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ABSTRACT

Reservoir wettability impacts the success of oil recovery by waterflooding and other methods. To understand wettability and its alteration, thin-film forces in solid-aqueous-oil systems must be elucidated. Upon rupture of thick aqueous films separating the oil and rock phases, asphaltene components in the crude oil adsorb irreversibly on the solid surface, changing it from water-wet to oil-wet. Conditions of wettability alteration can be found by performing adhesion tests, in which an oil droplet is brought into contact with a solid surface. Exceeding a critical capillary pressure destabilizes the film, causing spontaneous film rupture to a molecularly adsorbed layer and oil adhesion accompanied by pinning at the three-phase contact line.

We conduct adhesion experiments similar to those of Buckley and Morrow and simultaneously examine the state of the underlying thin film using optical microscopy and microinterferometry. Aqueous thin films between an asphaltic Orcutt crude oil and glass surfaces are studied as a function of aqueous pH and salinity. For the first time, we prove experimentally that strongly water-wet to strongly oil-wet wettability alteration and contact-angle pinning occur when thick aqueous films thin to molecularly adsorbed films and when the oil phase contains asphaltene molecules.

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INTRODUCTION

Reservoir wettability is an essential factor in enhancing oil recovery, significantly influencing oil displacement and multiphase-flow behavior. Different portions of the pore walls in a porous medium may exhibit different affinities for oil and water. For smooth, homogeneous solid surfaces, wettability is generally characterized by the macroscopic contact angle at the line of three-phase intersection. Contact angles measured through the water phase are approximately 0° for strongly water-wet surfaces, and near 180° for oil-wet surfaces, with intermediate wettability producing contact angles ranging from 45° to 135° (1). It is now recognized that at the molecular level, oil versus water wettability is best understood by examining the thin films of water separating the oil and rock surfaces (2). According to Frumkin and Derjaguin, it is the disjoining forces within the thin film that give rise to the contact angle, θ (3,4):

$$\cos \theta - 1 = \frac{1}{\sigma} \left[\int_h^\infty \Pi(\xi) d\xi - h\Pi(h) \right], \quad (1)$$

where $\Pi(h)$ denotes the disjoining pressure as a function of the equilibrium film thickness, h , and where σ denotes the bulk oil/water interfacial tension.

A generic disjoining pressure isotherm for an aqueous film is shown in Fig. 1. Disjoining pressure is typically comprised of three additive terms: attractive van der Waals forces, repulsive electrostatic forces, and short-range, strongly repulsive steric or hydration forces. Film (meta)stability demands that $\Pi > 0$ and $d\Pi/dh < 0$. Thus, stable films occur over two distinct thickness ranges: a thick or common film reflecting electrostatic interactions and a molecularly thin or adsorbed film reflecting specific short-range interactions. Along the outer branch of the isotherm the contact angle is zero, whereas along the inner branch finite contact angles arise, provided that the primary minimum is sufficiently deep (5,6).

Equilibrium film thicknesses in porous media obey the augmented Young-Laplace equation (2-6):

$$P_c = 2C_m\sigma + \Pi(h), \quad (2)$$

where P_c is the capillary pressure (i.e., oil-phase pressure minus water-phase pressure) imposed on the film Plateau borders, and C_m is the mean curvatures of the pore walls over which the films drape. Accordingly, Eqns. 1 and 2 reveal that contact angles in porous media depend on pore shape through pore-wall curvatures and on the oil and water saturations and saturation history through the capillary-pressure curve. Further, contact angles are spatially distributed because of variations of pore shape and pore-wall chemistry. Also from Eqns. 1 and 2, we discover that high capillary pressures (i.e., low water saturations) lead to a shift in wettability of the medium away from completely water-wet whenever Π_{max} is exceeded (cf. Fig. 1).

