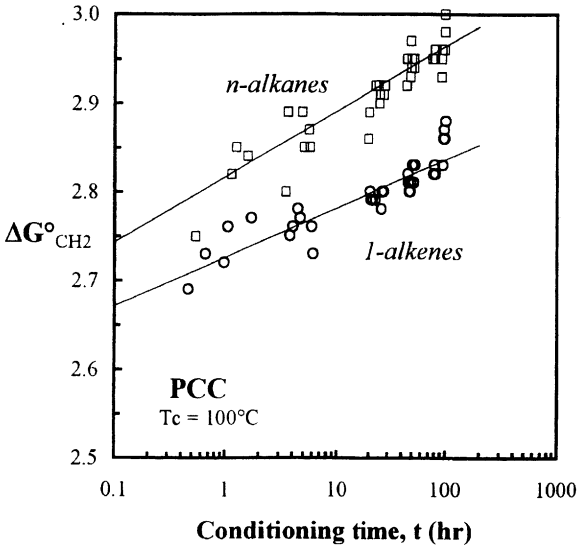

Figure 9: The Incremental free energy of adsorption per methylene group on PCC plotted as a function of conditioning at 100 °C. The n-alkanes represent the series from C_6-C_9, and the 1-alkenes represent the series from C_5-C_8.

A second trend apparent in Figure 9. is that values of $\Delta G^o_{CH_2}$ for both groups of hydrocarbons tend to increase with exposure time, albeit at a very low slope. This suggests a dependence of the interactions of the presumably non-polar alkane on the strength of the electric field at the adsorbent surface. The field strength is increased as shielding water layers are removed as discussed in previous sections. The 1-alkenes exhibit a slightly lower slope, suggesting a reduced response to an increasing electric field. This behavior may result if the surface mobility and site selectivity of the adsorbed 1-alkene is restricted by the polar interaction, or if the field strength is reduced by the π electrons.

The interaction energy of the π electrons of the 1-alkenes with acid sites on the surface, ΔG^o_π, were determined for the PCC and chalk samples at different preconditioning times and temperatures. The results are provided in Figure 10. where ΔG^o_π is plotted as a function of carbon chain length. As either calcium carbonate sample is conditioned

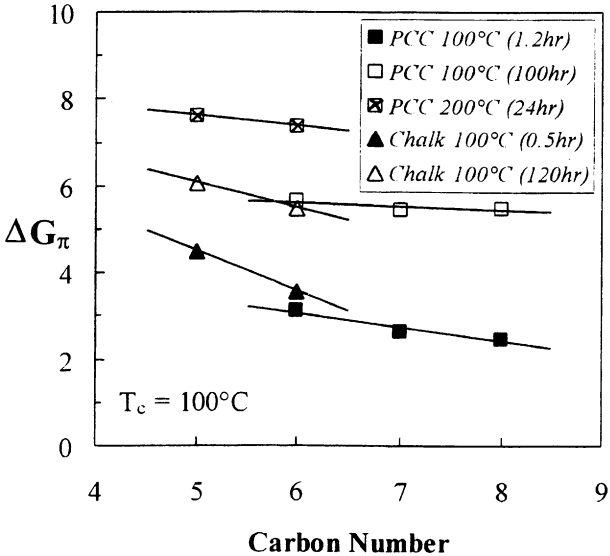

Figure 10: The standard free energy of adsorption due to the interaction of the π electrons of the alkenes with the PCC and chalk surfaces plotted as a function of the carbon chain length. Results for preconditioning at 100°C and 200 °C for different durations are shown (56). T_C = 100°C.

or dehydrated, either for longer exposures or at higher temperatures, ΔG_{π}^{o} is greater indicating increased interaction of the polar component. This suggests that Lewis acceptor (acidic) sites are either uncovered or are generated in the interphase during dehydration which likely occurs since an increase in electric field strength associated with conditioning has already been identified.

