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TECHNICAL PROGRESS REPORT

SUBMITTED TO

ATOMIC ENERGY COMMISSION

"CONTROLLED POLYMERIZATION OF ADSORBED MONOMERS"

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General Statement:

Our results of the past year have some significance in several different branches of physical science. Each will be mentioned briefly.

Adsorption Studies:

1. In the study of physical adsorption of vapors on solid surfaces we have published what may well be the first plot of amount adsorbed (q) vs. temperature (T) of the vapor source. This plot is Figure 3 of our publication in J. Colloid Interface Sci. 30, 312 (1969). and is for furan adsorbed on Graphon. It is based on work done on this research project several years ago. We are aware that we may be opening up a new field by indicating the advantages of this type of plot. We have recalculated experimental data for 15 other combinations of vapors and adsorbents. The data suggest that d^2q/dT^2 may be zero at the point corresponding to monolayer adsorption. There is some theoretical justification for this. The subject is obviously worthy of further investigation.

Polymerization:

The basic experiment in our laboratories consists of the following steps:

1. With 10-1000 mg. Graphon loaded onto spring or balance, heat the portion of the vacuum line containing the sample to 250°C . for four hours, meanwhile pumping down the vacuum line at pressures below one micron.

2. Equilibrate the Graphon at room temperature ($25-27^{\circ}\text{C}$).

3. Isolate the vacuum system from the vacuum pump and open a Teflon stopcock to expose the Graphon to vapors in equilibrium with a liquefied sample of the adsorbate maintained at a predetermined temperature of the order of -20°C .

The quantity of liquid is sufficient so that it does not all evaporate during adsorption.

4. Follow adsorption as a function of time for a period of 1-24 hours.

5. Close the stopcock between the liquefied adsorbate and the adsorbent.
6. Open the stopcock between the system and the vacuum pump and pump

down the system; follow desorption as a function of time for a period of 1-24 hours.

The most significant results appear in the following table.

Adsorbent: Graphon
 Adsorbate: Furan
 Temperature: 25-27°C.
 Furan pressure: 22 torr.
 Fraction of a monolayer at equilibrium: 0.47
 Apparatus: Cahn Electrobalance

<u>Run No.</u>	1	2	3
Time allowed for adsorption, hr.	0.85	0.98	3.55
Amt. adsorbed, mg./g.	15.0	14.9	29.2
Time allowed for desorption, hr.	1.00	4.25	6.05
Residual adsorbate at end of desorption, mg./g.	1.5	5.2	20.1
Net desorption, mg./g.	13.5	9.7	8.1

With this background, it is possible to consider the effect of time pattern on the results on irradiation of the Graphon with furan adsorbed on it, which have been presented in previous progress reports. All of our experimental results fall into a pattern in which a rapid polymerization initiated by high energy electrons is superimposed on a slow polymerization that is possibly initiated by defects in the Graphon. It should be noted that Ballentine and Manowitz (Brookhaven National Laboratory, Rept. No. 389) reported that Statex 125, the carbon black that they used reacted with butadiene on standing, even if there was no irradiation. On the other hand, Graphon did not fix any butadiene in their experiments, even when they used a γ -ray dosage of 200,000 rep/hr. for 12 hours.

The problem of identifying the polyfuran made by adsorption polymerization is still with us. We have carried out radiation polymerization of bulk furan and furan dissolved in carbon tetrachloride, using the Cobalt-60 generator recently

brought to our University by Professor Larry Kevan. Using infrared and nmr spectroscopy we are able to distinguish bulk polymer from solution polymer. Neither is exactly like adsorption polymer, but the distinctions are being unravelled.

Limits in Adsorption:

Our research group has a continuing interest in limits in physical chemistry and has studied such questions as the limit of volatility which can be phrased thus: "Under what conditions is a material nonvolatile?" Adsorption in gas-solid systems cannot occur unless the adsorbate is volatile. We have devoted a few experiments to a test of the Doss-Rao theory, which purports to provide a test for the presence or absence of adsorption.

The Doss-Rao theory (K. S. G. Doss and B. S. Rao, Proc. Indian Acad. Sci. 7, 113 (1938)) states that for a 2-component, 3-phase system in which the phases are solid, liquid, and gas:

$$\cos \theta_{S12/L21} = 2\sigma - 1.$$

- $\theta_{S12/L21}$ - contact angle between solid 1 and liquid 2, mutually saturated
- σ - fraction of the solid surface covered by adsorbed molecules of liquid 2

Clearly, a liquid with no vapor phase cannot adsorb from the vapor phase onto a solid, so that σ must be zero. The theories give

$$\cos \theta_{S12/L21} = -1,$$

and $\theta_{S12/L21} = 180^\circ.$

Two systems were chosen to test the theory: a lead-bismuth alloy on glass and pure, high-density polyethylene on platinum.