THEORY FOR MIXED WETTABILITY

Even more dramatic shifts in the wettability of a reservoir medium may occur if the crude oil is highly asphaltic. In 1973, Salathiel showed that asphaltic oils in both model sandstones and reservoir rock at low water contents cause a shift from highly water-wetting to a mixed-wet state in which residual oil saturations are close to zero (7). Salathiel envisioned oil-wet and water-wet regions that are contiguous and sample-spanning. Clean oils do not confer a similar wettability shift (7). Very recently, Kovscek et al. introduced a pore-level model that successfully accounts for the molecular origin of mixed wettability (2). These authors extend Frumkin-Derjaguin theory described above with several unique twists. They argue that thick aqueous wetting films on the outer branch of the disjoining pressure isotherm protect the rock surface from adsorption of water-insoluble asphaltenes. However, once a molecularly thin aqueous film is exposed, when Π_{max} is overwhelmed at low water saturation, disk-like colloidal asphaltene molecules irreversibly adsorb to the solid surface. On those patches of asphaltene

adsorption the surface is completely oil-wet, and the contact line separating oil-wet domains from water-wet domains is pinned and cannot move. Unfortunately, Kavscek et al. present only indirect evidence for the premises of their model (2).

The purpose of this work is to ascertain whether asphaltenic crude oil/aqueous/solid systems actually obey the physical picture painted in the model of Kavscek et al. We examine experimentally the thin aqueous film interposed between an asphaltic crude oil and a glass surface as a function of aqueous solution pH and ionic strength.

EXPERIMENT

Adhesion Tests

Following the pioneering efforts of Morrow et al. (8, 9) and Buckley et al. (10, 11), we perform "adhesion" tests, as illustrated in Fig. 2. A crude oil droplet is grown out of a 1-mm I. D. glass-tipped micrometer syringe in an aqueous solution and contacted with a solid substrate. We employ Orcutt crude oil (molecular weight = 278, API gravity = 22) containing 7.8 weight percent asphaltenes (12). The aqueous solution pH and ionic strength are adjusted with mixtures of sodium carbonate and phosphate buffers. The substrate is soda glass (microscope slides). The droplet is held against the surface for up to an hour and is then slowly retracted. The entire sequence of events is monitored by standard video equipment.

Depending on the solution pH and electrolyte content, one of two processes occurs. At higher pH and lower sodium concentration, the droplet simply detaches reversibly from the glass surface, as illustrated in Fig. 3. In this series of photographs pH = 10.0 and $[Na^+] = 0.01$ M. Contact angles (advancing) are difficult to gauge at this magnification, but they appear close to zero. Conversely, at lower pH and higher electrolyte contents the droplet does not retract along the glass surface and detach, as illustrated in Fig. 4 for pH = 8.0 and $[Na^+] = 0.01$ M. Rather, the contact line pins fixing the drop perimeter. The initially zero contact angle then increases consistent with oil-volume withdrawal until a Rayleigh instability leaves behind a sessile drop on the surface. Morrow et al. (9) and Buckley et al. (10, 11) call this phenomenon oil "adhesion".

Clean oils, such as dodecane and toluene, or deasphalted crude oils, do not adhere to the glass surface. Hence, adhesion of the Orcutt crude oil is primarily a result of the asphaltene component.

Film State

The thin aqueous film separating the oil drop from the glass substrate in Figs. 3 and 4 is best observed in a modified Derjaguin cell (13, 14), where a controlled capillary pressure may be exerted on the film, as shown in Fig. 5. A porous glass frit, drilled with a 1-mm hole, is sealed to the glass substrate and saturated with the aqueous solution of interest. The frit-substrate assemblage is immersed in the aqueous solution, overlaid with crude oil, and sealed in a Plexiglas™ cell. Increasing the gas pressure in the cell forces the oil into the porous-disk cylindrical hole eventually forming a plane-parallel aqueous film adjacent to the glass surface. Film illumination is by a Hg-Xe arc lamp (Oriel) and observation is through a metallurgical microscope objective (10X) and video recording. Film thickness measurements are made possible using thin-film interferometry, following techniques developed by Scheludko (15), with reflected intensities monitored by an RCA photomultiplier tube (not shown in Fig. 5). To date, however, unavoidable particulates on the glass surface have prevented quantitative measurements of h .