A comparison of the polar (ΔG_{π}^{o}) and apolar ($\Delta G_{CH_2}^{o}$) interaction energies of PCC and chalk may provide insight into apparent differences in surface properties. For chalk, ΔG_{π}^{o} values increased significantly with dehydration. The $\Delta G_{CH_2}^{o}$ values for chalk were initially high, compared to PCC, and underwent minimal change during sequential isothermal analysis. In Figure 10, the values of ΔG_{π}^{o} for both $CaCO_3$ samples are nearly equal at C_6

after similar conditioning. Furthermore, the trend of decreasing ΔG_{π}^{o} with carbon chain length could well be consistent between the two samples. This may suggest that the extent of interaction of the π electrons with the surface acid sites is similar for the chalk and PCC samples. Thus the differences in the surface energy for the two samples reflected in the non-polar interactions of $\Delta G_{CH_2}^{o}$. Clearly differences in the surface chemistry, especially the increased silicon content of chalk, may influence the dispersive component, γ_S^d, the surface free energy. An alternate explanation is that the basicity of the chalk is sufficiently different than that of PCC to cause differences in the magnitude or heterogeneity of the electric field at the surface. Such differences may increase the polarization of the alkyl groups in the probe gas thereby effecting the Debye contribution, γ_S^i, to the apolar component, γ_S^{LW}, of the surface free energy. To compliment this information, the investigation was expanded to examine the surface basicity of the two samples in greater detail.

Results: Nitro-alkanes (Lewis-Acid)

In order to characterize the basic sites of the PCC and chalk surfaces, nitro-alkanes were used as test probes. The approach was similar to that taken for the 1-alkenes where the polar end group, i.e. $-C{=}CH_2$ or $-NO_3$, was maintained while the alkyl chain length was varied. The results were far less extensive than those obtained using the basic probe discussed above. When injected at exceeding low concentrations nitro-alkanes were not observed to elute through a column packed with any of the $CaCO_3$ samples. When relatively high quantities of the probes were injected, peaks could be obtained. Multiple injections of the probe, or injection of higher concentrations may have caused saturation of the active surface sites either by reaction or by steric coverage. Probes that were subsequently injected were free to elute. An elution time could then be measured, although the relevance of the data to the energetics of the surface under examination may be questioned.

Figure 11. illustrates the *Adlayer Exchange Model* that describes the behavior of those probes that fail to elute in the complex system of calcium carbonate with an adsorbed layer of water at the surface. The polar probe is free to elute when the surface is covered with water since the electric field is effectively dissipated and interaction energies are low, cf. Figure 11a. When water desorbes from the surface, either by preconditioning or during nitrogen sweep at elevated temperatures, highly energetic sites are exposed. The probe may then react with those sites to bind the probe so that desorption is not observed, Figure 11b. When the sites are saturated and surface coverage is complete, probe elution may then be observed. However, the adsorption characteristics reflect the interaction of the probe the adlayer rather than with the surface of interest.

