

## THE ADSORPTION OF STEARIC ACID AND SEVERAL LOW MOLECULAR WEIGHT POLYMERS ON CHROMIUM FROM BENZENE SOLUTIONS

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### INTRODUCTION

Adsorption from solution, especially in the monolayer region, is an area in which fundamental knowledge is lacking (1). A particular area in which adsorption from solution is complex and requires more fundamental knowledge for interpretation is that of polymer adsorption. Silberberg (2) has summarized results for polymer adsorption from solution and has formulated a theory of adsorption for flexible macromolecules. The restrictions which must be imposed for the application of the theory point out the need of adsorption studies for diverse systems.

Ruch and Bartell (3) have shown that ellipsometry is a convenient and informative method of studying the adsorption of long chain polar organic molecules from aqueous solutions onto well-defined planar metal surfaces. The interpretation of results for these systems is facilitated by studies with adsorbed films isolated out of solution. Such films as prepared by Blodgett (4) or Zisman (5) techniques have been fairly well characterized.

Since most high molecular weight polymers are very slow in reaching adsorption equilibrium and little data exist with which adsorption results may be compared, a logical approach to studying polymer adsorption should be to study first the adsorption of simple and low molecular weight polymers. The results of the initial studies may be compared with those for the adsorption of similar but more adequately characterized long chain polar organic molecules. The low molecular weight polymers should bridge the gap between the simpler polar organic molecules and the more complex higher molecular weight polymers.

The purpose of the present study was to compare adsorption results for stearic acid as a typical long chain polar organic molecule with low molecular weight polymers of polystyrene. The use of the chain transfer agent mercaptopropionic acid regulates the degree of polymerization of the polystyrene and introduces a terminal carboxyl group in the polymer molecule.

The application of ellipsometry to solution measurements and

higher molecular weight polymer adsorption has been discussed by Stromberg *et al* (6).

### EXPERIMENTAL

**Adsorbent.** Separate chromium plated steel slides, 2.5 cm. on a side, were used for each adsorption trial. The slides were cleaned as in previous studies (3).

**Adsorbates.** Stearic acid, recrystallized from ethyl acetate and having a m.p. of 68.5-69.0°, was made 10% by weight in reagent grade benzene and used as a stock solution for all adsorption trials with stearic acid.

The polymers used for adsorption studies were prepared by the following procedure, the molecular weights being regulated by the amount of chain transfer agent employed in the preparation. Freshly distilled styrene (0.9 mole), 0.0003 g. of the initiator AIBN, and the chain transfer agent, mercaptopropionic acid (0.0045 and 0.0090 moles) were heated in a sealed reaction vessel at 51° C for 2½ hours. The polystyrene with mercaptopropionate end group formed a suspension with the addition of methyl alcohol which was coagulated by the addition of 1 cc. of 0.1 N potassium aluminum sulfate and gentle boiling. The polymer was isolated by centrifuging and decanting. After washing with water and reprecipitation with methanol, a white powder was obtained which was sparingly soluble in 5% sodium bicarbonate, insoluble in water, and readily soluble in benzene. Stock solutions were made 2 mg./ml. in benzene for both polymers.

The molecular weights of the polymers were determined by non-aqueous titration with 0.0130 N sodium ethoxide using phenolphthalein as an indicator. The sodium ethoxide was standardized using benzoic acid having a m.p. of 122.0-122.5° C.

**Apparatus.** The instrument used for assessing the amount of adsorption was essentially the one used in a previous study (3). A dark green lens and an adjustable slit were employed to facilitate readings. The instrument was set at an angle of incidence of 75° at the solution-metal interface and the setting of the quarter wave plate was kept constant while measuring an adsorption isotherm.

The adsorption cell used was a Pyrex turbidity cell, 3 x 3 x 6 cm., obtained from the Phoenix Precision Instrument Company.

**Procedures.** The cleaned slides were placed in ten ml. of benzene in the covered adsorption cell and an optical measurement taken. Increments of the stock solutions were added with a one ml. pipet graduated to 0.01 ml. Weighed increments of the stearic acid were added in some trials to obtain the higher concentrations. No corrections were made for adsorption on container walls. Optical read-

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ings were taken periodically after adsorbate additions until no significant changes in readings were noted at which time equilibrium was assumed to have been reached. No attempt was made to hold the temperature constant and it varied several degrees in any one trial.