RESULTS AND DISCUSSION

Fig. 6 presents an adhesion map (10) summarizing preliminary results of our adhesion tests for the Orcutt oil. Open circles correspond to droplets that reversibly detach from the glass surface (cf. Fig. 3) while closed circles reflect droplets that irreversibly adhere to the glass surface (cf. Fig. 4). The solid line delineates the adhesion/nonadhesion domains obtained by Buckley et al. (10) for a Moutray crude oil. Our results for the Orcutt oil are quite similar to those for the Moutray oil. Low pH and high sodium concentrations lead to adhesion and *vice versa*. The explanation offered by Buckley et al. (10) is identical to that adopted in the model

of mixed wettability proffered by Kavscek et al. (2). Namely, high pH values increase the negative surface charge densities on both the glass/aqueous and oil/aqueous interfaces. High surface charge density along with low ionic strength produces strong repulsive disjoining forces along the outer branch of Fig. 1 per DLVO theory. The resulting thick aqueous film does not allow the water-insoluble asphaltenes to reach the glass surface. Nonadhesion of the oil and a zero contact angle emerge. Conversely, low pH and high ionic strength diminish Π_{\max} collapsing the thick protective aqueous film to a few water molecular layers. Now the asphaltic components irreversibly adsorb. Adhesion, local oil-wettability, and contact-angle pinning emerge.

Fig. 7 sketches the visually observed state of the aqueous film in the Derjaguin cell corresponding to the nonadhering oil droplet of Fig. 3. Film diameter is about 0.5 mm, and the applied capillary pressure is about 500 Pa. Dark and light circles near the film edge are the Newton rings of the film meniscus. The central, gray shading defines a plane-parallel aqueous film of about 60 nm in thickness. Dispersed white objects in the figure correspond to very thick water films covering over unremoved particles on the glass surface. Upon lowering the applied capillary pressure, the film reversibly thickens, and new films may repeatedly be reformed.

Fig. 8 sketches the film state underlying the adhering oil droplet in Fig. 4, again garnered from the Derjaguin cell. In this case (i.e., pH = 8.0 and $[\text{Na}^+] = 0.01 \text{ M}$) no stable, thick water film is found. Rather, the film quickly ruptures, and oil components contact the surface. The dark, black regions in Fig. 8 correspond to deposited crude oil. As the film collapses and oil invades, thick patches of water are trapped, as shown by the white regions in Fig. 8. Trapped water pockets at least 100 nm thick are unable to escape over the oil-wet glass surface. The jagged edge of the film corresponds to the initial uneven breakup of the aqueous film. It is along this perimeter that contact-angle pinning occurs. As the oil phase is retracted by reducing the capillary pressure, the appearance of Fig. 8 is unchanged. An oily scum remains on the glass surface.

Figs. 7 and 8 confirm the basic physical picture assumed by Kavscek et al. (2) in their model of reservoir mixed wettability. Namely, thick water films, stabilized by electrostatic

interactions, between crude oil and the pore walls reflect a completely water-wet medium. However, when the thick aqueous films rupture due to increased capillary suction at low water saturations, asphaltene components in the oil irreversibly adsorb. The result is local oil-wet surfaces, contact-angle pinning, and a mixed-wet medium.

CONCLUSIONS

The properties of thin liquid films, as embodied in the disjoining pressure isotherm, determine the relative oil/water wettability of solid surfaces. Frumkin-Derjaguin theory is an especially useful tool for understanding the wettability of porous media because it explicitly accounts for the nature of the medium. Wettability is a local pore-wall issue and cannot be assessed solely from classical contact-angle measurements. When asphaltenes are present in the oil, dramatic changes in wettability can occur whenever the thick aqueous wetting films rupture permitting asphaltene adsorption. For the first time, this work directly confirms the physical state of the thin oil/water/solid films that originate mixed wettability. It remains to provide quantitative measurements of the disjoining pressure isotherms.