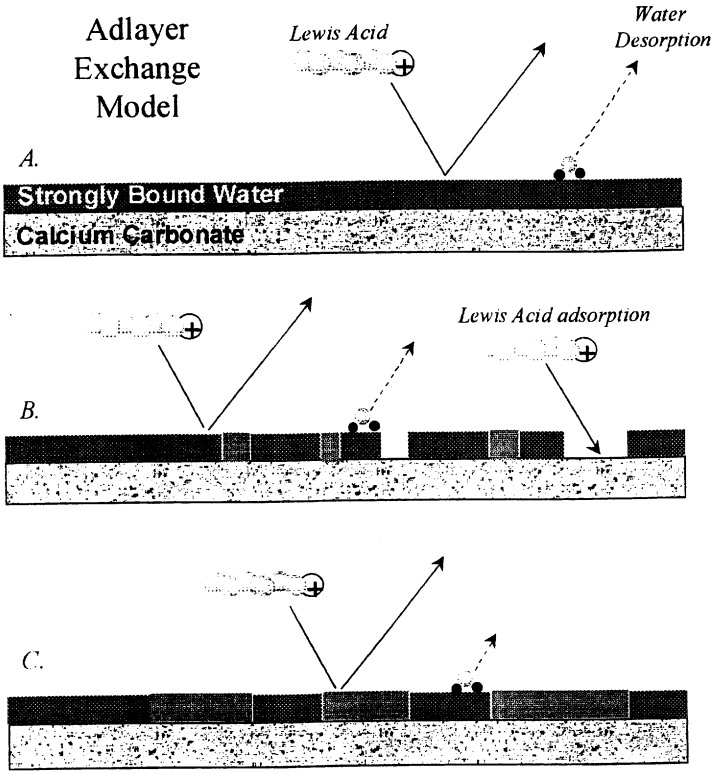

Figure 11: The *Adlayer Exchange Model* used to describe the behavior of polar probes in IGC experiment as they interact with high energy surfaces that have bound water present. A) If the bound water layer is present, prior to desorption by nitrogen sweep at elevated temperature, the electric field near the surface is dissipated and the polar probe has weak interaction with the surface. Elution of the probe may be detected in IGC experiments. B) As water at the interface desorbed, high energy sites or exposed. The polar probe reacts with those sites and it does not freely desorb. Elution of the probe is not apparent. C) Once sites are covered, the probe may then freely elute and an apparent interaction is measured. The elution time may not accurately reflect the true surface energy.

CONTACT ANGLE MEASUREMENT

In order to model the wettability of $CaCO_3$ systems, experiments that measured the sessile drop contact angles of various liquids on cleaved calcite surfaces were performed (60). Tests were conducted on cleaved calcite surfaces and after treatment by heat, AKD deposition and water to simulate the conditions that paper may be exposed to, e.g. heat drying and storage. The effect that these treatments had on wettability of the $CaCO_3$ surface is relevant to the understanding of printability, the adhesive and internal strength properties, or the performance of AKD and its susceptibility to sizing reversion. The results from this investigation are presented in the context of a comparison with the surface energetic parameters determined using IGC analysis.

Three techniques are commonly used for determining surface energetics from contact angle. These are the two liquid method (1-3), the abridged two liquid method (4-6), and the acid-base method (three liquid method) (7,8). A comparison of the three methods as applied to calcite surfaces was made by Okayama *et al.* (60). This report will discuss the results of the latter two methods. The calcite surfaces were studied under four conditions, these were, freshly cleaved, heated for two hours at 105°C or at 150°C, and following treatment with alkylketene dimer (AKD) sizing agent.

Theory: Abridged Two liquid Method

An abridged two liquid method has been used (4-6,61) to determine the surface energetics of solids surfaces. 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 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 are discussed separately below.

For the water immersed method, Jho (5) and Andrade (6) 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 (13) and (14) give the relationships used to determine the dispersive and polar components from the two contact angles.

$$\gamma_S^d = \left[\frac{\gamma_O + \gamma_{WO} \cos\theta_{SO/W} - \gamma_W \cos\theta_{SA/W}}{2\left(\gamma_O^d\right)^{1/2}} \right]^2 \tag{13}$$

$$\gamma_S^p = \left[\frac{\gamma_W - \gamma_O - \gamma_{WO} \cos\theta_{SO/W}}{2\left(\gamma_W^p\right)^{1/2}} \right]^2 \tag{14}$$

where γ is the interfacial tension and the subscripts S, L, W, and O identify the material as the solid, liquid, water or octane, respectively. Contact angle θ, with subscript SO/W indicates measurement of an octane drop on the solid in a water medium. The superscripts d and p identify the dispersive (London) and polar (Acid-Base) components of the surface free energy of the system.