Most of the measurements made to determine reversibility of adsorption were obtained by adding increments of pure benzene to the adsorption cell thereby reducing the effective concentration of the medium. Those points at the ordinate of the isotherms were obtained by flushing with pure benzene and reading the firm adsorption when the adsorbent was in contact with pure benzene.

### RESULTS

*Molecular weight determinations.* The expected formula of the polymer product is:  $H(HC\phi CH_2)_nSCH_2CH_2COOH$ , where  $\phi$  is the phenyl group. An approximate value for  $n$  may be obtained by utilizing the formulas derived by Walling (7) for the degree of polymerization under chain transfer conditions. Assuming a large value for  $n$  in the absence of a chain transfer agent and a value of 20 for the chain transfer constant for mercaptopropionic acid in styrene polymerization, values of 5 and 10 are predicted for  $n$  in the polymer preparations.

The results of the non-aqueous titrations gave an average molecular weight for the low molecular weight polymer of 786, a value suggesting that  $n$  was predominantly 6 or 7. The value for the higher molecular weight polymer was  $1.16 \times 10^5$  which is quite close to the weight of 1146 for a ten unit polymer of the expected composition. The titration value for the molecular weight of the stearic acid used in adsorption measurements was 286 (actual—284.5). The use of methanol in the isolation of the polymer no doubt resulted in the loss of some of the shorter chain molecules in the fractions.

*Adsorption isotherms.* In all isotherms shown the open symbols represent measurements taken as the concentration of adsorbate was increased. The solid symbols represent measurements taken as the concentration of adsorbate was decreased by the addition of pure benzene. Those solid symbols on the ordinate represent readings taken in benzene after the system was flushed with benzene. Adsorption is reported as  $\Delta E$ , the difference in degrees between the analyzer reading for the clean slide in benzene and the slide with adsorbed film in the adsorption medium.

Figure 1 shows the results of several trials for the adsorption of stearic acid from benzene solutions on chromium plated ferrotype surfaces. The isotherms exhibited a plateau region which was followed by a rapid rise in the isotherms and this is indicated in one of the isotherms. At intermediate concentrations desorption values

