

An Example of Why Research Cannot Be Planned

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Dr. William A. Zisman joined the Chemistry Division in 1939 and became its Superintendent in 1956, a position that he held until 1968. Since then he has been Chief Scientist of the Laboratory for Chemical Physics. He was honored for his contributions to pure science and his applications of surface chemistry to practical problems by being named to a newly created Chair of Science in 1969.



In 1941 D. L. Pickett and I were preparing a 0.1-percent solution of n-heptadecylamine in purified white mineral oil for use in spreading experiments. While gently shaking the solution in a Pyrex flask, we were very much surprised to observe that the oil rolled down or "peeled off" the interior surface of the flask and left a clear and apparently unwetted area behind it. This kind of behavior had been observed by Langmuir years before with oil drops rolling down the surface of an inclined glass plate coated with a Langmuir-Blodgett stearate multilayer, and he had described this as oleophobic behavior. I could not believe that we were observing the formation of a Langmuir-Blodgett multilayer on our flask wall; we thought the flask was not clean or the oil contained water. The experiment was repeated many times with increasing care, but the same oil retraction of the amine solution resulted. When the heptadecylamine was dissolved in various pure nonpolar solvents such as n-hexadecane and dicyclohexyl, essentially the same results were encountered. Any one of a number of paraffinic polar compounds such as palmitic and stearic acids and eicosyl alcohol behaved in the same way.

These observations led me to infer that we were observing the formation on the glass of an oriented film adsorbed from its original state in solution in the organic solvent, the orientation of the film being such that the polar end of each amine molecule was adsorbed on the glass wall, whereas the hydrocarbon chain with its terminal methyl ($-CH_3$) group was extended so that its principal axis was perpendicular to the wall. I proposed that the reason the oil was rolling off the wall was that it could not wet the surface of the adsorbed film because the outer surface of the film was composed of methyl groups.

Similar films were adsorbed more readily on clean glass microscope slides and also on polished, clean, flat strips of platinum, stainless steel, chromium, and nickel. It was sufficient simply to immerse each slide in the oil solution and slowly remove or retract it from the liquid at right angles through the oil-air interface. After removing each slide from the oil solution, we could readily measure with a simple goniometer the contact angle exhibited by an oil drop. Contact angles around 30° were common at room temperature. Experimentation with the effect of tilting the plane of the "retracted" oil-free specimen revealed that a slight tilt from the horizontal caused the drop to roll off the surface readily. The surface was apparently unchanged by contact with the oil, because the oil-drop experiment could be repeated again and again. Hence, it was correct to describe the adsorbed film on the solid as an "oleophobic film."

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Further experimentation with retracted oleophobic heptadecylamine films on such solids was done with the use of a flame-cleaned, polished, platinum foil. Similar results were obtained with other long-chain amine, acid, alcohol, and amide compounds. Approximate measurements of the contact potential difference occurring between two pieces of platinum foil, one of which was coated with an oleophobic monolayer of stearic acid, showed that the presence of a single adsorbed film caused a potential difference of 0.2 volt. We concluded that each such retracted adsorbed film on platinum was a monolayer of the polar compound oriented at right angles to the metal foil and arranged in close-packing.

As urgent research problems arising from World War II swarmed out of the Navy Department into the Laboratory, further investigations of these interesting films became impossible. However, later in the War, I persuaded Professor L. O. Brockway and Dr. Jerome Karle of the University of Michigan to examine our oleophobic monolayers of stearic acid and octadecylamine on platinum by using electron diffraction techniques. Subsequently, they reported that each of the two polar compounds had formed a monolayer on the platinum and that the polar molecules were oriented along the normal to the solid surface with a random tilt of several degrees of the principal axis of the molecule.

In an early postwar paper Bigelow, Glass, and I reported a method by which the energy of adsorption per long-chain polar molecule adsorbed on platinum from nonpolar solvents was estimated at from 10 to 14 kcal. per mole. These values obviously corresponded to a physical adsorption process. Since the energy of adsorption per mole increased linearly with the number of methylene ($-\text{CH}_2-$) groups per polar molecule, the energy increment per aliphatic carbon atom was in accord with available literature estimates of the energy of molecular cohesion for adlineated (or crystalline) paraffinic compounds.

Further experimentation revealed that a wide variety of polar paraffinic compounds could be adsorbed on smooth clean Pyrex glass, silica, and sapphire and on numerous clean polished metals by retraction of the solid from the molten compound. This was a welcome find since it led us to a simple method for preparing a variety of adsorbed condensed monolayers of many pure compounds without any possibility that solvent molecules could be present in the adsorbed film.

By retracting a monolayer from a dilute solution of octadecylamine in dicylohexyl on a polished platinum dipper and then removing it by heating the foil red hot so as to destroy the film, and by repeating the same procedure again and again, we could count the number of retracted films possible until the supply of amine solute in a given small volume of solution had been exhausted. By dividing the number of retractions possible into the total number of solute molecules initially present in the sample of solution, we could estimate the approximate cross-sectional area per adsorbed molecule of the retracted compound. The resulting value of somewhat less than 30 square angstroms per molecule of amine left no doubt that the film was a condensed monolayer. Many solutes besides aliphatic polar-nonpolar compounds could adsorb as oleophobic films; included were a great variety of other less simple compounds whose adsorptive polar groups existed at one extremity of the organic molecule and whose methyl groups existed at the other extremity.