The value for the interfacial tension of octane and water, γ_{WO}, was taken from Andrade *et al.* (6) as 50.5 mJ/m^2. Also recall also 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 (62) 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

$$\gamma_S^d = \left[\frac{\gamma_O + \gamma_W \cos\theta_{SW/A} - \gamma_{WO} \cos\theta_{SW/O}}{2\left(\gamma_O^d\right)^{1/2}} \right]^2 \tag{15}$$

$$\gamma_S^p = \left[\frac{\gamma_W - \gamma_O + \gamma_{WO} \cos\theta_{SW/O}}{2\left(\gamma_W^p\right)^{1/2}} \right]^2 \tag{16}$$

The dispersive and polar components of the work of adhesion were determined by applying the appropriate components of surface free energy to the equations:

$$W_{SW}^{d} = 2\left(\gamma_{S}^{d}\gamma_{W}^{d}\right)^{1/2} \tag{17}$$

$$W_{SW}^{AB} = 2\left(\gamma_{S}^{P}\gamma_{W}^{P}\right)^{1/2} \tag{18}$$

where W_{SW}^{AB}, is the acid base component of the work of adhesion

Theory: Acid-Base (Three liquid method)

According to Fowkes (63) the work of adhesion between a liquid and a surface was proposed to be given by

$$W_A = W_A^{d} + W_A^{P} + W_A^{AB} \tag{19}$$

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 combining rule holds for dispersive forces, and that the polar interactions, W_A^{P}, are negligible, Eq.(19) may be written as (64):

$$W_A = 2\left(\gamma_{w}^{d}\gamma_{s}^{d}\right)^{1/2} + W_{sw}^{AB} \tag{20}$$

where W_{SW}^{AB} includes the work of adhesion from acid-base (AB) interactions. More recently van Oss *et al.* (7,8) 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.(19) arise from the electron-acceptor (Lewis-acid) and electron-donor (Lewis-base) intermolecular interactions. Thus, for the AB component of a surface one writes

$$\gamma^{AB} = 2(\gamma^{+}\gamma^{-})^{1/2} \tag{21}$$

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

$$W_{SW}^{AB} = 2(\gamma_s^{+}\gamma_L^{-})^{1/2} + 2(\gamma_s^{-}\gamma_L^{+})^{1/2} \tag{22}$$

The surface energy components are related to the contact angle by combining Eqs.(20) and (11) to form

$$\gamma_L(\cos\theta+1) = 2\left(\gamma_S^{LW}\gamma_L^{LW}\right)^{1/2} + 2\left(\gamma_S^{+}\gamma_L^{-}\right)^{1/2} + 2\left(\gamma_S^{-}\gamma_L^{+}\right)^{1/2} \tag{23}$$

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.(23)

Experimental

All contact angle measurements were made using a Rame-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 point where the sessile drop profile intersected the solid surface. The calcite crystals were freshly cleaved and either dropped directly into the controlled environment for contact angle testing, or immediately subjected to conditioning by heat or AKD treatment. Drops were delivered to the sample surface using a microliter syringe. A more complete discussion of experimental conditions is provided elsewhere (60).

Results: Abridged Two Liquid Method

Both the dry and water immersed approaches to the abridged two liquid method were used to test the calcite samples. Table 2 provides the wetting parameters, including the 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.

	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

Table 2: Wetting parameters of calcite samples derived from the abridged two liquid methods.

For the dry method, air spread in octane on the *freshly cleaved* surface, which prevented the determination of γ_s^d. The dispersive components, γ_s^d, dispersive component are in the range of 40 ±6 mJm^{-2} which is lower than expected for a dehydrated state which for IGC was ~60 mJm^{-2}. The polar component, γ_s^p, gives a reasonable trend decreasing from a high of 37 mJm^{-2} for the *freshly cleaved*, and diminishing with heating which likely introduces airborne contaminants onto the surface, or reorganization of the surface, for the *heated* samples. Treatment with AKD reduces the polar component to 1.5 mJm^{-2} as the polar sites are either consumed by reaction, or covered by the AKD.

The reverse of the previous method involves measuring the contact angles of alkane droplets on calcite immersed in water. In this state, the treatments had little effect on the measured surface free energy components. The values of γ_s^d were about 21 mJm^{-2} for all treatments, while γ_s^p decreased slightly from 47 mJm^{-2} to 41 mJm^{-2} from the *freshly cleaved* to the *AKD treated* surface. 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. 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 indicates changes in the calcite surface imparted by the continuous phase. One can conclude from these results that the abridged two liquid method in water is more applicable to low energy surfaces such as polymers than to the present system, since surface modification by the polar solvents, such as water, will be less likely.