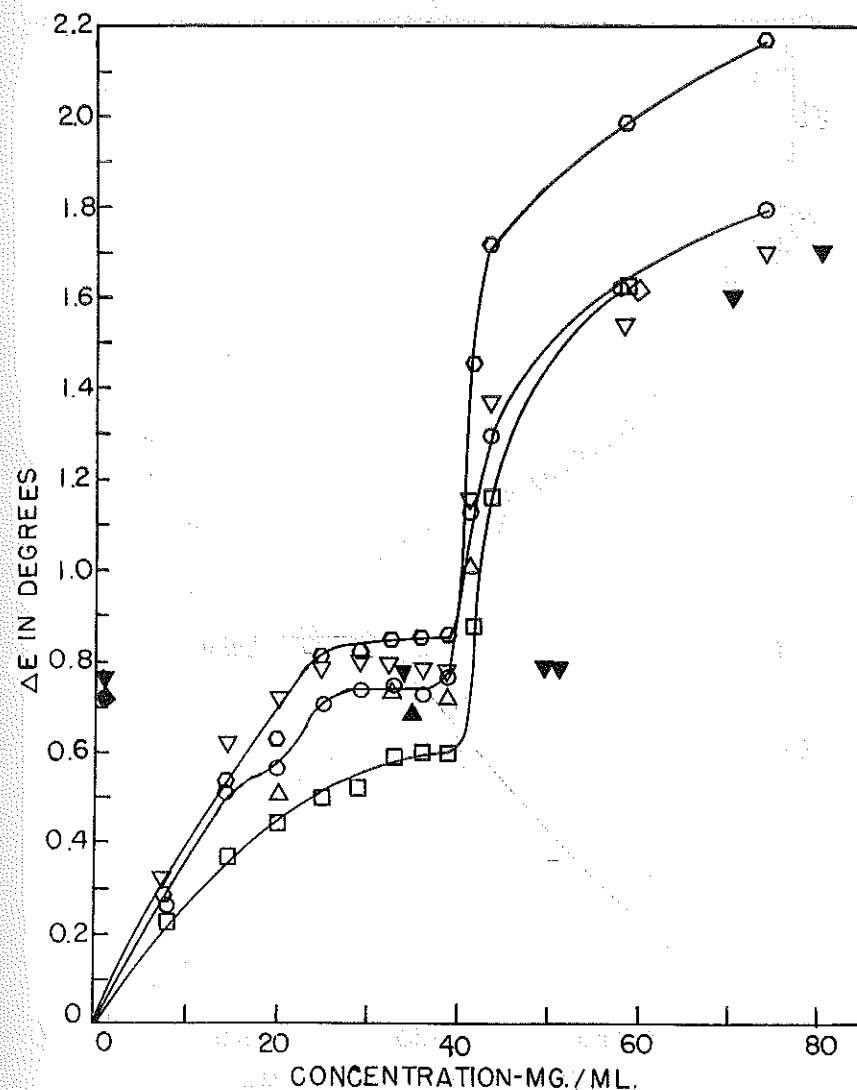


Figure 1. The adsorption of stearic acid on chromium from benzene solutions. Open symbols represent adsorption points and solid symbols represent desorption points. Temperatures from 25-28°C.

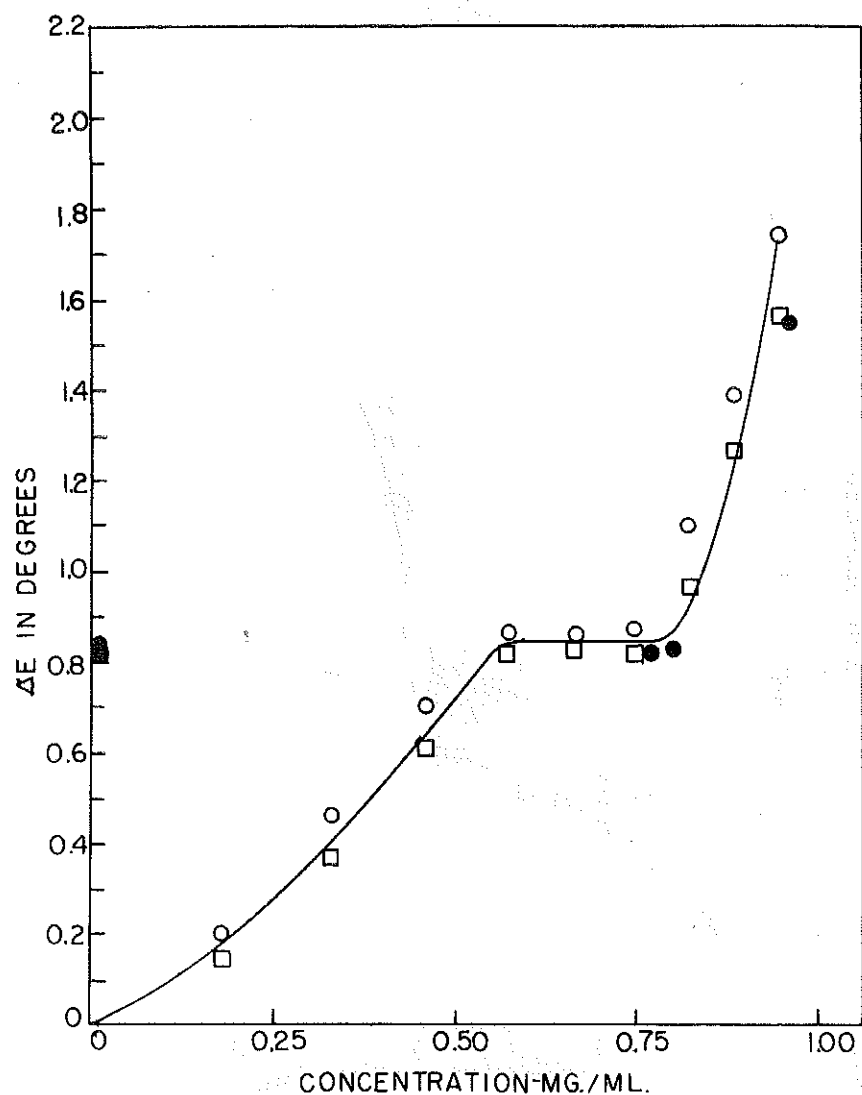


Figure 2. The adsorption of polystyrene with mercaptopropionate end group (M.W. = 786) on chromium from benzene solutions. Temperatures from 24-25° C.