Systematic measurements were made of the wetting properties of various smooth, clean, and polished surfaces, each coated by a retracted monolayer of a variety of polar-nonpolar compounds. Small drops of various well-defined pure liquids exhibited contact angles reproducible to $\pm 1^\circ$ when placed gently and slowly advanced on the monolayer-covered surface of the solid specimens. Such contact angles exhibited by drops of each liquid were essentially independent of the nature of the solid substrate! The resulting surface properties of these monolayers and the retraction process by which they were produced attracted our increasing interest, since the retracted films had been obtained under conditions of adsorption equilibrium at the solid-liquid interface. Such films were later found to occur widely in the arts and in technology.

The large and reproducible contact angles observed with a few organic liquids on various types of retracted monolayers intrigued us and led Elaine Shafrin and me to investigate the retraction of a variety of dissolved organic polar-nonpolar molecules adsorbed from their aqueous solutions as a function of the solute structure and concentration as well as the hydrogen-ion concentration. Because water has one of the highest surface tensions among liquids (72.8 dynes/cm at 20°C), the retraction technique allowed us to adsorb and to isolate for further examination monolayers of hydrophobic adsorptive compounds of a great

variety of organic structures. The competitive adsorption by hydrogen-ion and hydroxyl-ions in the water was especially of wide interest.

By 1950 our investigations of retracted monolayers began to open up for us a major field of research on the subject of the wetting of solids. Although contact angles and wetting had been described in an apparently simple way by Thomas Young in 1805, his theoretical equation was not very useful; later it was improved by others with emphasis on a more thermodynamic approach. Attempts by latter investigators to use the Young equation to explore the subject resulted in only minor advances. Available experimental data and their significance were the sources of much argument, and even by 1940 the subject was still obscured in a cloud of philosophical and theoretical arguments and experimental difficulties. By 1955 we had opened new approaches to the relationship of the contact angle to solid surface and liquid composition and properties through the retraction method. The success in obtaining reproducible contact angles for sessile drops led us to broaden greatly the variety of liquids studied and the kinds of films retracted.

In 1957, following a different pathway, Levine and I used retracted monolayers on hard solids to investigate the boundary friction of monolayer-coated solid surfaces; this investigation advanced the understanding of that subject. In 1963 another path was followed with Karl Bewig to succeed in explaining the effect of an homologous series of adsorbed organic monolayers upon the contact potential differences among a variety of metal substrates. Incidentally, both friction and surface potential investigations could readily distinguish under what special conditions a solvent could be included between the molecules of a retracted monolayer.

When, in 1950, H. W. Fox and I examined the contact angles of various pure liquids on many clean, polished, hard, metallic or nonmetallic "high energy" surfaces, we tried to maintain them free of adsorbed organic films. Later we found that a major difficulty arose from the fact that such surfaces readily adsorbed any contaminating films of water, gases, or organic material which often originated from pollution of the atmosphere or in the storage chamber. We reasoned that, because such solids have very high surface energies, each would be expected to have great susceptibility to the adsorption of gases and liquids and so lower the surface energy of the solid. Therefore, we focused attention first on the spreading of pure liquids on such low-energy solid surfaces as those of linear polymeric solids like perfluorocarbons and polyethylene which were made smooth, glossy, and clean. Because the majority of liquids were nonspreading on polytetrafluoroethylene (Teflon), we presumed that Teflon had an extremely low surface energy and therefore we investigated how the contact angles of the homologous n-alkanes varied on these surfaces. Subsequently, we also examined the contact angles of many other chemically well-defined linear polymers by using the homologous series of n-alkane liquids and obtained new data which enabled us to show that rather simple relationships existed between the cosines of the contact angles and the liquid surface tensions.

Further investigations of polymeric surfaces revealed by 1953 that when the wettability data concerning a polymer or of a monolayer-coated high-energy solid were compared, the results were surprisingly similar so long as the surface composition of the solid was essentially the same. This led us to the concept of the critical surface tension (γ_c) of the solid surface. By 1960 Mrs. Shafrin and I had found how the value of γ_c could be predicted from the solid surface composition. Soon it became possible for us to bring much order into the hitherto obscure subject of the contact angle and wettability. The results from this continuing series of investigations on wettability *versus* solid and liquid constitution were summarized in 1963 in the ACS Kendall Award Symposium. As a by-product of the evolution of these laws relating γ_c to wetting, we finally were able to explain the mechanism of the retraction process from which we had started in 1941!

In this 50th Anniversary Symposium commemorating the founding of NRL, I would like to express my appreciation for the support ONR has given me through so many years of my postwar scientific career—the support that made possible the kind of research I have described in this paper.