Wettability of CaCO₃ surfaces

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Abstract

The wettability of calcium carbonate, an important parameter in the evaluation of the interaction characteristics of materials used in conservation, was examined by measurements with the Wilhelmy plate technique. Heterogeneous surfaces consisting of glass and calcium carbonate were examined. Stable calcium carbonate layers were deposited on microscope glass slides using supersaturated solutions in which the equimolar concentrations of total calcium and total carbonate used ranged between 0.1 and 0.4 M, over a pH range between 9 and 12 and temperature between 25 and 80°C. In all cases amorphous calcium carbonate was deposited, the extent of surface coverage increasing with increasing supersaturation and temperature. Higher surface coverage of the glass slides with calcium carbonate yielded lower contact angles suggesting increased wettability of the heterogeneous surface. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The wetting of solid substrates by liquids is a significant parameter in a number of processes, such as spreading of liquid droplets on solids, with important application in the spraying of paints or agricultural chemicals, the penetration of ink in paper, the liquid absorbency or repellence of fabrics or the displacement of one liquid by another in oil recovery, etc [1,2].

The wettability of marble by various liquid chemical agents and/or rainwater is a very important factor both for understanding the erosion and weathering processes and also for the efficient application of chemical treatment methods used in conservation.

The effective spreading of a protective film on marble’s surface or the penetration of a consolidant in the pores are greatly influenced by the wettability of marble by these substances. In cases where adsorption of ions or groups of ions from aqueous solutions on marble takes place, the wettability turns out to be a significant parameter...
because of the possibility of change the surface tension of water by surfactants. The various polymorphic phases of CaCO₃ (the basic chemical constituent of marble) are expected to have different wetting properties which may be related to the corresponding kinetics of dissolution.

In the present work we have measured the wettability of calcium carbonate layers, deposited on glass slides aiming at investigating the applicability of the Wilhelmy plate method [3,4] for the measurement of wetting of calcium carbonate surfaces and at the examination of the influence of the conditions of the preparation of the carbonate layers on the glass slides on the contact angles measured.

2. Methods, techniques and materials studied

2.1. Definition

Wettability involves the interaction between a liquid and a solid when they are in contact. When a droplet of a liquid is deposited on a solid surface, there are two possibilities shown schematically in Fig. 1. In the first, the droplet spreads on the surface while in the second it shrinks. In the first case the solid is well wetted by the liquid and the contact angle \( \theta \), defined as shown in Fig. 1, is low. In the other case, the solid is poorly wet and the contact angle is high. The wettability of a solid by a liquid is determined by the balance between adhesive forces between the liquid and the solid and cohesive forces in the liquid. Adhesive forces cause the liquid to spread over the surface while cohesive forces to shrink as the molecules of the liquid prefer rather to stay near each other than to contact the solid. Wetting behaviour is characterised by the value of the contact angle, \( \theta \), a macroscopic parameter.

When a liquid drop is deposited on a substrate, as shown in Fig. 1, it forms the contact angle \( \theta \) with the surface and three interface energies, \( \gamma_{SV} \) between the solid and vapour, \( \gamma_{SL} \) between the solid and liquid and \( \gamma_{LV} \) between liquid and vapour in equilibrium at the contact point \( p \), where the three phases meet. When a solid is contacted by a liquid in the presence of vapour, the liquid will adhere well on the substrate if the total free energy required for the creation of the new interface decreases. The physical significance of this energy change is the work needed to separate the solid and liquid from the solid/liquid interface. This work is known by Dupre’s equation [5]:

\[
W_{SL} = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}
\]  

At the meeting point of the three interfaces (Fig. 1) the equilibrium condition is:

\[
\gamma_{SL} + \gamma_{LV} \cos \theta = \gamma_{SV}
\]  

and from Eqs. (1) and (2) it follows that:

\[
W_{SL} = \gamma_{LV}(1 + \cos \theta)
\]

Although there is no method for measuring directly the solid/vapour surface tension, the difference \( \gamma_{SV} - \gamma_{SL} \) can be determined and is known as the adhesion tension. The determination of the difference \( \gamma_{SV} - \gamma_{SL} \) can be done following the vector resolution shown in Fig. 1.