It would seem that research on the soldering process would already have resolved the question of contact angle and volatility. However, solder compositions

are generally chosen such that one of the solder components is soluble in the material to be soldered. Clearly this is not amenable to the simple 2-component, 2-phase system described by Doss and Rao.

Even at moderate temperatures (less than 200°C) some metallic systems are reactive. Cleary (AEC Rept. IS-T-56 (1966)) investigated the use of lead-bismuth alloy in steel heat exchangers in atomic reactors. He studied the contact angle of the eutectic on four stainless steels under vacuum and in the temperature range 460° to 572°C . We have studied the same alloy but at a lower temperature.

The experiments were done in a vacuum line consisting of a mechanical pump (Cenco Hyvac 28), two dry ice-acetone traps, a hot stage, and a cold cathode pressure gauge (NCR 724). The hot stage was a finger extending horizontally into a two liter vessel on the line. A plane glass disk was fused into the finger to form the actual hot stage. The finger contained a resistance heater and was filled with dimethyl terephthalate. The dimethyl terephthalate served as a heat exchanger and as a temperature reference. The experiments were done at the melting point of the dimethyl terephthalate, $141-2^{\circ}\text{C}$.

The bismuth was Fisher reagent grade (granular) and the lead was Baker reagent grade (granular). The alloy was 55:45 mole percent Bi:Pb. Fifty-five grams of bismuth were melted with 45 grams of lead in a Kimax beaker. The oxide was skimmed off as the melt was poured into a flat Kimax dish. The oxide was again skimmed off and samples were taken. A disposable pipette was immersed in the melt and a sample was drawn up into the pipette. This method produced glass-encased wires of the alloy which retained their bright metallic surfaces after cooling. The alloy melted at $127-129^{\circ}\text{C}$. Calculation from the manufacturers' analyses of

the lead and bismuth gave the following concentrations for impurities in the alloy (parts per million): As 2, Cu 2.5, Fe 10, Sn and Sb 25, Ni 2.5, Ag 0.55.

A length of alloy was broken out of its glass casing and three small pieces were cut off. These were transferred to the hot stage through a neck in the two liter vessel. The neck was closed with a standard taper joint, and the vacuum line was evacuated to 5×10^{-4} torr. Outgassing was continued for two days resulting in a final pressure of 3×10^{-4} torr. A predetermined voltage was applied to the heater in the hot stage. In half an hour the dimethyl terephthalate had stopped melting at about 90% melted and the alloy had melted. Heating was continued for two and one-half hours (though no change in the drops was observed one hour after the heat was turned on). The heat was turned off, the finger allowed to cool, and the finger with the solidified sessile drops removed from the vacuum line.

In a second experiment one of the drops formed above was returned to the vacuum line, outgassed at 8×10^{-4} torr for two days, then heated again to $141-2^{\circ}\text{C}$ under half an atmosphere of argon.

Photomicrographs of the drops were taken on Kodak 35 mm Plus - X film. The American Optical microscope was equipped with a four power, .15 numerical aperture objective lens and a ten power eyepiece. The drops were illuminated to form silhouettes. Enlargements onto high contrast paper gave a final magnification of 125 times. The magnification was determined by photographing a ruled bar supplied by Gaertner for calibrating their travelling microscopes. The ruled bar also provided a check of optical distortions in photographing and enlarging the drops. Measurements on enlargements of the rulings failed to show any optical distortion.

The contact angle was measured on the enlargements with a protractor.

The alloy melted in vacuum stuck to the glass. The sessile drops were well-formed spheres giving a contact angle of $136.5 \pm 2^\circ$ (average deviation). The drops measured about a millimeter across. It was thought that the design of the apparatus could prevent attainment of a 180° contact angle. As the drop approached 180° , its area of contact with the hot glass would decrease, reducing heat transfer, possibly allowing the alloy to freeze. It was desirable, therefore, to provide more uniform heating. To this end one of the drops was returned to the line, and the experiment was run again under $1/2$ atmosphere of argon. No change in the drop was observed. Clearly the result was not that predicted by the Doss-Rao theory.

It still could be said that the Doss-Rao theory had been disproved. Was it valid to claim that the liquid alloy had no vapor pressure? Lead and bismuth vapor pressures were available individually. Extrapolation to 140° gave pressures of 10^{-16} to 10^{-15} torr. However, could it be claimed that alloying, which had such a marked effect on melting point, would have no effect on vapor pressure?

It was decided that a second system should be studied; polyethylene on platinum. Certainly a high polymer could have no vapor pressure.

