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A NEW DEVICE FOR DETERMINING WETTING PREFERENCE OF CRUDE OIL/BRINE/SOLID SYSTEMS

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ABSTRACT

A dynamic Wilhelmy plate technique has been developed for quantitative determination of the wetting preference of crude oil/brine/solid systems. This method is simpler and less operator-dependent than the standard sessile drop (parallel crystal plate) technique used in the petroleum industry. This paper focuses on the laboratory setup required for the dynamic Wilhelmy plate technique to test crude oils, allowing for aging studies with oxygen-sensitive crude oils.

When comparing forces in the reservoir, capillary forces are always described as the product of interfacial tension and the cosine of the contact angle, which is termed the adhesion tension. The Wilhelmy test gives a direct quantitative determination of the adhesion tension, and a qualitative visual indication of wetting preference. The results graphically illustrate the wetting preference of the oil/brine/solid system. Three types of wetting preference have been observed: water-wetting, oil-wetting, and hybrid-wetting. In the first two cases, both the water-advancing and water-receding fronts indicate the same wetting preference. The hybrid-wetting system shows an oil-wetting character when water advances and a water-wetting character when water recedes across the solid. A systematic study of the wetting character of several mineral surfaces important to the petroleum industry has been performed, including studies on glass (sandstone analogue), marble (calcium carbonate), and dolomite.

The dynamic Wilhelmy test uses a thin solid plate suspended from a balance which is moved through the crude oil/brine interface inside an anaerobic vessel. The measured change in force as the plate passes through the oil/brine interface relates directly to the adhesion tension at that interface. The apparatus is computer controlled and monitored, allowing high quality data to be obtained and analyzed.

INTRODUCTION

Measurement and interpretation of wetting preference of oil-producing formations is an important part of engineering a reservoir. Although widespread recognition that a significant proportion of reservoirs are not water-wetting came less than twenty years ago (Treiber, et al, 1972), the question of wetting has generated a large body of laboratory work (Anderson, 1986a; Anderson, 1986b; Anderson, 1986c; Anderson, 1987a; Anderson, 1987b; Anderson, 1987c). This paper describes a new laboratory technique for assessing wetting preference in a fluid/liquid/solid system. Several examples of the uses of this device are reviewed here (Andersen, et al, 1988; Teeters, et al, 1988a; Teeters, et al, 1988b; Teeters, et al, 1989).

Every technique for estimating formation wettability has drawbacks. The easy tests are qualitative and the quantitative tests are expensive and time-consuming. Imbibition tests assume the wetting character is contained in the formation rock and require preserved core from the formation of interest. Obtaining such core material, without alteration from drilling muds or oxidation, is extremely difficult (Thomas, et al, 1984). Using either the Amott (1959) or USBM (Donaldson, et al, 1969) methods a quantitative measure of imbibition can be obtained for comparison with other rocks, but it does not relate to the physics of wetting, as discussed below.

Contact angle measurement is usually done in the petroleum industry by the sessile drop method (Hjelmeland and Larrondo, 1986; McCaffery, 1972), or a modification of this technique (Treiber, et al, 1972). This measurement assumes that the crude oil contains any wettability-controlling agents, so uncontaminated crude oil samples must be obtained. Test times exceeding one month are not uncommon and it can be difficult to determine that the interface has actually advanced across the face of the crystal. Displacement frequency and distance are variable and dependent upon the operator. Tests are conducted on pure mineral surfaces, usually quartz or calcite, which do not adequately model the heterogeneous rock surfaces in reservoirs. Although a physically meaningful measure of wetting is obtained from contact angle data, these data alone are not sufficient to completely define the wetting forces.

Wetting character is divided into three regimes usually based on advancing contact angle: water-wetting for angles less than 75°, oil-wetting for angles greater than 105°, and intermediate-wetting for contact angles between 75° and 105° (Anderson, 1986a). However, the degree of wetting of a system depends on the adhesion tension (the product of the interfacial tension, IFT, and the cosine of the contact angle) rather than the contact angle alone. The wetting force is obtained from the adhesion tension multiplied by the length of the oil/water contact line.

As an example, consider the systems listed in Table I. The contact angles indicate that system A has intermediate wettability while system B is oil-wetting. The IFT of system A is higher than the IFT of system B, leading to a greater adhesion tension for the "intermediate" system than

TABLE I. EXAMPLE OF TWO WETTING SYSTEMS

	Interfacial Tension	Contact Angle	Adhesion Tension	Wetting Character
System A	39 dyne/cm	105°	-10.1 dyne/cm	"Intermediate"
System B	12 dyne/cm	130°	- 7.7 dyne/cm	"Oil-wetting"

for the "oil-wetting" system. Clearly, the oil in the "intermediate" system A adheres more strongly to the solid surface than the "oil-wetting" system B.

The dynamic Wilhelmy plate measurement has the potential to give reproducible data which can be used to characterize wetting of mineral surfaces. Like the contact angle test, it assumes that the crude oil contains the wettability-controlling components, but the adhesion tension measured in this test can be directly related to the other forces in the system.

THE WILHELMY PLATE METHOD

Wilhelmy (1863) described the basic technique for measuring surface and interfacial tensions. The technique has been used by surface chemists for many years, primarily to study vapor/liquid/solid interfaces. A computer-controlled device has been developed for studying both vapor/liquid/solid and liquid/liquid/solid interfaces (Teeters, et al, 1988a). A thin plate is suspended from a computer-monitored microbalance over a vessel containing oil and brine. A computer-controlled stepper motor moves the vessel upward causing the plate to pass through the air/oil interface and the oil/brine interface. Multiple wetting cycles can be performed under computer control without disturbing the system.

In the equipment described above the force, F, on the plate which is partially submersed in a liquid is

$$F = p \gamma \cos \theta - B \tag{1}$$

where p is the perimeter of the plate, γ is the surface tension, θ is the contact angle and B the buoyant force on the portion of the plate below the general surface. The step change in force is related to the change in Gibbs surface free energy ΔG_S when a liquid displaces a vapor from a solid surface (Adamson, 1976),

$$\Delta G_S = (\gamma_{S2} - \gamma_{S1} + \gamma_{12} \cos(\theta - \Delta\theta)) * \Delta area \tag{2}$$

where S1 denotes the solid/phase 1 interface, S2 the solid/phase 2 interface, and 12 the phase 1/phase 2 interface. At equilibrium the limit of Δarea goes to zero, and the Young's equation results

$$\gamma_{S1} - \gamma_{S2} = \gamma_{12}\cos\theta \quad . \tag{3}$$

When two liquids such as oil and water are involved, the force on a plate which has passed through the oil layer into the water layer is given by

$$F = p\,\gamma_{AO}\cos\theta_{AO} - B_O + p\,\gamma_{OW}\cos\theta_{OW} - B_W \quad . \tag{4}$$

In Equation 4, AO and OW indicate the air/oil and oil/water interface respectively, B_O is the buoyant force caused by the oil and B_W that caused by the water layer.

The hexadecane/water/glass system was used as an initial model for crude oil/brine systems (Teeters, et al, 1988a). When the plate enters the fluids the menisci are upwards, indicating a water-wetting system as shown in Figure 2. Characterization of wetting behavior of this system from the dynamic Wilhelmy plate data shown in Figure 3 is interpreted by using Equation 4. The mass read by the balance was converted to a tension by multiplying by the gravitational acceleration, g, and dividing by the plate perimeter, p. As the plate was immersed, the tension increased when the solid surface was wetted by the hexadecane ($\gamma_{AO}\cos\theta_{AO} < 90^\circ$ in Equation 4). Further immersion of the plate into the hexadecane resulted in a slight decrease in the tension because of the buoyant force. Another increase in tension was observed at the hexadecane/water interface since the water wetted the glass surface in preference to hexadecane and the advancing contact angle as measured through the aqueous layer was again less than 90°. The buoyant force of the water caused the measured tension to slightly decrease as the slide went further into the water layer. The direction of motion was reversed for the emersion half of the cycle and the contact angles in Equation 4 changed from advancing to receding angles. The difference between these two angles caused the hysteresis observed in the wetting cycle shown in Figure 3. The hexadecane/water/glass system is a typical example of water-wetting behavior.

Oil-wetting systems can be modeled by replacing the glass plate with a plate of polytetrafluoroethylene (PTFE). The hexadecane/water/PTFE system has a wetting cycle as shown in Figure 4, and the menisci are shown in Figure 5. In this system, at the hexadecane/water interface the water phase did not wet the PTFE surface. As the plate advanced into the water, the interface pinned at the bottom edge of the plate, until gravitational and wetting forces balanced. The contact angle was greater than 90° and the tension decreased. The peak observed at the hexadecane/water interface on emersion was typical of other oil-wetting systems and is believed to be caused by edge effects from the bottom of the plates.

The dynamic Wilhelmy wettability test determines both advancing and receding contact angles, so it distinguishes another characteristic wetting in crude oil/brine systems, termed "hybrid" wetting, in which the water-advancing contact angle is greater than 90° and the water-receding contact angle is less than 90° (Figure 6). In a hybrid system, whichever liquid is in contact with the surface tends to remain in contact with the surface until it is displaced because of other overriding forces. When the direction of motion of the interface across the plate changes, the contact angle changes until a new stable meniscus forms. The contact line on the solid appears to be pinned at the position of maximum advance. It remains pinned until the balance of gravitational and adhesion forces stabilized the meniscus at the new (receding) contact angle. This hybrid wetting behavior suggests that some liquid/liquid/solid systems have an extremely strong history dependence.

In this paper, systems with both advancing and receding adhesion tensions greater than zero are termed water-wetting; both adhesion tensions less than zero are termed oil-wetting; and those for which the adhesion tensions switch sign as described above are termed hybrid-wetting. Since contact angles are not directly measured by the dynamic Wilhelmy plate device, the "intermediate" wetting terminology is not used here.

The computer interface system lends itself well to the determination of interfacial tension and contact angles using Equation 4 and the technique described by Pike and Thakkar (1976) for Wilhelmy plate type experiments. Contact angles for crude oil/brine systems using the dynamic Wilhelmy plate technique have been determined by this technique and all three of the wetting cycles described above have been observed in various crude oil/brine systems (Andersen, et al, 1988). The adhesion tension can be determined by noting the magnitude of the jump in tension measured at the interface. This is straightforward when the lower liquid wets the plate, for example both interfaces in Figure 3. The adhesion tension can still be determined when the upper fluid preferentially wets the plate, as for the oil/brine interface in Figure 4, which is reproduced in Figure 7. The buoyant slopes in the oil and brine phases are extrapolated to the bulk interface and the step in tension between these extrapolated lines is the adhesion tension, -37.7 dyne/cm. The plate must travel far enough into the lower (brine) phase for the downward meniscus to stabilize.