Results: Acid-Base Method

The contact angles on the three calcite samples were determined with the liquids listed in Table 3. Zisman plots were made in the anticipation of deriving some meaningful information. However, no consistent picture emerged in examination of the critical surface tensions, γ_c, and thus the values are not reported.

Figure 12 shows the 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,

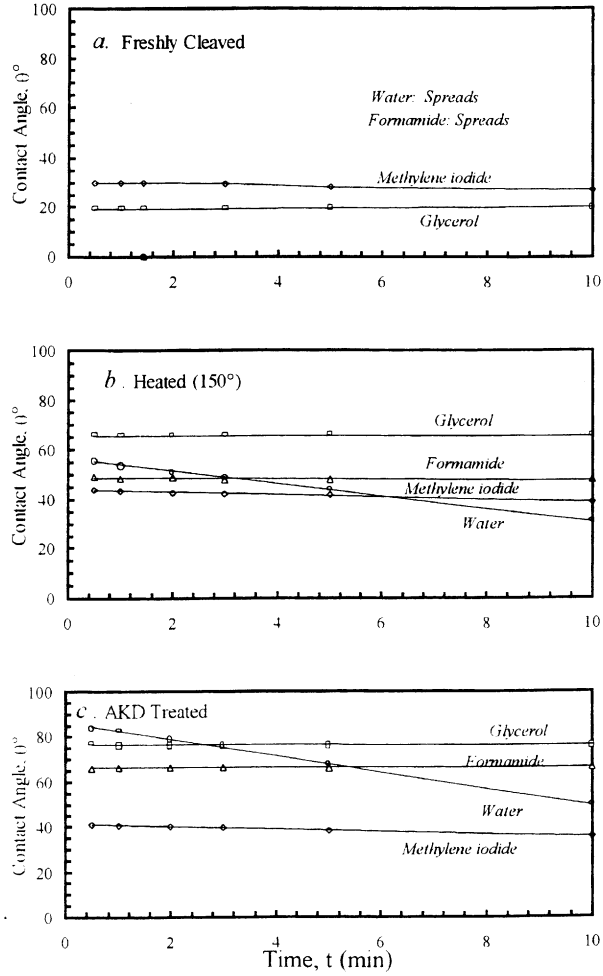

Figure 12: The contact angles of several liquids in air on the surface of calcite samples; a) freshly cleaved; b) heated at 150°C for 2 hours; and c) AKD treated. Results from these liquids were analyzed using the acid-base method (60).

	γ_L †	Contact Angle, θ° at 0.5 min		
		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

Table 3: Surface tensions (mJm^{-2}) and contact angles of liquids on calcite samples in air.

complete wetting may be expected. For the *AKD treated* sample, (Fig. 11c), complete coverage is apparently not achieved although the contact angle is higher than for the *heated* sample. The rehydration of the calcite surface and expansion of the interphase, which results in weaker AKD anchoring, may also explain the behavior. 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 (65).

According to van Oss and Good (7) 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 for the surface. This was done for our systems by using Eq.(20) and the necessary surface energy components for the probe liquids as given for the liquids used in this study as given in Table 4. The γ_s^{LW} of a surface may be determined by using:

$$\gamma_S^{LW} \approx \gamma_S^d = \frac{\gamma_L}{4}(1+\cos\theta)^2 \tag{24}$$

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 5 shows the experimental contact angles observed for methylene iodide as

	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 4: Surface energy components of wetting liquids (mJm^{-2})

	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 5: Contact angles (°) of wetting liquids on calcite, measured in air for the 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

Table 6: Surface free energy components of calcite samples. (acid-base method)

well as water, formamide and glycerol. The values of γ_s^{LW} determined from Eq.(21) are given in Table 6 and are similar to those determined by the abridged two liquid methods for water in air and in octane, cf. Table 3.