The experiments were done in a vacuum line consisting of a mechanical pump (Cenco Hyvac 28), two dry ice-acetone traps, a tube furnace, and a cold cathode pressure gauge (NCR 724). The tube furnace was a 30 cm. length of 45 mm. glass tubing closed at one end and attached to a standard taper joint at the other end. Two centimeters from the closed end, the tube was wrapped with resistance wire. The wrapped section of the tube was 5 cm. long. A glass microscope slide was cut to fit snugly in the tube to provide a platform. A thermometer was held against the platform bottom with nickel-chromium wire.

The polyethylene was a sample from Dr. W. O. Statton, E. I. du Pont de Nemours, Inc., Experimental Station, Wilmington, Delaware. It was high-density

polymer which had been grown as single crystals, cast from suspension as a mat, and melted. The fact that the sample consisted entirely of single crystals was the best indication of its purity. The polyethylene cleared at 120-125°C. This was taken as its melting point.

The platinum was heated to orange luminescence in a natural gas-air flame just prior to placing it on the glass platform. Small pieces of the polyethylene were cut from the sample and placed on the platinum. The platform was placed in the tube furnace using the thermometer as a handle. The furnace was attached to the vacuum line, and the pump was turned on.

The line was outgassed with the furnace at a low voltage. The temperature was raised to its final value slowly (20 minutes or longer). Earlier experiments showed that faster heating rates produced wild pressure fluctuations, presumably from outgassing the furnace walls; and pock-marked polyethylene, perhaps from rapid escape of absorbed gases from the molten polyethylene. The pressure during the experiments was $5-7 \times 10^{-4}$ torr.

Two experiments were performed. In the first, pieces of the polyethylene were heated to 220°C for 6 1/2 days. In the second they were heated to 370°C for nearly 2 days. The furnace was turned off and allowed to cool before opening to remove the samples. The samples were examined in a microscope under 40 times magnification.

The results of both experiments were the same. The polyethylene stuck to the platinum. It showed no yellowing from oxidation. It failed to flow sufficiently to give a contact angle. The pieces, square at the start, merely rounded at the edges.

Here, where non-volatility was assured, viscosity precluded an equilibrium measurement. Neither of our two contact angle experiments showed positively that

we had achieved conditions in which the gas phase contained no molecules from the liquid (or polymer phase). We are encouraged to believe that even relatively non-volatile monomers such as caprolactam or furancarboxylic acid can be used as subjects for adsorption polymerization experiments.

Polymerization Trials at Liquid-Gas Interfaces

In our previous report the subject of stability of insoluble monolayers was discussed. Monomers that form insoluble monolayers should be capable of polymerization, but the control of polymerization may be rather poor unless disc-shaped molecules are used. It was shown in that report that hydroxybenzenes and hydroxynaphthalenes are too soluble to form stable monolayers on water and hydroxyanthracenes are marginal. Compounds that might be suitable were not readily available.

We had intended to synthesize some vinyl-substituted hydroxyanthracenes and hydroxyterphenyls during 1969. This work was planned for Dr. J. Kresta, who was to join our group on April 1. However, there was an unexpected delay in obtaining clearance from AEC for Dr. Kresta's assignment to this grant (Dr. Kresta is a Czech national). When he did arrive, on July 1, we were deeply into a program with monolayers that did not involve vinyl polymerization, so Dr. Kresta was assigned to a different phase of this project.

We decided to start with readily available thiols instead of the hard-to-get hydroxy compounds, which would take advantage of the fact that the thiols have much lower solubility in water. In our first trials, made with n-octadecanethiol, there was no spreading. We therefore developed a scouting procedure that allowed us to make an approximate measurement of surface pressure at a single surface concentration and then quickly go on to another experiment. A wide variety of conditions were explored, but the only one that gave a spreading pressure in the range to be expected

of a monolayer of a long-chain alkyl compound was for spreading on an alkaline KMnO_4 solution ($\text{pH} = 14$).

Our interest in thiols grew out of our knowledge that the well-known reaction:

$$2\text{RSH} \xrightarrow{\text{oxidation}} \text{RSSR}$$

could be employed with dithiols to form linear polymers. The observation that $\text{C}_{18}\text{H}_{37}\text{SH}$ on a strong oxidizing substrate formed an insoluble monolayer led to this question: Was the monolayer $\text{C}_{18}\text{H}_{37}\text{SH}$ or an oxidation product such as the disulfide?

Answering this question was a major problem, since we had only a monolayer, not quantities of product, to use for identification. The force-area curves for the insoluble monolayer had the general shape expected for a simple long-chain alkyl compound. This made it seem unlikely that the monolayer was a dialkyl disulfide. Infrared spectra of surfaces bearing traces of the monolayer suggested that the permanganate may have oxidized octadecanethiol to octadecanesulfonic acid. Authentic sodium octadecanesulfonate was obtained, converted to the acid, and used for determination of the infrared spectrum. The same was done with the oxidation product obtained by shaking octadecanethiol and alkaline KMnO_4 solution in air to simulate the film balance experiment but with a greatly increased area of air-water interface. This confirmed that KMnO_4 would oxidize the thiol to the acid.