COMPARISON OF THE DYNAMIC WILHELMY METHOD TO FIELD PROCESSES

Wetting preference affects the location of fluids flowing in porous media, influencing the behavior of waterfloods and other methods of improved oil recovery. Water displaces oil from the pore space in a waterflood. At the leading edge of the water bank, the capillary forces given by the water-advancing adhesion tension influence the displacement process. An oil bank can build in front of the water bank, so there is also a water-receding zone ahead of the oil bank. Both the water-advancing and the water-receding wetting information needed to model this displacement behavior is provided by the dynamic Wilhelmy technique.

Far from a wellbore, the velocity of these fluids is about one linear foot per day. Near a wellbore, the velocity can increase one-hundred fold. A static or quasi-static test such as the sessile drop (contact angle) test may not represent the dynamic behavior of the fluids in the field. The dynamic Wilhelmy device gives results which are comparable in interface velocity to the field displacement rate. The interface in the Wilhelmy test described here moved at a steady rate of 0.127 mm/sec or 36 ft/day. The wetting cycle for a hybrid-wetting crude oil system was not affected by moving at a rate less than 1 ft/day.

Another measure of wetting character in the field is the dimensionless capillary number N_c, which is the ratio of viscous to capillary forces. One expression for this number is (Stalkup, 1983)

$$N_c = \frac{V \mu}{\gamma} \qquad (5)$$

where V is the macroscopic velocity of the fluid and μ is the viscosity. Residual oil saturation, which is the oil left behind after a waterflood, is approximately constant for capillary numbers up to 1.0 E-5, then begins to decrease (Stalkup, 1983). For a 2 centipoise oil with an interfacial tension of 31 dyne/cm flowing at 1 ft/day, N_c = 2.27 E-5, and at 100 ft/day, N_c = 2.27 E-3. For such an oil/brine system, the dynamic Wilhelmy device had an equivalent capillary number of 8.21 E-4 - in contrast, the sessile drop test is quasi-static.

Since there can be both a water bank displacing oil and an oil bank displacing water, both the water-advancing and water-receding wettability affect the flow characteristics of the reservoir. Specifically, a water-wetting system shows hysteresis in the oil relative permeability curve, but not in the water relative permeability curve. An oil-wetting system is the opposite. All crude oil/brine/solid systems examined for this study exhibited wetting hysteresis. In some cases the difference between advancing and receding adhesion tensions was small. These cases correspond to the water-wetting or oil-wetting cases generally studied in the laboratory which display relative permeability hysteresis only in the non-wetting phase. The hybrid wetting cases had very large hysteresis and the solid tended to hold whichever fluid was in contact with it in preference to the displacing fluid, regardless of which fluid was in contact with the solid. Although a systematic relative permeability study has not been conducted of such systems, it is likely a rock saturated with a crude oil/brine system which displays hybrid behavior would have a relative permeability hysteresis for both phases. These systems have been observed in relative permeability tests (Potter, 1987), but a connection with hybrid wettability has not been hypothesized before.

EXPERIMENTAL

The Wilhelmy (1863) hanging plate method has been used for many years to measure interfacial and surface tensions, but with the advent of computer data collection and computer control of dynamic test conditions, its utility has been greatly increased. Figure 8 shows the major pieces of equipment used in our studies.

A Cahn Model 29 microbalance and a stepper motor were interfaced to an IBM PC/XT through an RS-232 interface and an IEEE488 general purpose interface bus (GPIB), respectively. The microbalance rested on top of a housing containing a flat platform on a vertical stage moved by the stepper motor. The vessel holding the liquids rested on the platform. The plate hanging from the balance was immersed in and removed from the liquids in a continuous motion so that immersion-emersion cycles or "wetting cycles" could be obtained. The initial plate position was typically 4 mm above the liquid/vapor interface. A wetting cycle run consisted of moving the liquid interface a certain distance up onto the plate and then the same distance down at a standard speed of 0.127 mm/sec. During this movement, 720 data values were recorded by the microcomputer for total cycle distances of 50.4 mm and 360 values for cycles of 25.4 mm.

The software on the microcomputer was designed to control the equipment and display the results in real time. The wetting cycles drawn simultaneously with the data acquisition alerted the operator immediately if the data were unusual, allowing a visual inspection of the plates during the test. At the conclusion of the test, the data could be stored on the hard disk, printed, or plotted using a six-pen plotter. Data files can be recalled for display, printing or plotting.

The equipment and cleaning procedures were tested using hexadecane/distilled water as a strongly water-wetting system. Any changes toward oil-wetting behavior indicated contamination or insufficient cleaning procedures. This study was designed to test the dynamic Wilhelmy plate procedure so sodium borosilicate glass cover slides were used for convenience. Each cover slide was rendered clean and reproducibly water-wetting by soaking in chromic acid followed by a rinse with distilled water and then a rinse with alcohol. As a final step the plate was held over a flame to burn off any hydrocarbon residue. The mineral plates were cleaned with a different procedure to avoid changing the surface with chromic acid or heat. The plates were scrubbed with a cotton swab using methylene chloride, then soaked in methylene chloride. After air drying they were soaked in isopropanol, methanol, then distilled water, and blown dry with nitrogen between each soaking. Both procedures left plates that were reproducibly water-wetting in a hexadecane/water system. The surface and interfacial tensions measured with this technique agree with literature values to within 0.1 dyne/cm (Teeters, et al, 1988a).

The marble (calcium carbonate) was obtained from Ward's Natural Science Establishment, Inc., and the dolomite was from a west Texas oil field. Thin plates of these materials were cut but not polished. The ability to use natural, slightly rough mineral surfaces is an advantage of the Wilhelmy technique over the traditional contact angle test, which requires smooth single crystals of the solid.

The brine was made from distilled water with 50 kppm NaCl and 5 kppm $CaCl_2$. Purity of the brine was verified using the maximum pull method on the Wilhelmy device to measure its surface tension which should be greater than pure water (Teeters, et al, 1988a). Since a brine solution drives surfactants to the surface, the surface tension of contaminated brine would be less than that of pure water and would be discarded. All glassware was soaked in chromic acid and thoroughly rinsed with distilled water. The brine contacted only glass, Teflon, and Silastic tubing; the oil contacted only glass, Teflon, and the stainless steel pressure vessel. The Teflon parts were cleaned with chromic acid and rinsed with distilled water, and the Silastic tubing was rinsed with distilled water before use and replaced after each test.

The refined paraffin of Figure 3 was tested in an open beaker (Teeters, et al, 1988a). This technique was used as a method of scoping crude oil behavior. Crude oils may be affected by exposure to air (Treiber, et al, 1972) so an anaerobic vessel was designed for aging tests on crude oil systems. Figure 9 shows the apparatus used with the anaerobic vessel. Three vacuum/argon cycles purged oxygen from the vessel after the internal portions shown in Figure 10 were assembled. These cycles also purged the lines to the brine and oil supplies. Argon bubbled through the brine storage vessel for about fifteen minutes. Brine was drained from a glass storage tank into the vessel to cover the glass plates. The vacuum pump pulled gas from the brine in the vessel for five minutes. A positive pressure of argon on the brine assisted a gravity drain from the vessel until the brine level dropped below the bottom of the glass plates. Then the oil inlet valve was opened and the pressure in the cylinder forced oil into the vessel until the glass slides were covered with oil. The hooks holding the slides were not wetted by brine or oil.

Six glass slides hung from a Teflon and glass support around the periphery of the vessel (Figure 10). As noted above, brine contacted the plates first followed by oil to replicate the order of exposure of rocks in an oil field. A plate could be suspended from the microbalance through the central port of the vessel for the dynamic Wilhelmy test. A beaker centered in the vessel kept the brine level under the central port above the general oil/brine interface. Thus, for the dynamic Wilhelmy test the plate passed through a central thin layer of oil into the brine while the suspended plates aged in a thick layer of oil in the periphery of the vessel.

Argon flowed through a relief valve to keep a slight positive pressure in the anaerobic vessel. To perform the test, the operator removed the central stopper and "fished" the plate to be tested from its hanger and suspended it from the microbalance. A small flow of argon out of the port prevented air from diffusing into the vessel during the ten minute period of the test.

A sealed anaerobic system has been constructed which prevents exposure to air by affixing the chamber directly to a microbalance at the beginning of the test.

EXAMPLES OF USE

Results of studies using the dynamic Wilhelmy plate device have been published elsewhere (Andersen, et al, 1988; Teeters, et al, 1988a; Teeters, et al, 1988b; Teeters, et al, 1989). A few examples are discussed here to show the scope of the work possible with this device.

A West Texas crude oil (SS1473) tested in an open beaker (Figure 11) displayed a wetting behavior which changed in a way which was not systematic. Each wetting cycle used a new, clean, glass plate but the same beaker of oil and brine. A second sample of oil from the same field behaved in a qualitatively similar way. Figure 12 shows the results of the tests on SS1473 in the anaerobic vessel. These tests had two purposes: eliminate contamination by oxygen and provide a means of aging the glass plates in the crude oil. The interface age noted on Figure 12 was also the aging time of the plate prior to performing the dynamic Wilhelmy test.

The first plate tested immediately after preparing the vessel displayed hybrid wetting behavior in two wetting cycles similar to the initial wetting cycle for the measurement in air. After one day soaking in crude oil and on subsequent days up to the six days the behavior was oil-wetting with a small hysteresis. The water-advancing adhesion tension for all of these tests (listed in Table II) was almost constant. The IFT of this crude oil and brine was 36.4 (+/- 0.5) dyne/cm, measured using the maximum bubble pressure method. This value was used to calculate the contact angles shown in Table II. Other oil samples from the same field tested using the method of a sessile drop between crystal plates have water-advancing contact angles ranging from 112° to 145° (Treiber, et al, 1972), averaging 130° over six measurements.

This study demonstrated two aspects of measurement of wettability of crude oils. Exposure to air caused changes in the wetting cycle. This was not true of normal paraffins such as hexadecane, which yielded stable wetting cycles for days and weeks when exposed to air. Equilibration of the oil/brine/solid system also caused changes in the wetting behavior. From this study it is not clear whether the changes were due to equilibration of the oil and brine phases or the aging of the solid in the oil phase. It is likely both affect the measurement. The six days (wherein equilibrium actually occurred after one day) were much shorter than the times generally required for the sessile drop test. The conventional contact angle measurements on oil from this field mentioned above required up to 48 days (Treiber, et al, 1972).