ACKNOWLEDGMENT

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REFERENCES

1. Craig, F.F. (1971). The Reservoir Engineering Aspects of Waterflooding, Society of Petroleum Engineers of AIME, New York, 12-19.
2. Kovsky, A.R., H. Wong, and C.J. Radke (1993). "A Pore-Level Scenario for the Development of Mixed-Wettability in Oil Reservoirs," *AIChE Journal*, **39**, No. 6, in press.
3. Frumkin, A.N. (1938). "Wetting and Adherence of Bubbles," *Zh. Fiz. Khim.*, **12**, 337-345.
4. Derjaguin, B.V. (1940). "Theory of Capillary Condensation and Related Capillary Effects.

- Calculation of Spreading Action of Polymolecular Liquid Films," *Zh. Fiz. Khim.*, **14**, 137-147.
5. Hirasaki, G.J. (1991). "Thermodynamics of Thin Films and Three-Phase Contact Regions," in Interfacial Phenomena in Petroleum Recovery, ed. N.R. Morrow, Marcel Dekker, Inc., New York, Ch. 2., 23-76.
 6. Churaev, N.V. (1988). "Wetting Films and Wetting," *Revue Phys. Appl.*, **23**, 975-987.
 7. Salathiel, R.A. (1973). "Oil Recovery by Surface Film Drainage in Mixed-Wettability Rocks," *J. Pet. Tech.* **25**, No. 10, 1216-1224.
 8. Morrow, N.R. (1990). "Wettability and Its Effect on Oil Recovery," *J. Pet. Tech.*, **42**, No. 12, 1476-1484.
 9. Morrow, N.R., H.T. Lim, and J.S. Ward (1986). "Effect of Crude-Oil-Induced Wettability Changes on Oil Recovery," *Soc. Pet. Eng. Form. Eval.*, **1**, No. 1, 89-103.
 10. Buckley, J.S., K. Takamura, and N.R. Morrow (1989). "Influence of Electrical Surface Charges on the Wetting Properties of Crude Oils," *Soc. Pet. Eng. Res. Eng.*, **4**, No. 3, 332-340.
 11. Buckley, J.S. and N.R. Morrow (1990). "Characterization of Crude Oil Wetting Behavior by Adhesion Tests," SPE 20263, presented at SPE/DOE Symposium on Enhanced Oil Recovery, Tulsa, OK, 871-877.
 12. Robertson, S. (1992), private communication.
 13. Derjaguin, B.V., Z.M Zorin, N.V. Churaev, and V.A. Shishin (1978). "Examination of Thin Layers on Various Solid Substrates," in Wetting, Spreading, and Adhesion, ed. J.G. Padday, Academic Press, London, Ch. 9, 201-212.
 14. Zorin, Z.M., I.N. Kornil'ev, and N.V. Churaev (1984). "Transition of Metastable Wetting Films of Aqueous Solutions Into a Thermodynamically Stable State," *Kolloid. Zhurnal*, **46**, 437-443.
 15. Scheludko, A. (1957). "Über das Ausfließen der Lösung aus Schaumfilmen," *Kolloid Zeit.*, **155**, 39-44.

FIGURE CAPTIONS

Figure 1. Generic disjoining pressure isotherm.

Figure 2. Apparatus for adhesion tests.

Figure 3. Nonadhesion of Orcutt crude oil to glass surface. Aqueous pH = 10.0 and $[\text{Na}^+] = 0.01 \text{ M}$.

(a) Initial contact (b) Retraction from surface (c) Droplet nonadherence and clean surface.

Figure 4. Adhesion of Orcutt crude oil to glass. Aqueous pH = 8.0 and $[\text{Na}^+] = 0.01 \text{ M}$.

(a) Initial contact (b) Withdrawal to instability (c) Droplet adherence upon retraction

Figure 5. Apparatus for thin-film measurements.

Figure 6. Adhesion map of Orcutt crude oil. Open circles correspond to drop nonadhesion while

filled circles correspond to adhesion. The solid line gives results for a Moutray crude oil (10).

Figure 7. A stable equilibrium aqueous film about 60 nm in thickness (central grey region).