Finally, octadecanesulfonic acid was spread to form an insoluble monolayer. The force-area curve matched that obtained with octadecanethiol on KMnO_4 . Material skimmed off the film balance after an octadecanethiol - KMnO_4 experiment resembled octadecanesulfonic acid in its infrared spectrum.

We concluded that long-chain mercaptans could not be spread on aqueous substrates. Attempts to oxidize them to disulfides as a model reaction that could

(with dithiols) lead to polymerization led instead to formation of long-chain sulfonic acids.

Limits in liquid-liquid interactions:

Polymerization at the air-water interface has not occurred in any of our experiments. The interface between water and a water-immiscible liquid might provide a better locale. Some theoretical work, based in part on experiments performed in previous years, has provided insight into the limiting cases that might be investigated experimentally.

Much discussion of interfacial tension has been devoted to the balance of tensions at the liquid-liquid-vapor interface where a lens of the lighter liquid rests atop the surface (i. e., liquid-vapor interface) of the heavier liquid. In our case it is important to deal with pairs of liquids with very little mutual solubility. When solubility is substantial and the surface tensions of the two saturated phases (solutions) are significantly different from the surface tensions of the pure liquids, Antonov's rule is generally applicable (G. N. Antonov. J. Chem. Phys. 5, 372 (1907)). This states that

$$\gamma_1' - \gamma_2' = \gamma_{12}$$

where the primes refer to saturated solutions (Component 1 saturated with Component 2 and Component 2 saturated with Component 1, respectively). Donahoe and Bartell (J. Phys. Chem. 56, 480 (1952)) have given a very reasonable treatment of Antonov's Rule, pointing out that there is one class of systems, which they call Class I, for which $\gamma_{12} + \gamma_2 > \gamma_1'$. All their examples of Class I have water as Component 1 and hydrocarbons as Component 2. Shifting to the more convenient subscripts W and H, one can observe that $\gamma_W > \gamma_W'$ and $\gamma_H \approx \gamma_H'$, so it is a necessary condition of Class I systems that $\gamma_{WH} + \gamma_H > \gamma_W'$, and Antonov's Rule cannot be obeyed.

Donohoe and Bartell made solubility measurements on their systems.

All the Class I hydrocarbons had extremely low solubility in water and dissolved very small amounts of water. In the homologous series of n-alkanes, as the molecular weight increased, $\gamma_{wH} + \gamma_H$ first approached, then became greater than γ_w . From our own data we note that the bicycloalkyls are very close to the limit of Class I in that $\gamma_{wH} + \gamma_H > \gamma_w$. In any homologous series of hydrocarbons, solubility in water decreases with molecular weight and the sum of hydrocarbon surface tension and interfacial tension against water ($\gamma_H + \gamma_{wH}$) approaches the surface tension of water (γ_w). The Fowkes equation (F. M. Fowkes, J. Phys. Chem. 67, 2538 (1963)) for saturated hydrocarbons

$$\gamma_{wH} = \gamma_H + \gamma_w - 2 \sqrt{\gamma_H \gamma_w^d}$$

where γ_w^d , the dispersion force at a water surface, is considered to be a constant, can, therefore have γ_w^d evaluated simply from surface and interfacial tension data for a homologous series. Those systems that present the equality.

$$\gamma_w = \gamma_H + \gamma_{wH}$$

must have $\gamma_H = \gamma_w^d$. Inspection of the data for the n-alkane homologous series, as tabulated by Donohoe and Bartell, shows that $\gamma_w = \gamma_H + \gamma_{wH}$ for n-octane, for which hydrocarbon $\gamma_H = 21.8$ dynes/cm. at 20°C. This is Fowkes's preferred value for γ_w^d at 20°C.

The two bicycloalkyls that we have studied do not have $\gamma_w^d = \gamma_H$, even though $\gamma_{wH} + \gamma_H \approx \gamma_w$. Fowkes's generalization that $\gamma_H = \gamma_w^d$, the dispersion force at a hydrocarbon surface, has been stated too broadly. It probably should be restated as applying only to those saturated hydrocarbons that can pack closely at the water-hydrocarbon interface. Bicyclopentyl and bicyclohexyl cannot pack closely, as judged by molecular models, and therefore have γ_H^d values of 41.0 and 47.2 dyne/cm.

at 30°C., respectively.

The limiting cases that must be considered in the choice of immiscible liquids for use with water in polymerization experiments are:

1. Antonov case ($\gamma_1' - \gamma_2' = \gamma_{12}'$);
2. Fowkes case ($\gamma_H = \gamma_H^d$).

Liquids that we have studied are: bicyclopentyl and bicyclohexyl (Antonov case), n-octane (Fowkes case), benzene and n-heptylbenzene (neither).