Figure 13 shows a comparison of a glass slide and a marble plate in the same crude oil. After seven days equilibration at room temperature, the glass plate displayed hybrid wetting character, and the marble plate was oil-wetting. The temperature was raised to 100°F and after four days equilibration both were oil-wetting. The water-advancing adhesion tension was about the same for both solids at the higher temperature. The differ-

TABLE II. ADHESION TENSION MEASUREMENTS AND CONTACT ANGLES USING IFT = 36.4 DYNE/CM

Interface Age	Measured Adhesion Tension Water-Advancing	 Water-Receding	Calculated Contact Angle Advancing	 Receding
In Air				
15 min.	-31.22 dyne/cm	25.66 dyne/cm	--	--
32 hours	-28.81 dyne/cm	?	--	--
4 days	-34.18 dyne/cm	?	--	--
Anaerobic				
15 min.	-21.72 dyne/cm	25.04 dyne/cm	127°	47°
30 min.	-30.65 dyne/cm	23.03 dyne/cm	147°	51°
22 hours	-29.76 dyne/cm	-26.54 dyne/cm	145°	137°
3 days	-32.45 dyne/cm	-25.92 dyne/cm	153°	135°
6 days	-30.80 dyne/cm	-19.53 dyne/cm	148°	122°

ence in slope of the two sets of curves was due to the thickness of the plates - since the marble was thicker the buoyant force was greater.

In many oil-wetting systems a film of oil adhered to the plate below the oil/brine meniscus. In some cases, the film was not persistent; during the minute or so the bottom of the plate was submerged in brine, it was swept clear of the oil film and the receding cycle switched from oil-wetting to water-wetting as the cycle progressed. After about one day of equilibration between the oil and the brine, this short-time behavior was no longer seen.

For water-wetting oil/brine systems, the receding portion of the wetting cycle was more consistent (smoother) than the advancing portion, which is opposite to the effect with oil-wetting crude oils. This has been seen with other water-wetting materials in our laboratory. In both the oil-wetting and water-wetting cases, the smoother curves were noted when the relative motion of the plate pulled the wetting fluid into the non-wetting fluid. The more ragged features were seen when the non-wetting fluid advanced over the thin edge of the wetting fluid. This raggedness appeared to be a result of irregular detachment of the wetting fluid along the contact line, a localized "stick-slip" behavior.

The wetting behavior at a solid interface is dependent on the surface energy of the solid involved. Solids with low surface energies, such as PTFE (Teflon), tend to be wetted by only those liquids that have low surface tensions; in an oil/water system they tend to have oil-wetting behavior as shown in Figure 4 for hexadecane/water/PTFE. Solids with higher surface energies, such as glass, are wetted by water with its high surface tension in preference to hydrocarbons of low surface tension such as hexadecane. Surface energy values can thus be very important in understanding the wetting phenomenon.

Penn and Bowler (1981) used both the advancing and receding contact angles for a series of liquids to compare the surface energies of solids. They suggested that advancing and receding contact angle data for a series of probe liquids against a solid be presented in bar graph form; describing a "fingerprint" for that solid. The bar graphs for one solid are compared to those for another solid. If the graphs are similar, the solids have similar surface energies and good adhesive performance (Penn and Bowler, 1981). This same technique has been used to understand wetting properties important in the oil industry (Teeters, et al, 1989). Plates of glass, PTFE, dolomite and marble were used. Dolomite and marble were chosen because they represent minerals found in oil reservoirs. Glass and PTFE were investigated because they represent high and low surface energy solids respectively and are good model systems for data comparisons. The liquids used ranged from water at 72.6 dyne/cm to hexadecane at 27.6 dyne/cm (Penn and Bowler 1981).

Figure 14 shows the bar graph presentation of these data. The abscissa of the graph is an ordered listing of the surface tensions of the probe liquids. Several runs of each liquid/solid system were averaged. The bottom of each bar is the cosine of the advancing contact angle and the top is the cosine of the receding angle of the liquid/solid system. The dolomite and marble had very similar hysteresis responses while the glass and PTFE were much different. This corresponds well with the hybrid wetting seen for dolomite and marble in a hexadecane/water system as compared with the water-wetting behavior of glass and the oil-wetting nature of PTFE in the same liquid/liquid system. The importance of this type of surface characterization has been shown in the marble/glass comparison above. The two solids exhibited different wetting cycles as would be predicted from the work presented here. From the similarity of the bar graphs for marble and dolomite, we believe that dolomite must have a surface energy near that of marble. The very oil-wetting PTFE surface is easily distinguished from the hybrid-wetting marble and dolomite and the water-wetting glass. Studies such as these make it possible to more fully characterize the wetting behavior of reservoir rock.

SUMMARY

The work reported here demonstrates the potential for this method. Characterization of individual oil/brine pairs is important for the evaluation of each reservoir. The system can be used to examine components of crude oils at various conditions to determine the surface activity of each cut of the oil. The effects of contaminants can be examined systematically on fluid pairs of known wettability. In a laboratory environment, it is very easy to control the concentration of the contaminant and examine the effect as a function of temperature and to a certain extent pressure. The pH of the brine should affect the wetting character, particularly when the zeta potential crosses a zero point of charge.

Unlike the sessile drop between crystal plates, the dynamic Wilhelmy plate technique allows the use of heterogeneous surfaces. Such a surface may give more realistic values of wettability than homogeneous single crystals. Results from attempts to use porous sandstone and limestone have been difficult to interpret, but a procedure might be found for using actual preserved formation rock as the solid in the dynamic Wilhelmy method. With a preserved rock sample from the formation and reservoir crude oil and formation brine at reservoir temperature and pressure, the closest approximation to a reservoir wettability measurement could be made in the laboratory. The dynamic Wilhelmy device has also been used to determine the degree of wettability alteration of quartz plates after vapor phase silation (Takach, et al, 1989).

Laboratory measurements of relative permeability show hysteresis in the oil phase for water-wet systems, and vice versa for oil-wet systems. Some systems show hysteresis in both phases. The dynamic Wilhelmy device could be used to examine such systems. We believe there may be a correlation between the hybrid wetting behavior of some crude oils and the hysteresis in relative permeability tests. This is an area to which attention must be directed.

NOTATION

g - gravitational acceleration
p - perimeter of plate in Wilhelmy test
B - buoyant force
F - force on Wilhelmy plate
ΔG_S - Gibbs surface free energy
N_c - capillary number
V - fluid velocity
γ - surface tension or interfacial tension
Θ - contact angle
μ - viscosity

Subscripts

A - air
O - oil
W - water or brine
S1 - solid/phase 1 interface
S2 - solid/phase 2 interface
12 - phase 1/phase 2 interface

REFERENCES

Adamson, A. W., 1976, Physical Chemistry of Surfaces, 3rd ed., Wiley-Interscience, New York, p. 339-345.

Amott, E., 1959, Observations relating to the wettability of porous rock, Trans. AIME, v. 216, p. 156-62.

Andersen, M. A., Thomas, D. C., Teeters, D., 1988, A new formation wettability test: The dynamic Wilhelmy plate wettability technique, 1988 SPE/DOE Enhanced Oil Recovery Symposium, SPE Preprint 17368, p. 529-37.

Anderson, W. G., 1986a, Wettability literature survey - Part 1: Rock/oil/brine interactions, and the effects of core handling on wettability, JPT, v. 38(10), p. 1125-49.

-----, 1986b, Wettability literature survey - Part 2, Wettability measurement, JPT, v. 38(11), p. 1246-62.

-----, 1986c, Wettability literature survey - Part 3, The effects of wettability on the electrical properties of porous media, JPT, v. 38(12), p. 1371-78.

-----, 1987a, Wettability literature survey - Part 4, The effects of wettability on capillary pressure, JPT, v. 39(10), p. 1283-1300.

-----, 1987b, Wettability literature survey - Part 5: The effects of wettability on relative permeability, JPT, v. 39(11), p. 1453-68.

-----, 1987c, Wettability literature survey - Part 6: The effects of wettability on waterflooding, JPT, v. 39(12), p. 1605-22.

Donaldson, E. C., Thomas, R. D., and Lorenz, P. B., 1969, Wettability determination and its effect on recovery efficiency, SPEJ (March), p. 13-20.

Hjelmeland, O. S., and Larrondo, L. E., 1986, Experimental investigation of the effects of temperature, pressure, and crude oil composition on interfacial properties, SPE Reservoir Eng., v. 1(4), p. 321-328.

McCaffery, F. G., 1972, Measurement of interfacial tensions and contact angles at high temperature and pressure, J. Can. Petrol. Technol., v. 11, p. 26-32.

Penn, L. S. and Bowler, E. R., 1981, A new approach to surface energy characterization for adhesive performance prediction, Surf. Interface Anal., v. 3, p. 161-4.

Pike, F. P., and Thakkar, C. R., 1976, Interfacial tension measurement by an improved Wilhelmy technique, Colloid and Interface Science, Kerker, M. (ed.), Academic Press, v. 3, p. 375-402.

Potter, G. F., 1987, The effects of CO_2 flooding on wettability of west texas dolomitic formations (figure 5), 1987 SPE Annual Technical Conference and Exhibition, SPE Preprint 16716, p. 183-93.

Stalkup Jr., F. I., 1983, Miscible Displacement, Monograph Series 8, Society of Petroleum Engineers.

Takach, Nicholas E., Bennett, Lori B., Andersen, Mark A., Thomas, David C., 1989, Generation of oil-wet model sandstone surfaces, International Symposium on Oilfield Chemistry, SPE Preprint 18465.

Teeters, Dale, Wilson, Joel F., Andersen, Mark A., and Thomas, David C., 1988a, A dynamic Wilhelmy plate technique used for wettability evaluation of crude oils, J. Colloid Interface Sci., v. 126, in press.

Teeters, Dale, Smith, B., Andersen, Mark A., and Thomas, David C., 1988b, Surface studies related to the oil industry using the dynamic Wilhelmy plate technique, Symposium on Advances in Oil Field Chemistry, Toronto, American Chemical Society Preprints, p. 146-51.

Teeters, Dale, Andersen, Mark A., and Thomas, David C., 1989, Formation wettability studies using the dynamic Wilhelmy plate technique, ACS Symposium Series, Advances in Oil Field Chemistry, in press.

Thomas, D. C., Hsing, H. H., and Menzie, D. E., 1984, Evaluation of core damage caused by oil-based drilling and coring fluids, 1984 SPE Annual Technical Conference and Exhibition, SPE Preprint 13097.

Treiber, L. E., Archer, D. L., Owens, W. W., 1972, A laboratory evaluation of the wettability of fifty oil producing reservoirs, SPEJ (Dec.), p. 531-40.