Aqueous pH = 10.0 and $[\text{Na}^+] = 0.01 \text{ M}$. Small white objects indicate particulates on the surface.

Figure 8. Oil adhering to glass surface after aqueous film rupture (dark regions). White

areas correspond to very thick ($> 100 \text{ nm}$) water pockets trapped on the surface.

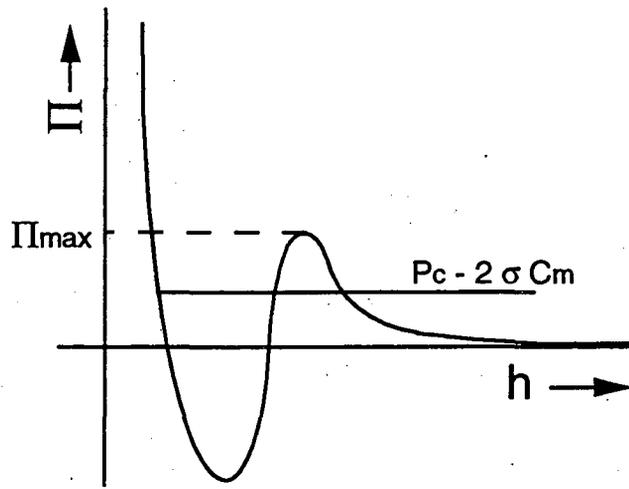


Figure 1

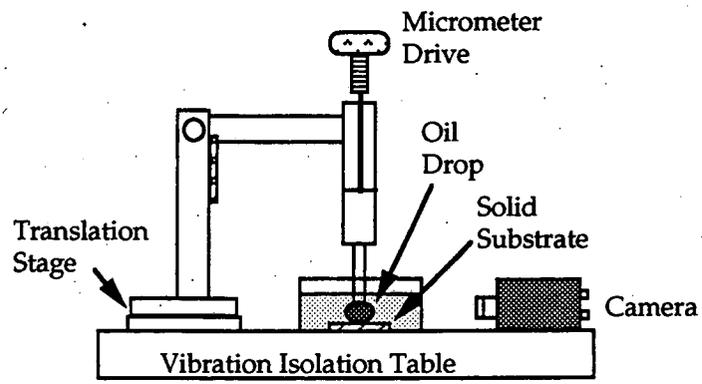


Figure 2

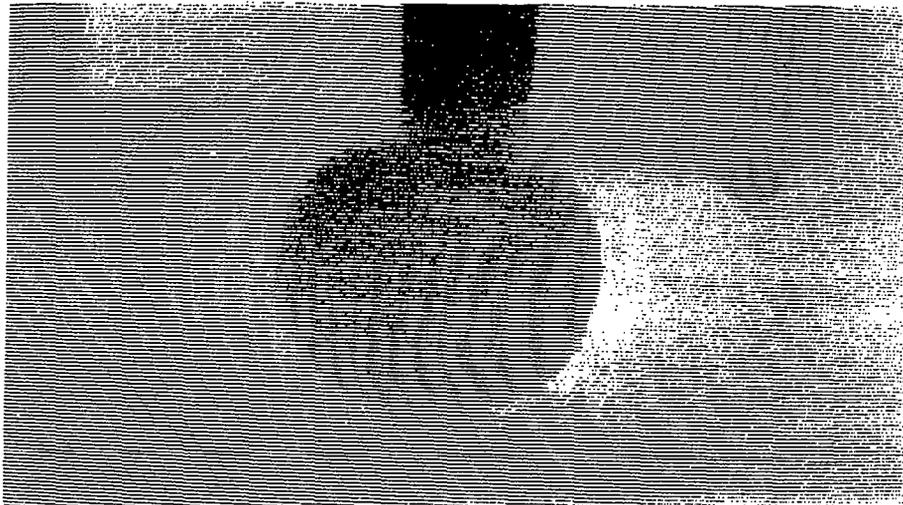


Figure 3a