As may be seen from Eq. (3), provided that \( \gamma_{LV} \) and the contact angle \( \theta \) can be measured, a quantitative assessment of the degree of adhesion of the wetting liquid can be obtained. Moreover, Eq. (3) shows that \( \theta \) is determined by the relative strengths of the interactions of the liquid with the solid and with the vapour. If \( \theta = 0 \), \( W_{SL} = 2\gamma_{LV} \) and the liquid attracts the solid to the same extent as it does for itself. The attraction for the liquid itself is \( 2\gamma_{LV} \). If \( \theta = 90^\circ \) the attraction of the liquid
Fig. 2. Schematic diagram of techniques used to measure contact angle. (a) Sessile drop method; (b) Wilhelmy plate method.

for the solid is half of the attraction for itself and if $\theta = 180^\circ$ there is no adhesion between the liquid and the solid.

2.2. Contact angle measurement

Several techniques are available for measuring the contact angle of liquids [6]. For the measurement of contact angles of liquids on solids both static and dynamic methods of measurement are commonly employed [7,8]. The most common static technique is that of the sessile drop, in which, a droplet of the tested liquid is placed on an horizontal surface as shown in Fig. 2a and observed with a microscope or a video camera. The contact angle $\theta$, formed by the tangent at the contact point of the drop with the solid substrate is measured by a goniometer. Another technique is the Wilhelmy plate technique, which is principally a dynamic method [8]. According to this technique a slide of the solid under investigation is lowered by the appropriate mechanism based on the motion control of a stepper motor until it touches the surface as shown schematically in Fig. 2b. Next, it is slowly cycled up and down and at the same time the force acting on the slide, $F$, is recorded. The contact angle $\theta$ can be measured using Eq. (4)

$$F = 2\gamma (L + e) \cos \theta - B$$

In Eq. (4) $\gamma$ is the surface tension, $L$ and $e$ are the length and the width of the slide, respectively, and $B$ the buoyancy of the plate. It should be noted that during the cycles both the advancing and the receding angles may be measured providing information on the specimens roughness and/or heterogeneity from the hysteresis which may possibly appear [9].

2.3. Comparison between the Wilhelmy plate and the sessile drop methods

The contact angles of the calcium carbonate polycrystalline specimens in the present work were measured by the Wilhelmy plate technique which shows several advantages over the static, sessile drop method:

1. It is highly reproducible while in the sessile drop technique the results depend considerably on the experimenter.
2. There is no problem associated with the size of the droplet and moreover the speed of sample’s movement can be readily controlled.
3. High sensitivity. Differences as low as $\pm 0.5^\circ$ can be accurately measured.
4. The static method is more suitable with pure homogeneous systems without chemical interaction. The presence of an additional compound in the liquid which can be adsorbed on the surface may change its nature and the results. On the other hand, the dynamic, Wilhelmy plate method has turned out to be an ideal tool for studying the progress of phenomena which vary with time, like adsorption, desorption or chemical reaction.
5. It is applicable in cases of systems with two immiscible liquids, where the displacement of one liquid by the other can be studied.
6. The presence of surface roughness and porosity are not important problems, contrary to the static, sessile drop method since in the Wilhelmy plate method the angle measured is the average from the entire area wetted each time.
7. Surface heterogeneities may be easily studied since scanning of the surface by the wetting line can be done.

2.4. Scope of the present work

In the present work, the possibility of using the dynamic Wilhelmy plate technique to evaluate the
wettability of CaCO₃ covered glass slides in the system of dodecane and aqueous solution saturated with CaCO₃ was tested. Dodecane was introduced into the system to test the effect of a hydrophobic substance on the wettability while the saturated solution of CaCO₃ was used instead of water to avoid dissolution of CaCO₃. Glass slides were chosen as substrates for the CaCO₃ deposits in the present work because of their small thickness and also because of the possibility of forming coatings by precipitation of different crystal phases of CaCO₃. Moreover, the possibility of application of the Willhelmy method on polycrystalline materials was examined.

2.5. Preparation of the samples

Calcium carbonate coatings on the slides were prepared by a combination of the spin-coating with the spontaneous precipitation technique, in which CaCO₃ slurries prepared by rapidly mixing solutions of Ca(NO₃)₂ and Na₂CO₃ at different concentrations (0.1–0.4 M), pH (9–12) and at temperatures ranging between 60 and 80°C were used.

2.6. Characterization of the samples

The surface coverage of the glass slides by CaCO₃ deposited following mixing of the component solutions was measured quantitatively using an image analysis system connected to a light microscope (LEICA, QMC500). Scanning electron microscopy and powder X-ray diffraction were used for morphological characterization and the identification of the crystal phase of the precipitated CaCO₃. In all cases the precipitated phase was amorphous calcium carbonate. The contact angle of the glass slides covered with CaCO₃ was measured using the Wilhelmy plate technique in the double liquid system of dodecane and saturated solution of CaCO₃.