Wilhelmy, L., 1863, Ueber die abhangigkeit der capillaritats-constanten des alkohols von substanz und gestalt des benetzten festen korpers, Ann. Physik., v. 119(6), p. 177-217.

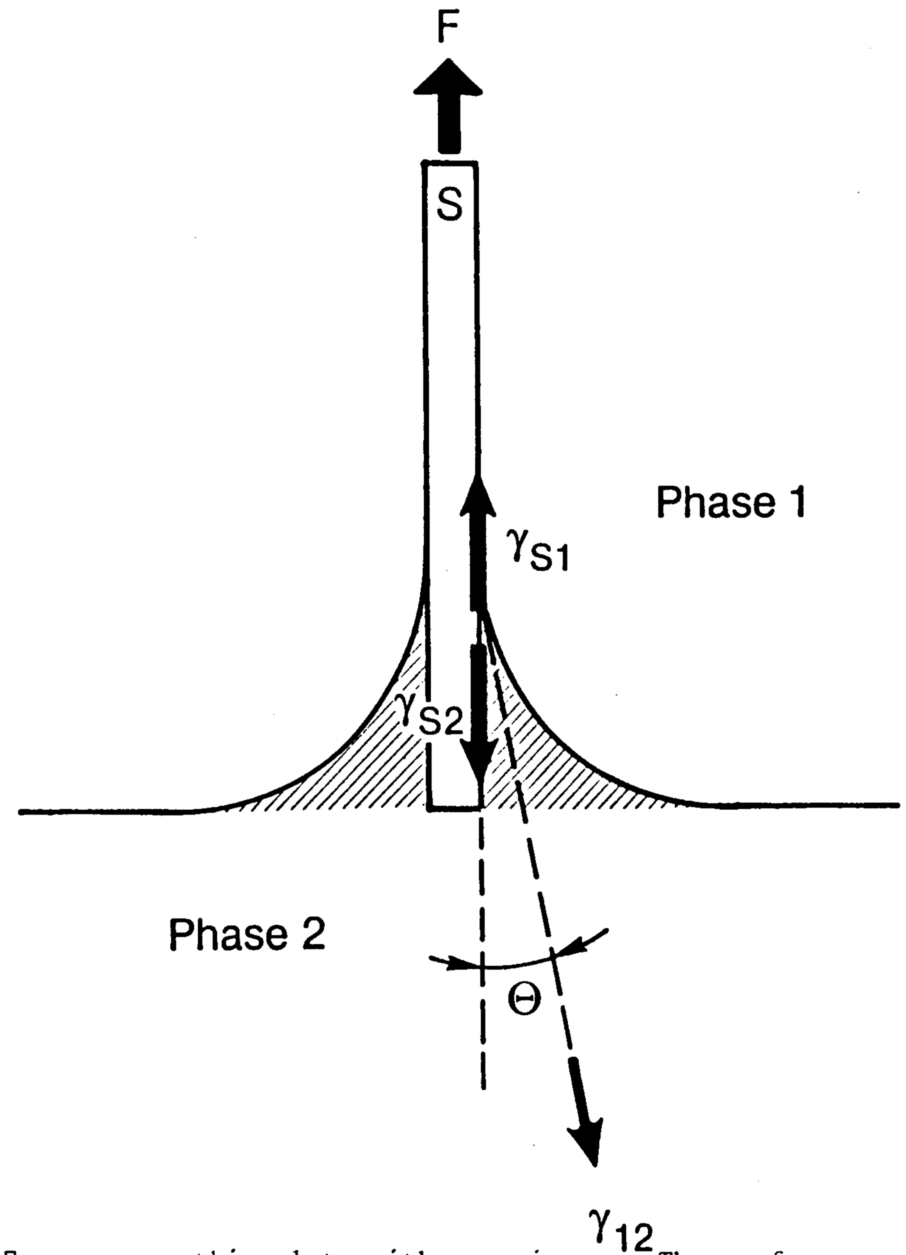

Figure 1: Forces on a thin plate with a meniscus. The surface tensions are γ_{S1} and γ_{S2} for the solid against fluids 1 and 2 respectively, and γ_{12} for the interfacial tension between the liquids at contact angle Θ. The force on the plate F is measured by a microbalance.

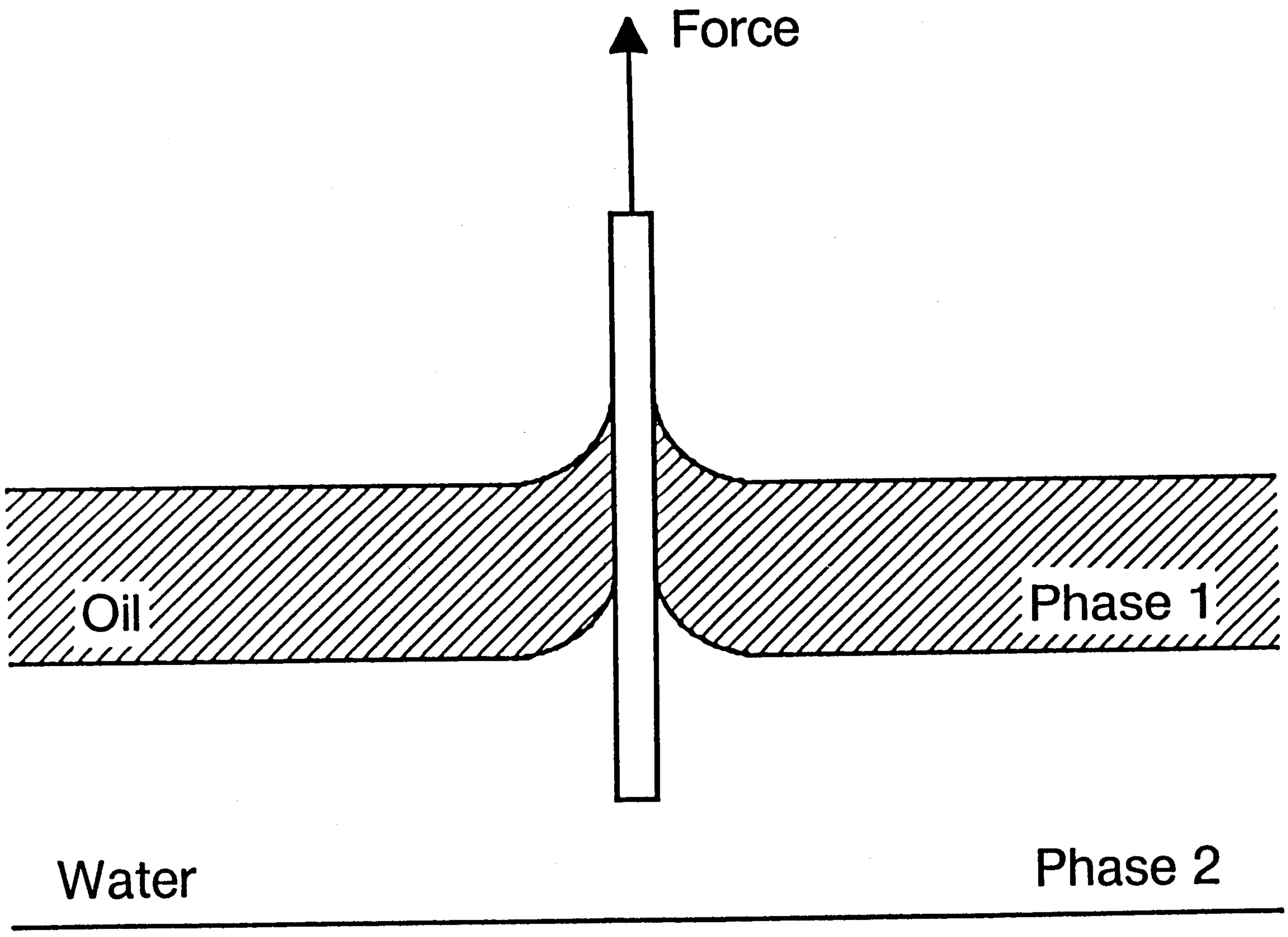

Figure 2: Schematic showing water-wetting behavior in an oil/water system.

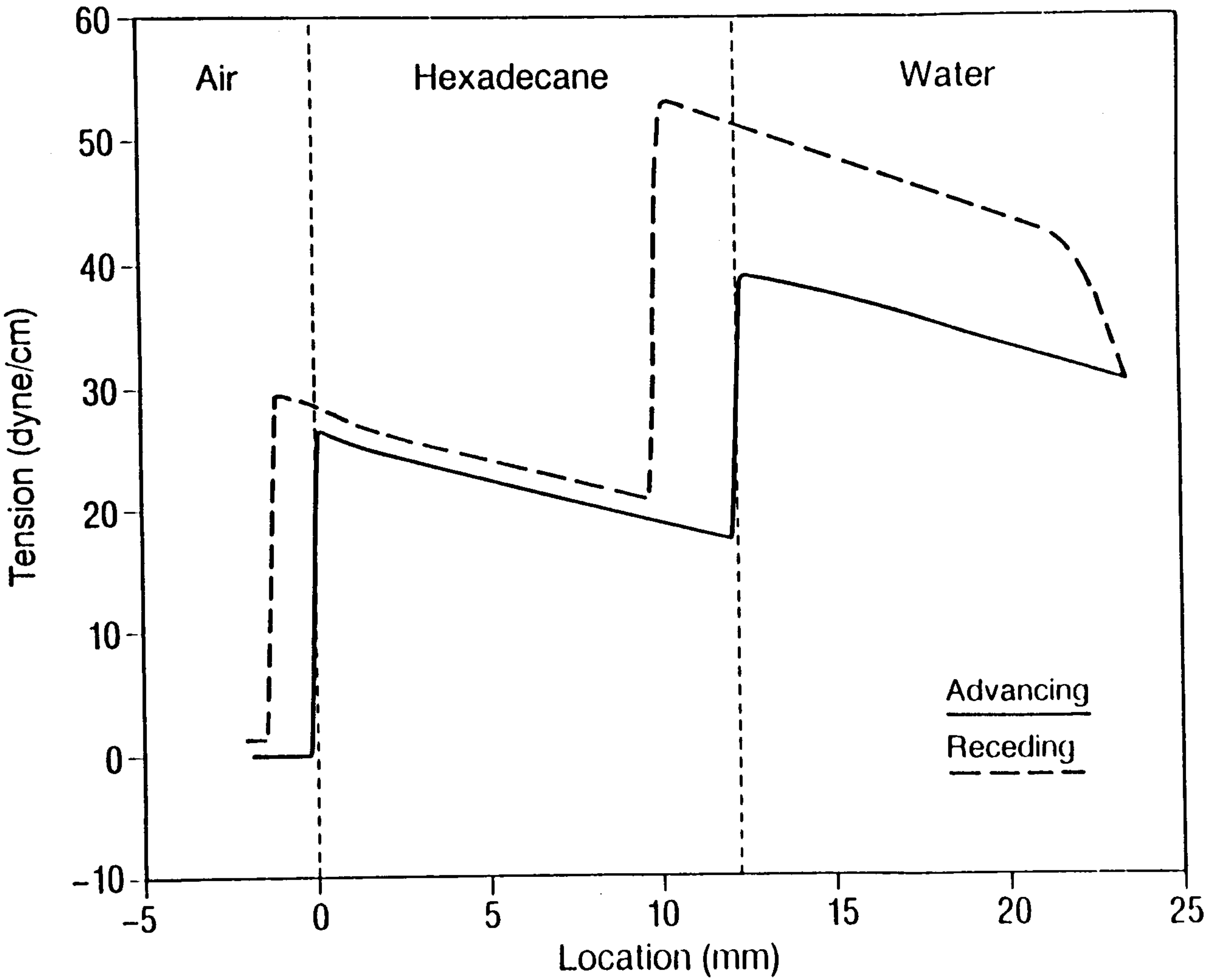

Figure 3: Water-wet cycle for hexadecane/water/glass system. The vertical axis has been converted to tension units. (from Teeters, et al, 1988a.)