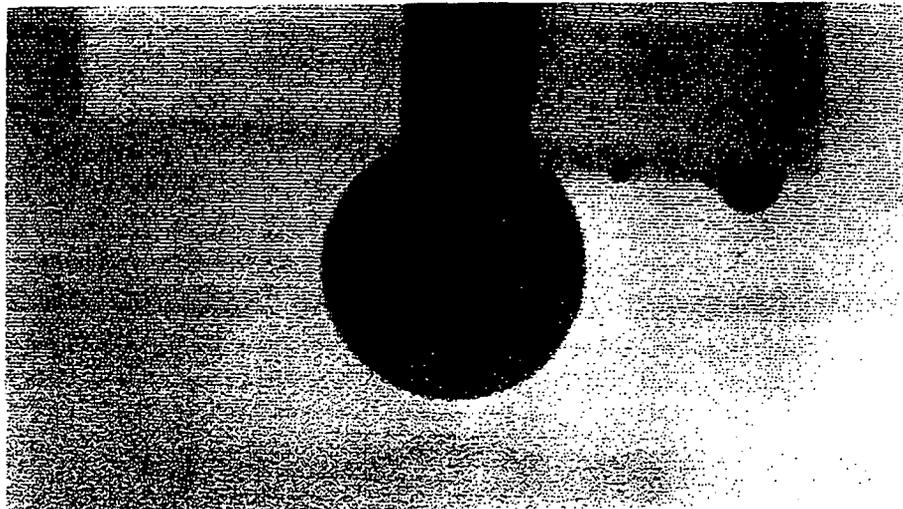


Figure 3b

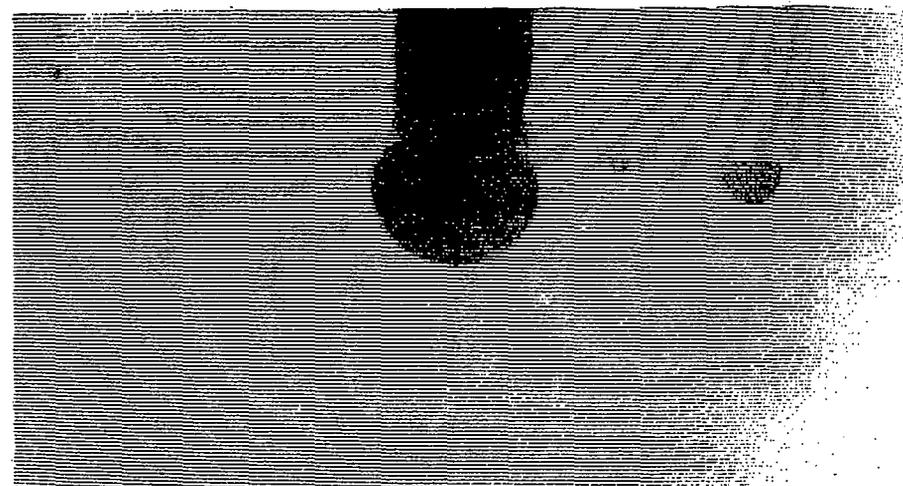


Figure 3c

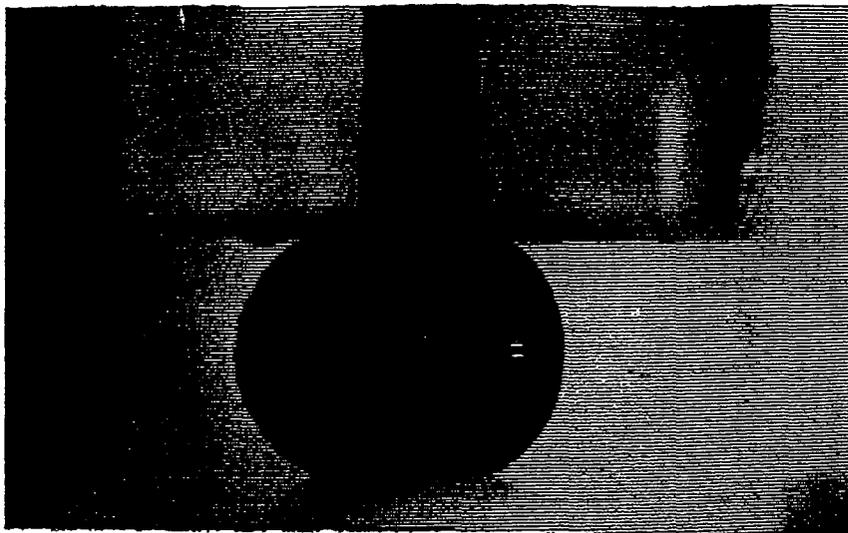


Figure 4a

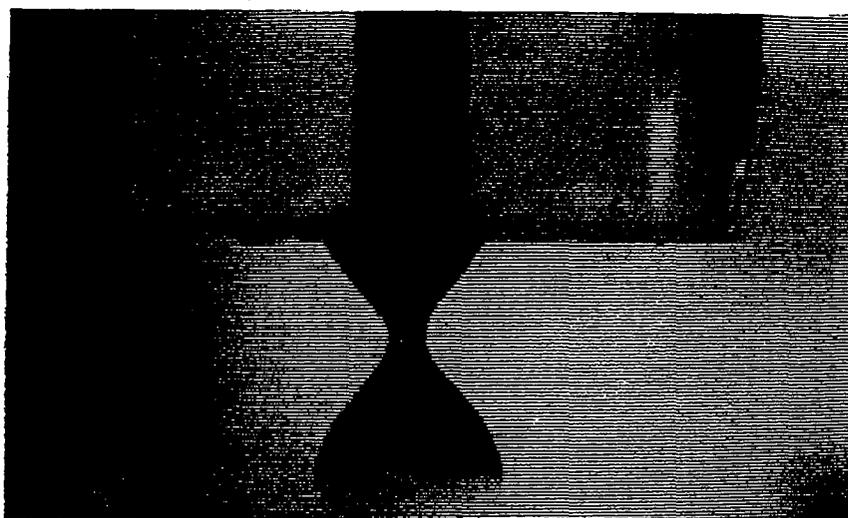


Figure 4b

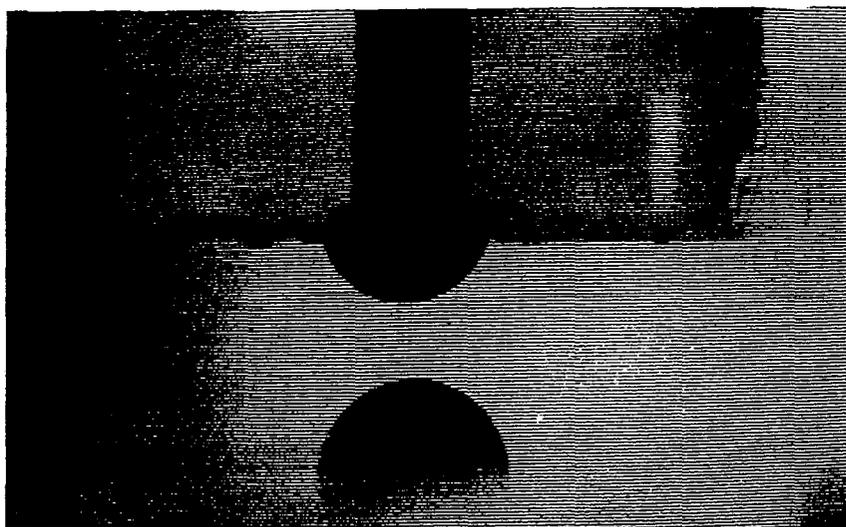