2.7. Experimental system

The experimental system used to measure contact angles is shown schematically in Fig. 3. It consisted of a balance from which the glass slide of dimensions (32 × 24 × 0.15 mm) is suspended. The vessel with the liquids was cycled up and
down by a stepper motor the velocity of which was precisely controlled by a computer (± 0.01 mm s⁻¹). The evolution of the force acting on the sample versus the displacement was recorded and subsequently plotted by a computer in real time. The movement of the wetting line was observed in real time in a monitor using a video camera. This extra feature enabled also measurements of the contact angle using a goniometer. The choice of the binary liquid mixture was done for two reasons:

1. to test the possibility of applying the measurements in of interest to petroleum reservoir systems where mixed hydrocarbons–water liquids are present;
2. keeping the coated plates totally immersed in the liquids prevented contamination from particles suspended in the air.

3. Results and discussion

Upon mixing aqueous solutions containing Ca²⁺ and CO₃²⁻ ions, precipitation of calcium carbonate takes place provided that the supersaturation, S, with respect to calcium carbonate, defined as [10]

\[ S = \frac{(Ca^{2+})(CO_3^{2-})}{K_S^0} \]  

(5)

exceeds 1. In Eq. (5) () denote activities and \( K_S^0 \) is the thermodynamic solubility product of the precipitated salt. In our experiments the conditions were selected so that \( S > 20 \) and precipitation was spontaneous, following immediately after mixing equimolar calcium nitrate and sodium carbonate solutions. In all cases amorphous calcium carbonate was formed which persisted without any conversion to the thermodynamically stable calcite during all tests. It is obvious that the mass which may be deposited is higher the higher the value of the supersaturation, \( S \). As a consequence, it was anticipated that the higher the supersaturation in the liquids mixed on the glass slides the thicker the layer of the deposit formed. As may be seen in Fig. 4, higher surface coverage was obtained for the glass slides with the higher supersaturation.

Coverage of the glass slides with the mineral salt is expected to affect its wettability. The contact angles measured for glass slides treated with
supersaturated solutions of different concentrations are shown in Fig. 5.

The behaviour found for the dependence of the contact angles on the supersaturation of equimolar solutions in which the glass slides were exposed may be seen in Fig. 6. As may be seen both from Figs. 5 and 6, the contact angles were reduced upon increasing the driving force for the formation of the mineral deposits on the glass slides. Higher driving force was accompanied with larger amounts of calcium carbonate deposits and higher slide surface coverage (see also Fig. 4). The importance of surface coverage is related with the smoothness of the surface. Smoother surfaces are expected to be wetted better than the rougher in which dodecane is trapped in the uncovered areas of the glass slides.

The increase of temperature during the preparation of the coating, resulted in the improvement of the wettability as may be seen from the values of the contact angles measured presented in Fig. 7. At all temperatures tested amorphous calcium carbonate was the only phase forming. Increasing temperature, is expected to increase the driving force and hence the amount of the deposits significantly. The spontaneous precipitation of calcium carbonate is reported to be a surface controlled process associated with high apparent activation energies [11,12].

4. Conclusions

The results presented in this work have shown that highly supersaturated solutions of calcium carbonate may be used for the formation of amorphous calcium carbonate deposits on glass slides. The thickness of the deposits and their homogeneity concerning the development of a smooth surface was higher the higher the supersaturation of the calcium carbonate solutions. Increased wettability was also achieved by increasing the temperature of the solutions up to 80°C. This trend is probably associated with the amounts and the smoothness of the deposits formed on the glass slides. Estimates of the wettability of the carbonate covered surfaces were made from measurements of the contact angles of

Fig. 5. Contact angle measured as a function of the initial concentration of calcium and carbonate ions in the supersaturated solutions used for the preparation of the calcium carbonate coatings.
Fig. 6. Schematic diagram of the contact angle as a function of the supersaturation with respect to calcium carbonate (calcite) of the solutions in which the glass slides were exposed.

Fig. 7. Dependence of the contact angle measured on calcium carbonate covered glass slides as a function of the temperature of the supersaturated solution used for the preparation of the coatings.
the mineral covered glass slides by the successful application of the Wilhelmy plate method in the binary system dodecane–water. In all cases the same, amorphous calcium carbonate was deposited and the wetting was found to increase with increased amounts of deposited calcium carbonate.

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References