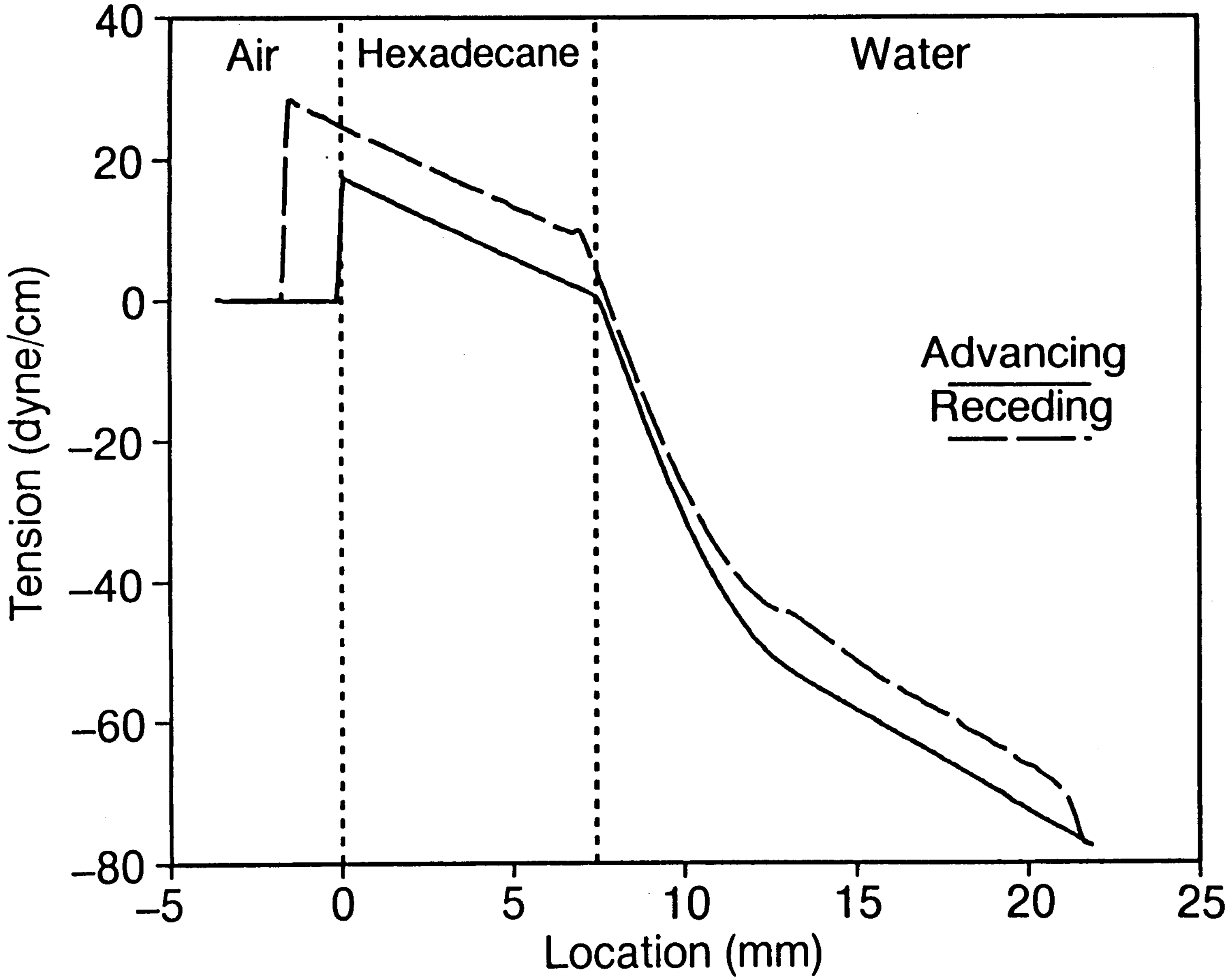

Figure 4: Oil-wet cycle for hexadecane/water/PTFE system. (from Teeters, et al, 1988a.)

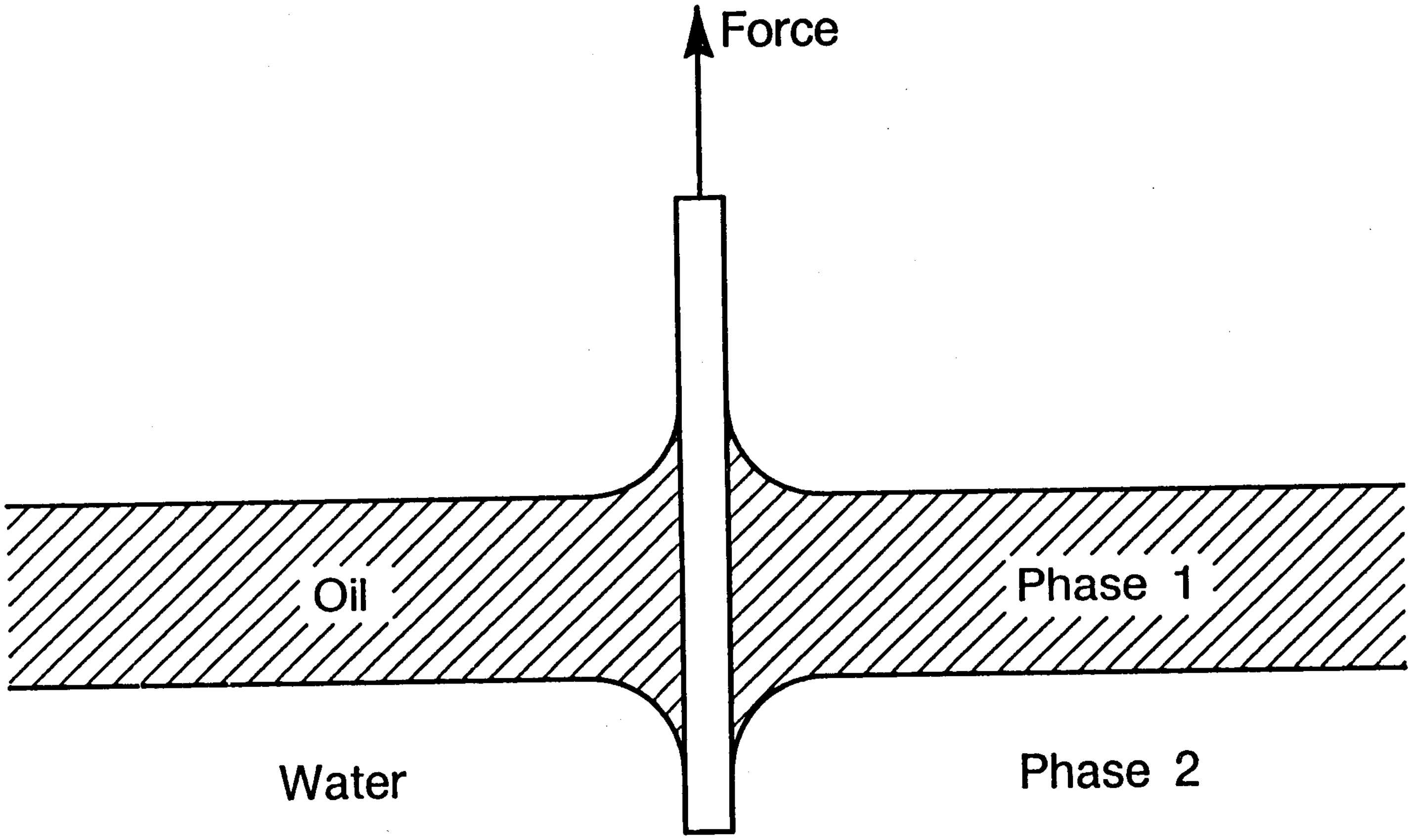

Figure 5: Schematic showing oil-wetting behavior in an oil/water system. (from Andersen, et al, 1988.)