Figure 4c

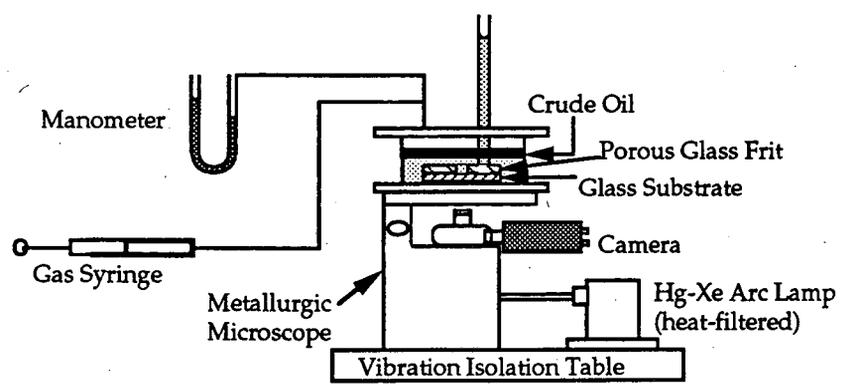


Figure 5

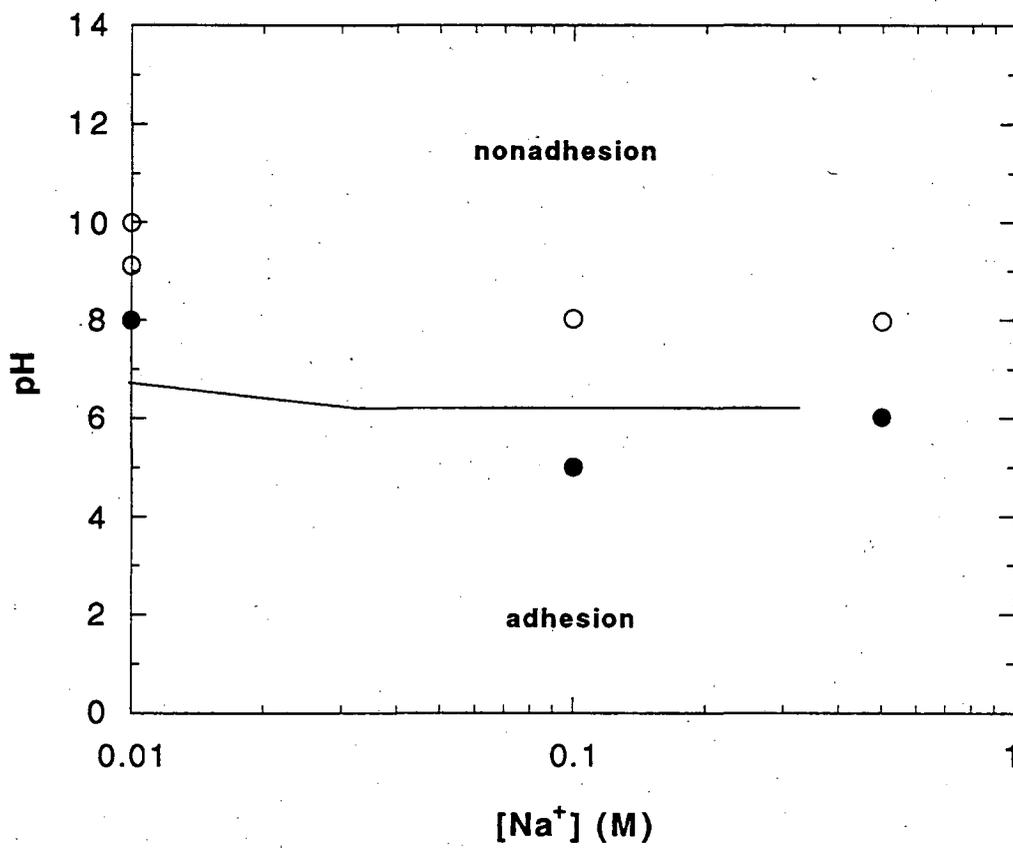


Figure 6

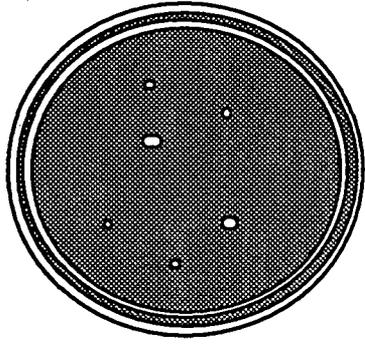


Figure 7



Figure 8

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