By using the van Oss *et al.* (7,8) relationship given by Eq.(20) 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 5., while the calculated values are shown in Table 6. The spreading of water on the *freshly cleaved*

sample indicates a surface 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 has compared to heat treatment alone.

Work 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 were calculated from the contact angles determined by abridged two liquid method and the acid-base method, are reported in Tables 7 and 8, respectively.

The work of adhesion components for the water/calcite system as determined using the abridged two liquid method from were determined from Eqs.(13) (18) are given in Table 7. The results for the *dry*, water in alkane systems shows that the acid- base component is reduced from the *freshly cleaved* as the surface is *heated*, and potentially contaminated. When the surface is *AKD treated* to lower the surface energy, W_{SW}^{AB} is reduced substantially.

For the water-immersed method, the W_{SW} approximates the W_C for water. The W_{SW}^{d} and W_{SW}^{AB} are in the correct proportion for water. The AKD sample shows a slightly lower W_{SW}^{AB} and W_{SW} due to the presence of alkyl chains and the values appear reasonable. It is

	Dry method			Water immersed method		
	W_{SW}^{d}	W_{SW}^{AB}	W_{SW}	W_{SW}^{d}	W_{SW}^{A}	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 7: Work of adhesion between water and calcite samples from the abridged two liquid method. (mJm^{-2})

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

Table 8: Work of adhesion between water and calcite samples from the acid/base method.(mJm^{-2})

apparent that we are observing a water-alkane system in the contact angle measurements. A strongly bound layer of water, which agrees with the previous notion that there is a strong interaction between bare calcite and water, effectively shields the calcite surface.

The work of adhesion between water and calcite derived from the van Oss *et al.*, acid-base approach are given in Table 8. 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 abridged two liquid method given the limitations of the techniques.

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CONCLUDING REMARKS

A rigorous comparison of the results from IGC and wetting experiments reported above cannot be made since the cleaved calcite can only be considered a model system. The surface energetics at the fine sizes of the filler/pigment particles could be quite different from the freshly cleaved planar surface. Furthermore, significant difference between the chalk, marble and PCC samples were observed from IGC data. Prediction of how the cleaved calcite should relate to these three samples cannot be made.

However, there are consistent trends that occurred in both experiments. The IGC test method, at infinite dilution was sensitive to very small changes in water content at the particle surface. Small losses of surface water caused significant increases in the adsorption

interaction for both the non-polar and polar probes. If water is present, or if a polar probe (Lewis-acid) was retained, the surface energy decreased, either because sites were chemically reacted, or they were covered by an adlayer. By analogy in the wetting experiments, the cleaved calcite represented a moderately clean surface, that after exposure to ambient contaminants, the surface energy, specifically the polar components were reduced. Intentional surface contamination using the AKD reduced the surface energy further.

Since both methods are sensitive to such contamination, in using either approach for characterizing practical surfaces one should consider the manner in which the test procedure modifies the surface and influence the results. For example, the IGC procedure involves dehydration of the test sample, or in the case of wood or paper, important volatile fractions may be lost. Once the specimen has been modified, the resulting data may have no bearing on the surface of interest. In a similar manner, the contamination of the calcite surface with water or alkane in the contact angle experiments clearly modified the surface so the changes to the base material such as heating or AKD addition went virtually undetected. This may not be entirely bad from a practical perspective since surface of interest may reside in a contaminated or wet environment, and so results may reflect practical observations. For IGC, however, the continual dehydration may cause a modification of the surface to one that departs greatly from the practical.

The results from wetting studies indicated a substantial basic component on the cleaved calcite surface, which is expected. The conflicting results in certain studies may result from the injection of excessive amounts of probe gases into the column, thereby giving an inaccurate assessment of the surface chemistry. This aspect is currently under examination.