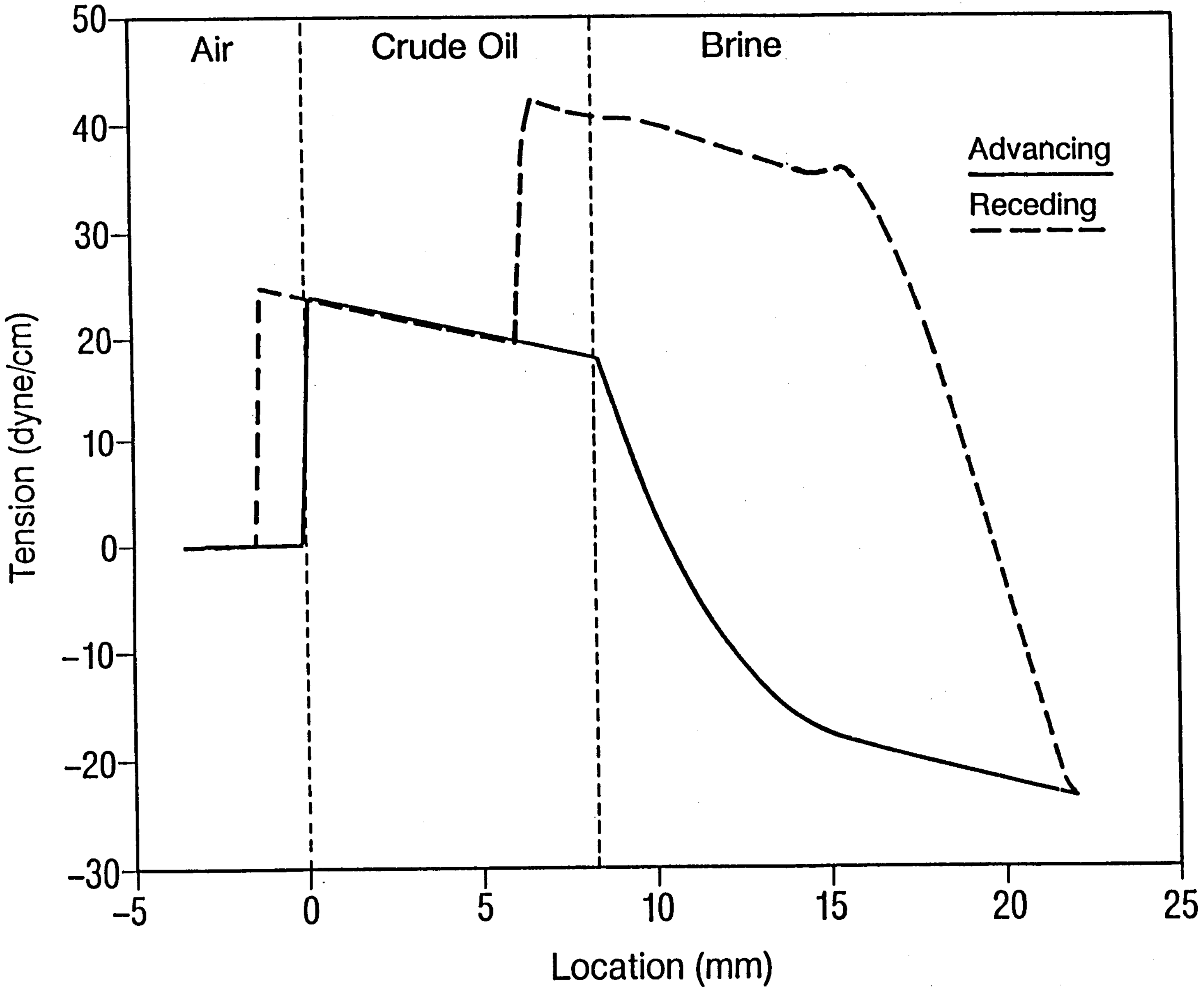

Figure 6: Hybrid-wetting cycle for crude oil/brine/glass system.

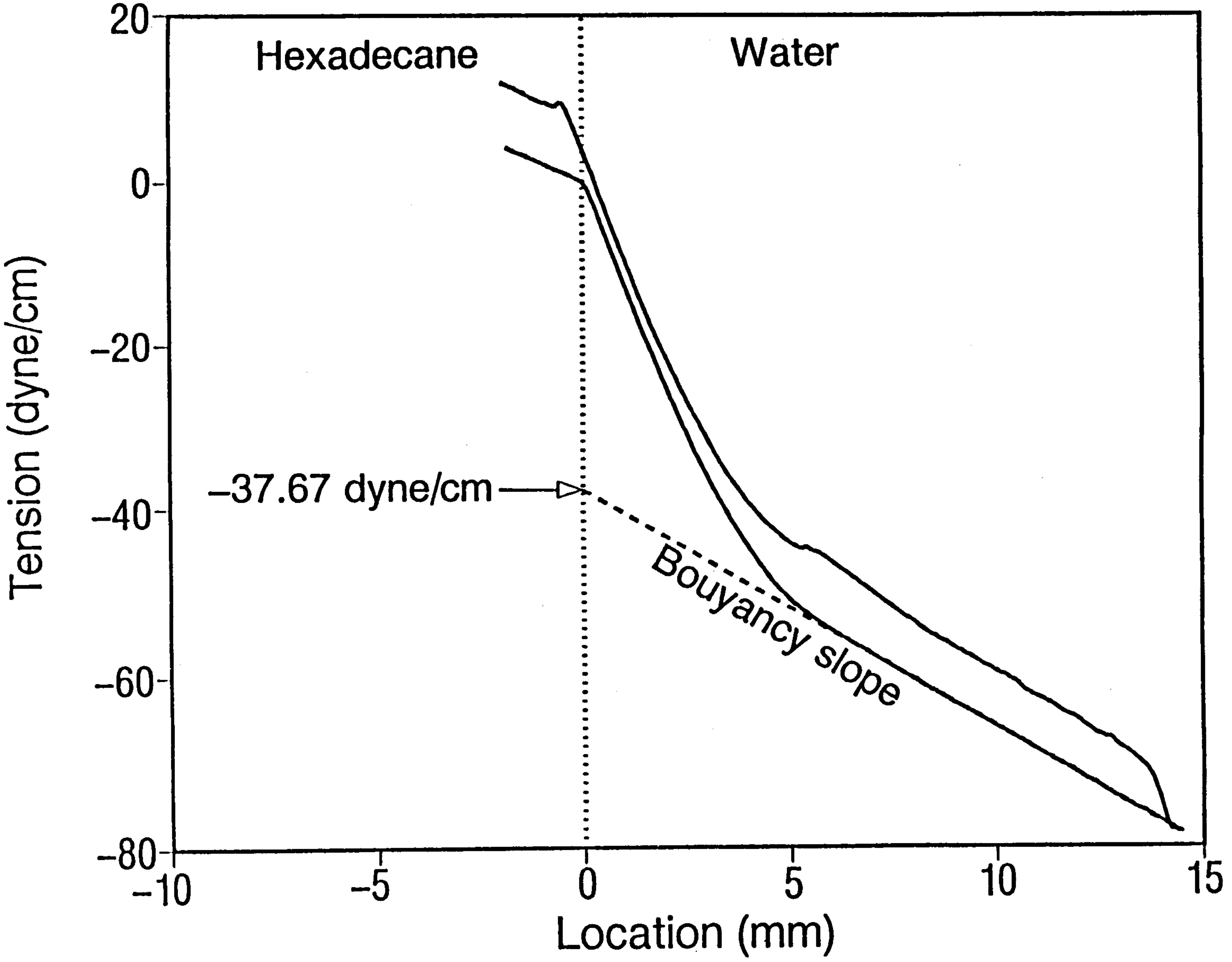

Figure 7: To calculate adhesion tension for an oil-wet system, extrapolate the buoyancy slope in the water phase to the bulk interface. The step change is the adhesion tension.

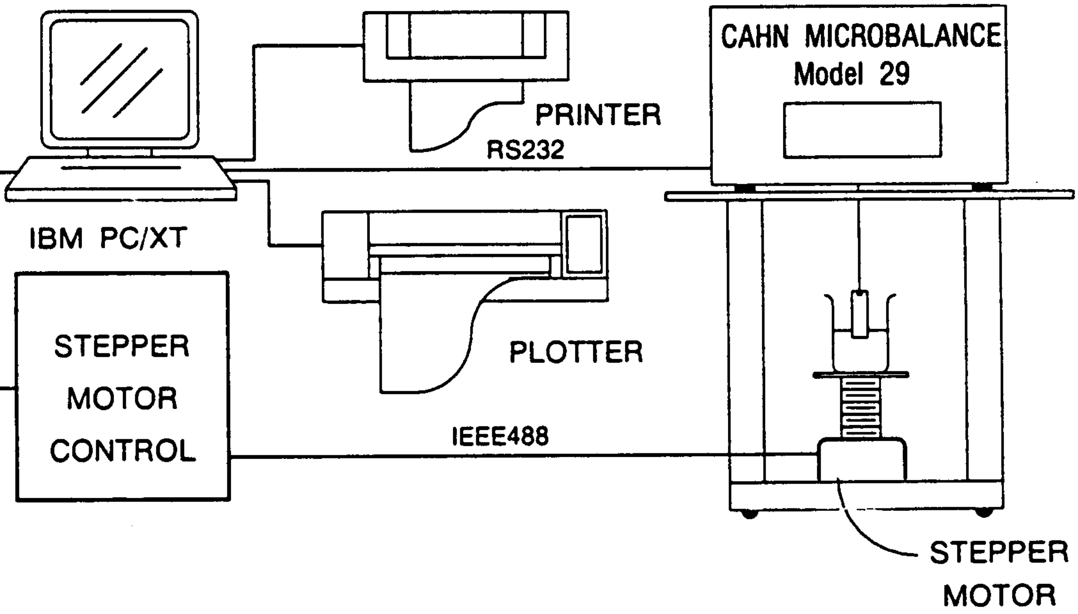

Figure 8: Schematic of equipment used for computer control of dynamic Wilhelmy device. (from Teeters, et al, 1989.)