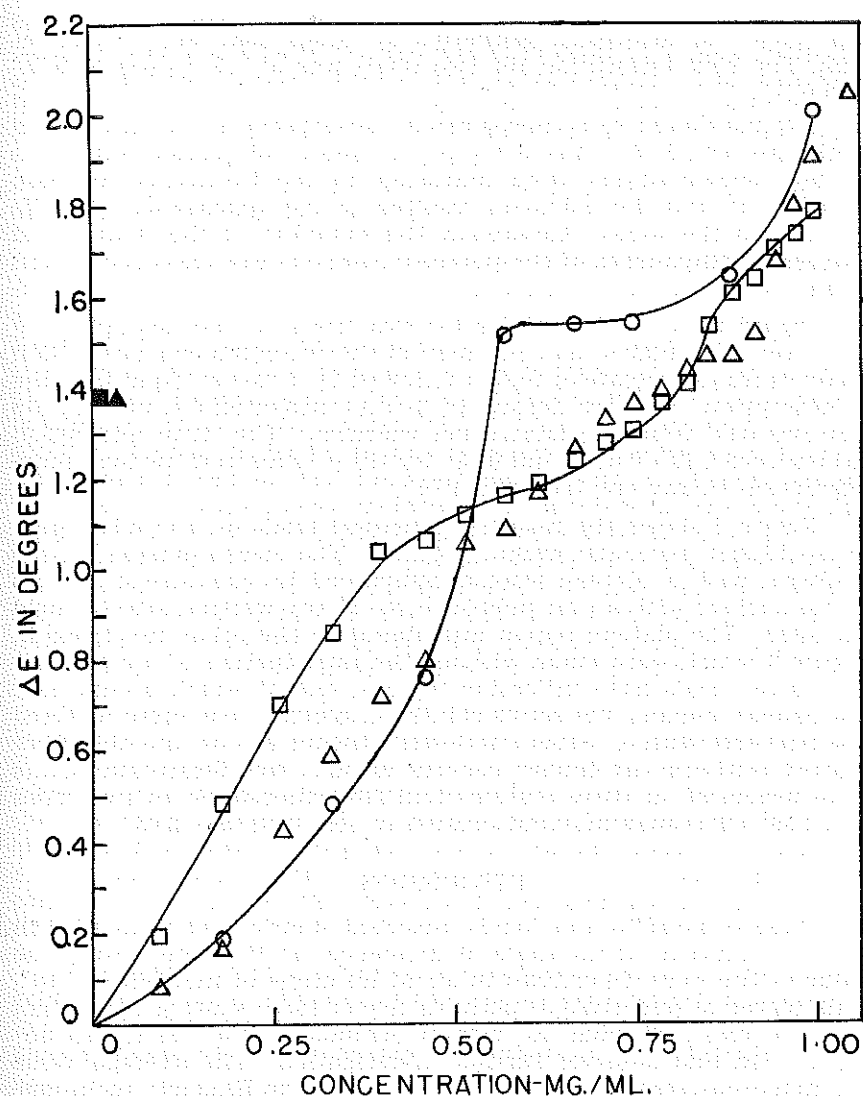


Figure 3. The adsorption of polystyrene with mercaptopropionate end group (M.W. =  $1.16 \times 10^5$ ) on chromium from benzene solutions. Temperatures from 24-25°C air bubbles introduced periodically in trial having a plateau region.

fell below the adsorption isotherms to values near the plateau region. The firm adsorption for two trials was at  $\Delta E$  values of  $0.73^\circ$  and  $0.74^\circ$ .

The maximum value measured for adsorption in the stearic acid isotherms was  $2.18^\circ$ . Any attempt to obtain adsorption values at higher concentrations than indicated in the isotherms for both stearic acid and the polymers resulted in the appearance of white patches on the slides. Apparently the solubility of the stearic acid and some components of the polymer fractions was exceeded at this point.

Figure 2 shows the results for two trials on the adsorption of the lower molecular weight polymer on the chromium surfaces. Both trials exhibited a plateau region followed by a rather rapid increase in adsorption. The few desorption points measured did not deviate significantly from the adsorption isotherm. The firm adsorption values were  $0.72^\circ$ ,  $0.81^\circ$ , and  $0.83^\circ$  for three trials and the maximum adsorption in any one trial was  $1.74^\circ$ .

Figure 3 shows the results for several trials on the adsorption of the higher molecular weight polymer. The measurements for the isotherm with a plateau were accompanied by concurrent contact of the surface with an air bubble to see if any wetting effects could be noted. The plateau region was absent in the other two trials in Figure 3 which were made without the introduction of air bubbles. The latter trials have inflection regions, one of which occurs near the plateau region. The set of points not plotted as a curve followed the isotherm with a plateau at lower concentrations and the other plotted isotherm at higher concentrations. No desorption points were measured in these systems and firm adsorption in two trials was  $1.38^\circ$ . The maximum adsorption in any trial was  $2.05^\circ$ .