An important difference in the two methods exists theoretically, but may or may not be recognized at the experimental level. The liquid-solid interactions of the wetting study will encounter different Lifshitz-van der Waals forces than the ideal gas state of IGC at infinite dilution. Considering the differences, IGC results may be more easily predicted from theory since neighbor-neighbor interactions are minimal. Examination of the result at finite concentration may improve the correlation of results between IGC and contact angle wetting. This aspect will be examined in future studies

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Transcription of Discussion

Surface Energetics of Calcium Carbonate Powders by Inverse Gas Chromatography (IGC) and Cleaved Crystals by Contact Angle Measurements

Steven Keller, Assistant Professor, Syracuse University, USA

Dr Theo van de Ven, Director, Paprican/McGill, Canada

I have difficulty understanding the equating of the London force components between the rigorously and mildly conditioned surfaces to calculate the Debye component. In one case you really look at an alkane-water interaction and in the other case you look at an alkane-calcium carbonate interaction and obviously you get two different answers for the van der Waals energy. Why would they be those two components and what is the role of water in this?

Steve Keller

We have not measured the induced Dipole component. We saw a substantial increase in the Lifshitz Van der Waals component which we ascertain cannot be resolved by merely an increase in the London component. Now in the presence of a high electric field we expect that there will be more contributions from the Debye component. We have not calculated the Debye component and I believe that will be a very difficult task.

Gil Garnier, Research Engineer, Paprican/McGill, Canada

You compare your contact angle results with your IGC measurements and you find differences. Couldn't it simply be explained by the fact that when you measure contact angle you work in the liquid phase which allows some ionisation to occur (effect of pH) and also some desorption of ions from the particles, while you don't have these phenomena in the gaseous phase of the IGC measurements?

Steve Keller

That's an aspect that has been neglected in the contact angle because when you place water onto the surface of calcite you can expect there to be some dissociation, although the surface was washed, and one could consider it in a pristine state. When you freshly cleave it and put it in water you are likely going to have dissolution, into the contact angle liquid and you're going to have migrations of ions to the point where contact angle is

measured. I suspect that will contribute to a lowering of the energetic parameters derived from wetting.

Gil Garnier

A second question. Do you see any relationship between the dispersive and the polar components and the DLVD theory when you break everything down in terms of Van de Waals and electrostatic forces?

Steve Keller

I think that is similar to Dr van de Ven's question. What we have is, the conventional way of breaking these down is to non-colombic and colombic interactions but unfortunately we find that in the non-colombic interactions we have two that are based on the polarity of the interactive bodies. So we may have to revert to the old system where surface energy is split into either polar or dispersive, not dispersion, interactions or specific or non-specific, and that might be a simple way around this problem. Unfortunately this means deconvoluting back to an older style. Although we have identified all these different surface energy components, we would be reclustering them back together just to do an empirical calculation. I think sorting these out is going to be a very difficult task, not necessarily left to IGC.

Professor John Roberts, UMIST, UK

You reported surface energies of PCC particles which had been treated with AKD. There is evidence in the literature from carbon 13 labelling that the AKDs undergo change through hydrolysis through the intermediacy of the calcium carbonate to the ketone. Did you see any evidence of these changes? I have a second question related to that. Did you ever look at ASA treated particles which would give hydrolysis presumably to a dicarboxylic acid which is significantly more polar and which I would expect would cause some differences.

Steve Keller

Our work with AKD was initiated to study sizing reversion and also to study sizing demand. From my current point of view that AKD is distributed spotwise on the surfaces of paper and fillers, I think the manner in which we deposited one or several mono-layers

of AKD, may not necessarily reflect the behaviour that AKD would interact with PCC in the drying section of the paper machine. I think there is room for work to go back and apply AKD dispersions to these particles and study them as if they were in the papermaking process. We are truly interested in the dusting problem, reversion problem and those things that happen on the reel. Regarding your second question, we have not studied ASA. Now as far as characterising the chemistry of interaction, that earlier work was also interested in studying the orientation of AKD on the surface as it exists in the mono-layer and I think we should just abandon that and go back to the dispersion deposition.