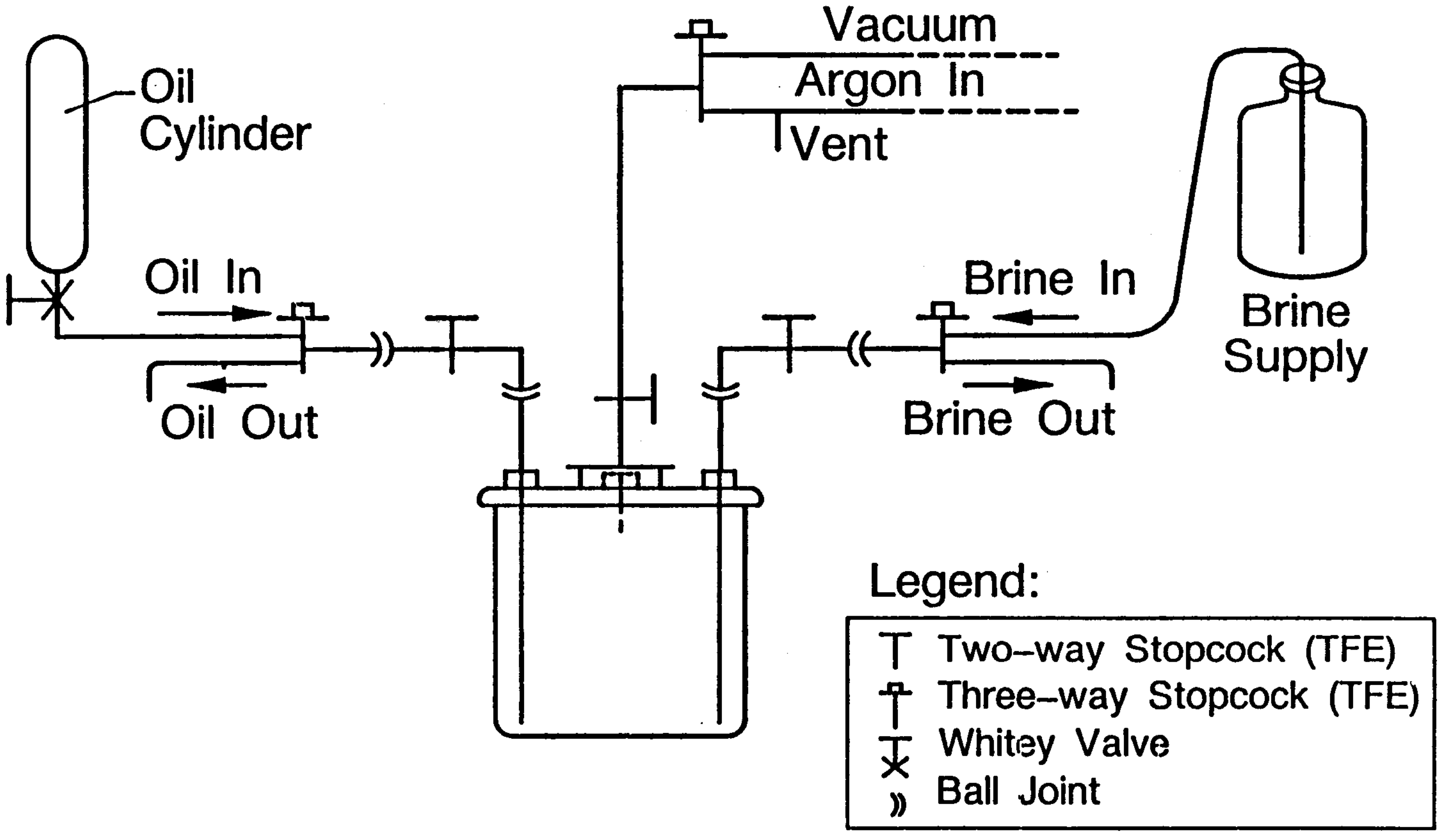

Figure 9: Oil, brine and gas connections for anaerobic vessel. (from Andersen, et al, 1988.)

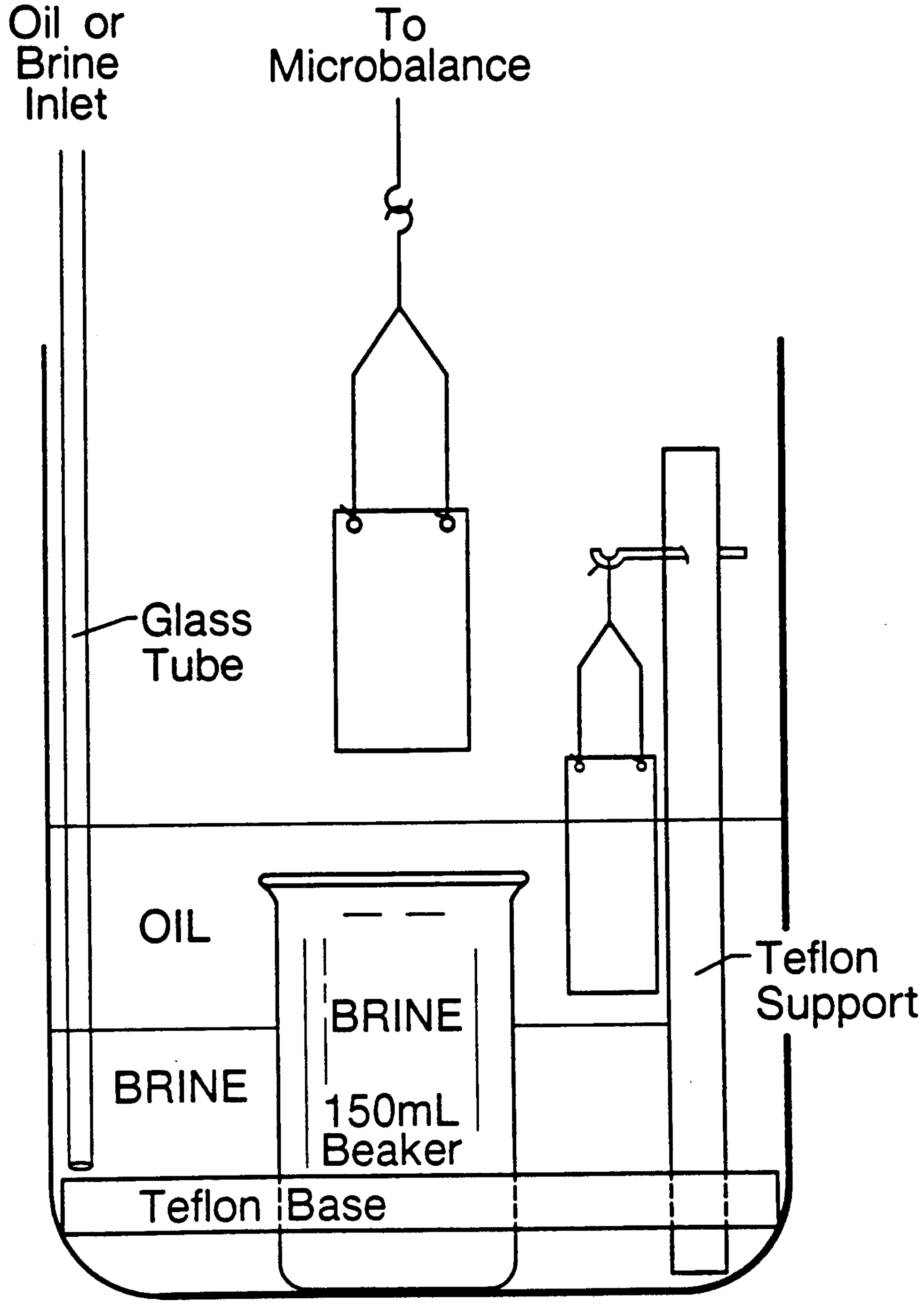

Figure 10: Arrangement of components inside anaerobic vessel, with thick layer of oil for equilibrating and a thin layer under the microbalance for performing the Wilhelmy plate test. The lid to the vessel is not shown. (from Andersen, et al, 1988.)

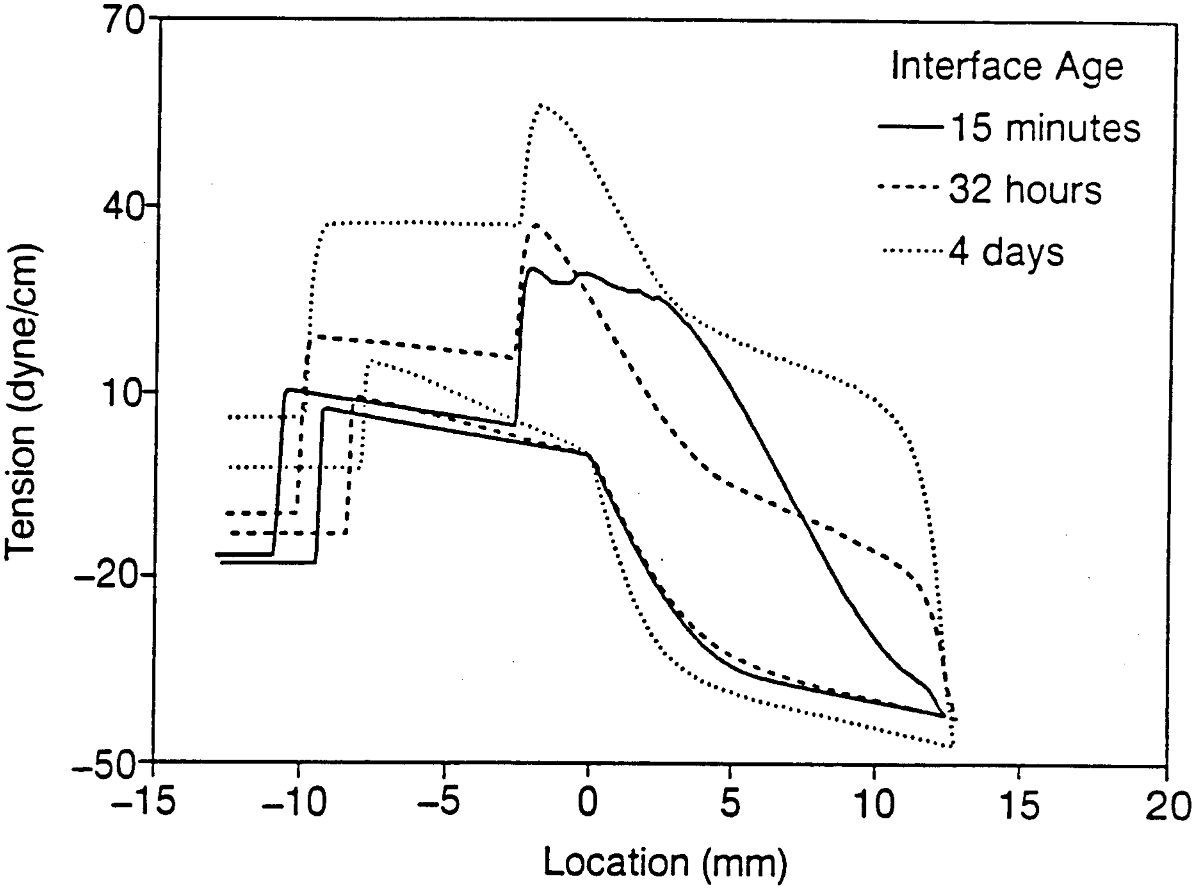

Figure 11: Crude oil from cylinder SS1473 showing unusual behavior when exposed to air. (from Andersen, et al, 1988.)