#### DISCUSSION

Rubbed paraffin and firmly adsorbed stearic acid films read in benzene solution at an angle of incidence of  $75^\circ$  were  $0.6-0.8$  the value of the same films read in air at an angle of incidence of  $67^\circ$ . This degree of sensitivity is perhaps five or more times greater than would be expected from the data of Stromberg *et al* (6) for an isotropic film and deserves further investigation. The average value for numerous stearic acid films formed by the Blodgett technique and measured in air at an angle of incidence of  $67^\circ$  was near a  $\Delta E$  of  $1.0^\circ$  indicating that monolayers in benzene should be near  $0.6-0.8^\circ$ . The plateau regions in Figure 1 for the stearic acid isotherms are near this value suggesting monolayer coverage in this region.

If a step in the isotherms for stearic acid is a real effect, it may result from a phase change of the adsorbed layer as suggested by Kipling and Wright (8) for the adsorption of lauric acid on carbon

black. The phase transition may represent a change in molecular packing from a hydrogen bonded adsorbed layer to a more compactly non-hydrogen bonded layer at the plateau region. The transition from an intralayer hydrogen bonded film to a more closely packed film results in approximately a 20% decrease in area per molecule (9) which corresponds roughly to the change in area reflected in Figure 1. There is a strong possibility of hydrogen bonding of the molecules in the benzene solution.

The plateau region also occurs for both trials of the shorter chain polymer and in one trial for the longer chain polymer. If the adsorption behavior of the polymers were similar to that of the stearic acid, one would expect these plateaus to also represent monolayer adsorption. The polymers have average molecular weights about 3 and 4 times that of the stearic acid and hence have correspondingly higher molar refractivities. The area occupied per adsorbing polymer molecule is also considerably larger than that of stearic acid molecules and furthermore depends on whether isotactic, atactic, or syndiotactic molecules are involved in the molecular packing. Fisher-Taylor-Hirschfelder models give an area about 2.5 times larger for the isotactic polymer molecules than the stearic acid monomer molecules. No measurement of the sensitivity of the polymer films was made. If the sensitivity of the polymer films is near that of the stearic acid, then the plateau adsorption values for the polymer seem reasonable for monolayer adsorption.

The rapid rise in adsorption following the plateau region can be attributed to the second and third layers adsorbing together. This leads to methyl or styrene groups being exposed to the benzene solvent rather than carboxyl groups which would be the case if only the second layer adsorbed. Hydrogen bonding would further promote the dual layer adsorption. The maximum measured value for stearic acid of  $2.18^\circ$  agrees favorably with the three layer adsorption concept since a monolayer value for stearic acid was in the range of  $0.6-0.8^\circ$ .

The deviation of intermediate desorption points in the stearic acid study shows a tendency of the less strongly adsorbed molecules in the second and third layer to be desorbed and the tendency of the more strongly adsorbed monolayer to adhere to the substrate.

The optical readings for the apparently irreversibly adsorbed or firmly adsorbed molecules was near the plateau region for all three of the systems studied. This value is higher than might be expected and suggests that chemical adsorption was significant in these systems. In studies with stearic acid-barium stearate films (10) formed by the Blodgett technique on the same substrate, indications were that the majority of the stearic acid molecules in these films were readily removed by benzene.

The possibility that oxygen and moisture has an affect on the adsorption can be seen in Figure 3. The air bubbles in the one trial apparently affected the surface to such an extent that adsorption of the polymer molecules resulted in an isotherm similar to that of stearic acid and the short chain polymer. The more non-descriptive adsorption carried out without air being introduced probably resulted from more heterogeneous adsorption at isolated spots with subsequent layers to the monolayer adsorbing before monolayer adsorption was complete. Similar effects due to the presence of air bubbles have been noted in flotation studies (11) where adsorption has been induced by the presence of air.

It was not possible in the present study to assess the presence or absence of solvent in the adsorbed films. In studies with higher molecular weight polymers, where vertical orientation of the adsorbed molecules is less likely, the presence of solvent in the adsorbed films is much more probable and important to detect in the adsorption process. A more refined instrument and technique such as that used by Stromberg *et al* (6) is desirable for such studies.

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