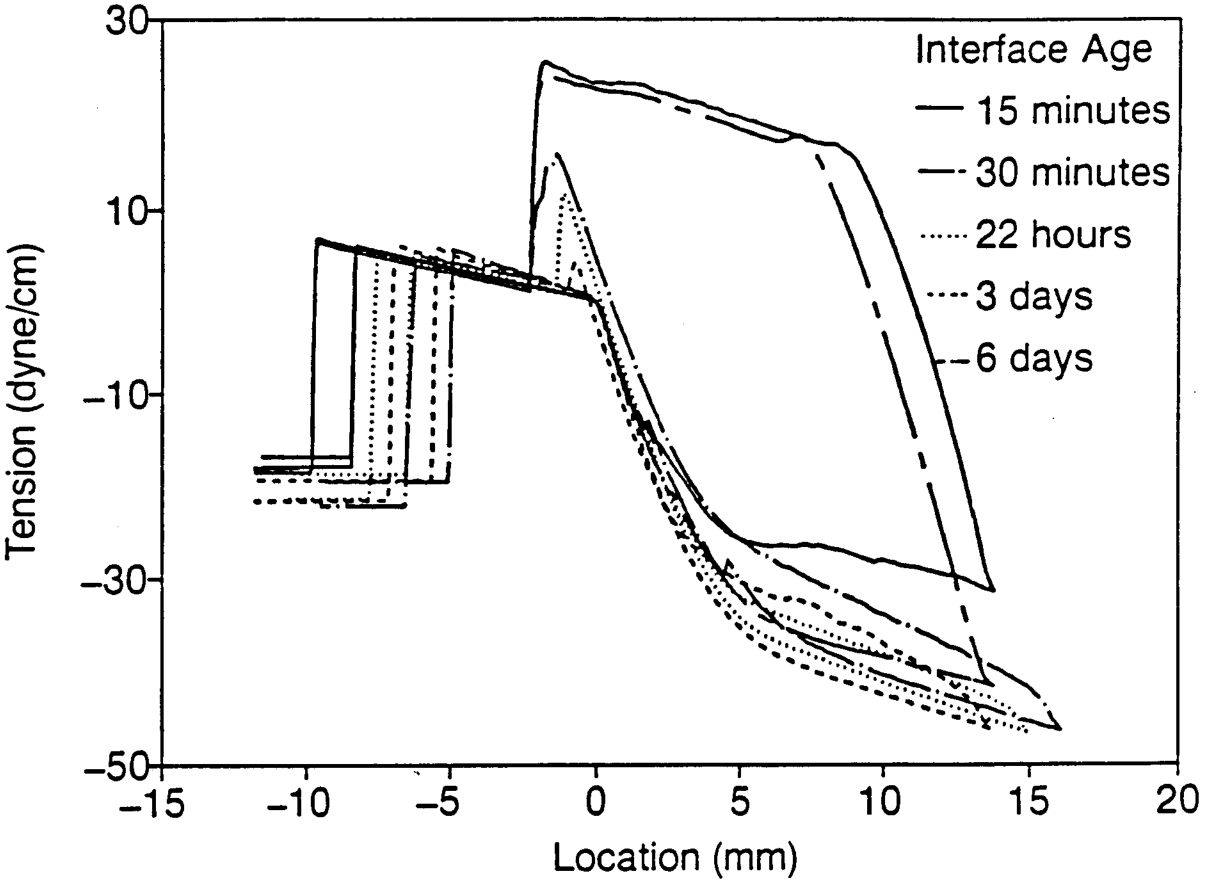

Figure 12: Crude oil from cylinder SS1473 showing reproducible behavior when tested under argon atmosphere. (from Andersen, et al, 1988.)

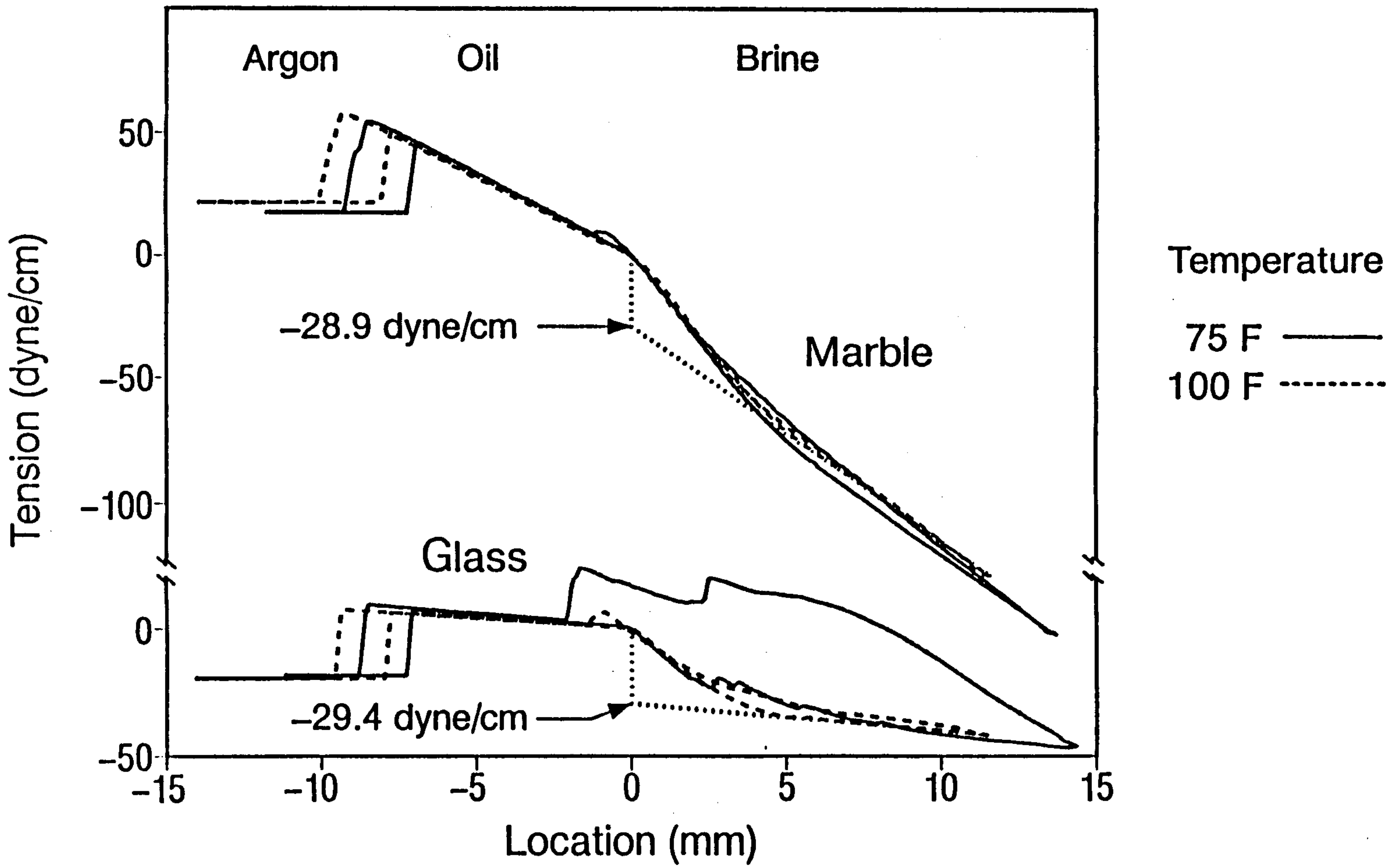

Figure 13: Comparison of crude oil wetting on glass and marble at room temperature and 100°F. The dotted line is the extrapolation of the constant buoyancy line to the oil water interface for determination of the adhesion tension.

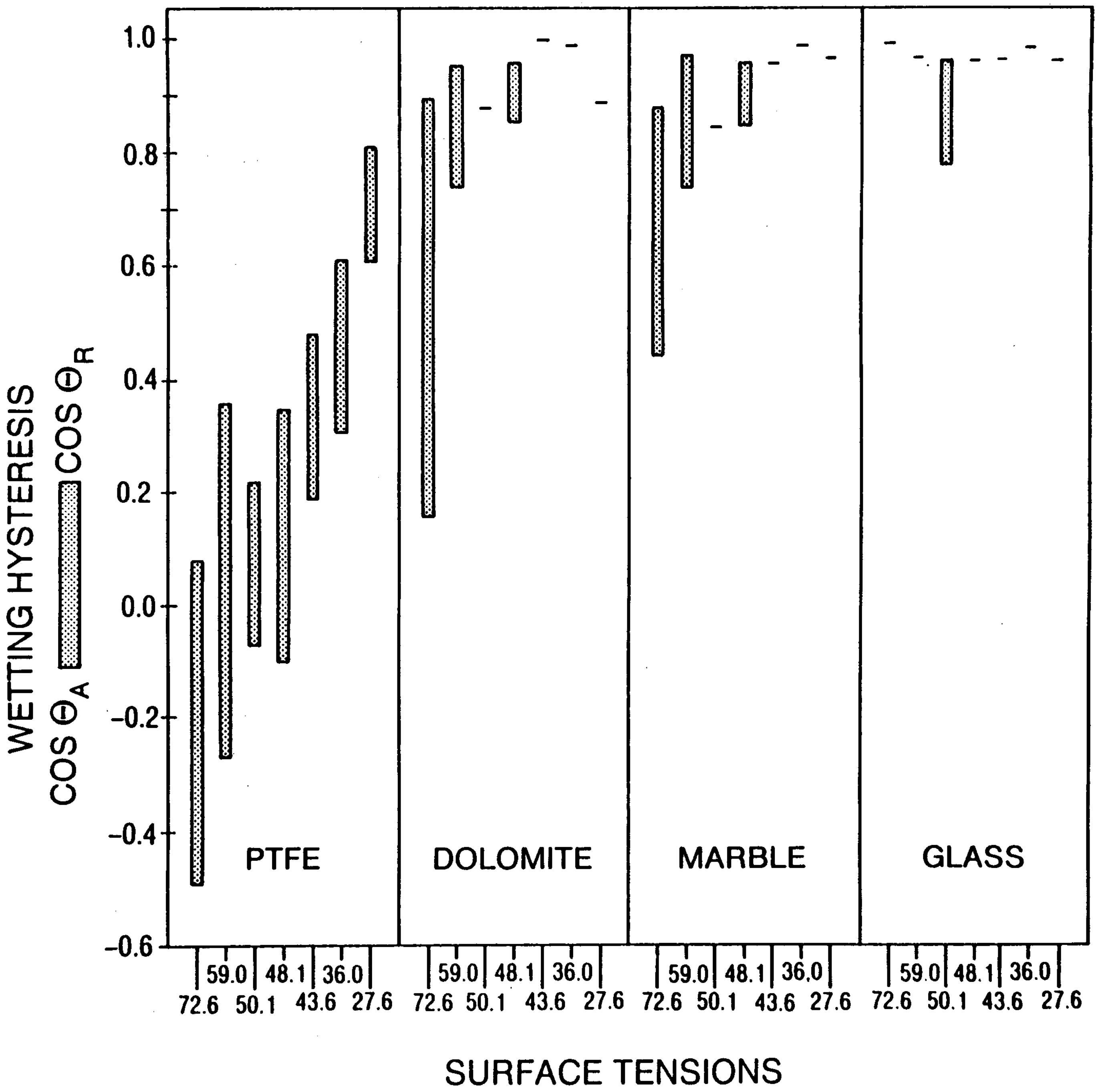

Figure 14: Surface adhesion tension fingerprints of several solids against a series of liquids. Dolomite and marble show similar behavior, which differs from PTFE and glass. (from Teeters, et al, 1988a.)