

# THE ADSORPTION OF HYDROPHOBIC MONOLAYERS OF CARBOXYLIC ACIDS

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January 14, 1951

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## ABSTRACT

A previously reported contact-angle method has been extended to the study of the adsorption from aqueous solution of a variety of types of mono- and di-carboxylic acids. Since emphasis was to be given to physical adsorption, it was most convenient to use platinum foil as the adsorbing surface. The effects have been investigated of varying the hydrogen-ion concentration over the range of pH 2 to pH 12 and of varying the molal concentration of solute over a 10,000-fold range. The results are explained in terms of the formation of an adsorbed monomolecular layer whose water repellency has been related to the molecular structure, orientation, and packing.

The equivalence of the maximum contact angle ( $\theta_{lim}$ ) of the film adsorbed from solution to that ( $\theta_{melt}$ ) obtained from films made from the molten polar compound investigated is demonstrated.

A new thermal-gradient method of preparing and isolating a close-packed adsorbed monolayer on platinum is described. It is more general than the oleophobic method described in previous reports, since it has been found applicable to all amphipathic compounds tried—whether straight-chain, branched, or cyclic. Further research possibilities are indicated.

## PROBLEM STATUS

This is an interim report; work is continuing along the lines recommended.

## AUTHORIZATION

NRL Problem Nos. C09-07R and C02-14R  
NR 409-070 and NR 402-140

## THE ADSORPTION OF HYDROPHOBIC MONOLAYERS OF CARBOXYLIC ACIDS

### INTRODUCTION

A previous study of hydrophobic monomolecular films of primary n-alkyl amines adsorbed on platinum and isolated from aqueous solution (1) had established an effective technique for investigating physically adsorbed monolayers of compounds which are not capable of forming oleophobic films (2, 3). In that study, the critical concentrations for hydrophobic film formation and the degree of wettability of hydrophobic films of the alkylamines were reported as functions of the alkyl chain length, the amine concentration, and the pH of the aqueous solution. This report is concerned with the extension of the same methods to the adsorption from aqueous solution of various carboxylic acids.

The acids studied included representative monocarboxylic acids of the n-alkyl, cyclo-alkyl, and aryl types, some homologous dicarboxylic acids from succinic through tetradecanedioic acid, and a group of alkyl-substituted succinic acids.

### TECHNIQUE

The experimental procedure employed was essentially that described previously (1). The films were always formed, isolated, and measured at  $20.0 \pm 0.1^\circ\text{C}$ . Contact of the adsorbing surfaces with the aqueous solutions of organic acids was limited to an immersion period of  $30 \pm 1$  seconds. The films were adsorbed upon dippers of carefully selected, scratch-free, commercial platinum foil, as in earlier studies (1, 2, 3). Before each contact of the platinum with the solution under study, the dipper was allowed to soak in distilled water to dissolve any alkali residue left from previous experiments. Then the platinum was heated briefly to dull redness in the nonreducing portion of the flame from a microburner and was used immediately upon cooling to room temperature.

The following monocarboxylic acids were used directly as received from the Eastman Kodak Co.: caproic acid (b. p.  $86-88^\circ\text{C}$  @ 6 mm), caprylic acid (m. p.  $16^\circ\text{C}$ ), capric acid (m. p.  $31.5^\circ\text{C}$ ), lauric acid (m. p.  $42-43^\circ\text{C}$ ), myristic acid (m. p.  $52-53^\circ\text{C}$ ), palmitic acid (m. p.  $61-62^\circ\text{C}$ ), stearic acid (m. p.  $68-69.5^\circ\text{C}$ ), cyclohexylcarboxylic acid (m. p.  $29.5-30.5^\circ\text{C}$ ), and benzoic acid (m. p.  $123-125^\circ\text{C}$ ). The behenic acid, supplied by the DuPont Co., was repeatedly recrystallized from ethanol, followed by ethyl ether, until a melting point of  $80.0-80.3^\circ\text{C}$  was reached. The cyclohexylacetic acid (b. p.  $129^\circ$  @ 10 mm; m. p.  $28.5^\circ\text{C}$ ), cyclohexylpropionic acid (b. p.  $144.5^\circ\text{C}$  @ 10 mm; m. p.  $15.0^\circ\text{C}$ ), cyclohexylbutyric acid (b. p.  $154^\circ$  @ 10 mm; m. p.  $29^\circ\text{C}$ ), and the cyclohexylcaproic acid (b. p.  $177^\circ\text{C}$  @ 10 mm; m. p.  $> 32^\circ\text{C}$ ) were used as obtained from the Dow Chemical Co. The phenylbutyric acid (m. p.  $49-50^\circ\text{C}$ ) was kindly supplied by Dr. A. Schneider.

Three  $\alpha, \omega$ -dicarboxylic acids were recrystallized twice from water and the following melting points determined: succinic acid (Eastman Kodak Co.) m. p. 185-186°C; adipic acid (Eastman Kodak Co.) m. p. 151°C; sebacic acid (Rohm and Haas Co.) m. p. 129°C. The dodecanedioic and tetradecanedioic acids were obtained from the Sapon Laboratories and were purified by repeated recrystallization from ethyl alcohol until maximum melting points of 125-126°C and 124.5-125.5°C, respectively, were obtained. The n-octylsuccinic acid (m. p. 88-89°C) was prepared by the hydrogenation and hydrolysis of octenylsuccinic anhydride obtained from the Humphrey-Wilkinson Co. The n-decylsuccinic acid (m. p. 92.5-95°C) and the n-octadecylsuccinic acid (m. p. 104-106°C) were prepared by converting the corresponding anhydrides by saponification, acidification, and recrystallization from a mixture of ligroin and toluene.

The n-alkyl amines were the same compounds used in previous work and described earlier (2, 3).

The solutions used in the adsorption measurements were made as in our earlier paper (1). Measurements of the hydrophobic contact angle ( $\theta$ ) on films isolated from aqueous solutions were made as before with drops of the generating solutions at the same concentration and pH at which the monomolecular film to be tested was formed. Since conditions of solution equilibrium obtained, effects due to dissolution of the film into the superjacent test drops were avoided. Changes in pH were effected by the dropwise addition of the appropriate solution (6.0, 0.6, or 0.06 N) of HCl or KOH to the acid solution with continuous stirring. The presence of electrolytes is known to have a marked influence on the adsorption of hydrophobic films on minerals (4), on the critical concentration for micelle formation in aqueous soap solutions (5), and on the surface tensions of the aqueous solutions (6). Precautions were therefore observed to keep the concentration of added electrolytes as low as possible, consistent with the adjustment of the pH. For the more soluble compounds and for low concentrations, the pH response was investigated for two separate portions of the solution, to one of which was added HCl only and to the other KOH only. For the more insoluble acids, it was sometimes necessary to add KOH initially to facilitate the dissolving at the higher concentrations; in such cases it was impossible to avoid the presence of neutral salts. Periodic checks were made to determine the effect of the presence of excess electrolytes on the reproducibility of the  $\theta$ -vs.-pH curves; with one exception, no significant differences were detected. In the case of benzoic acid solutions, however, attempts to retrace the acidic portion of the curve from pH 2 to its peak, in the presence of the relatively high concentration of HCl required to reach pH 2, were only partially successful. The general shape of the curve was repeatable, but subsequent values of the peak angle ( $\theta_p$ ) were never as high as the original value. The curve was more nearly reproducible when approached from the alkaline direction in the presence of excess KOH.

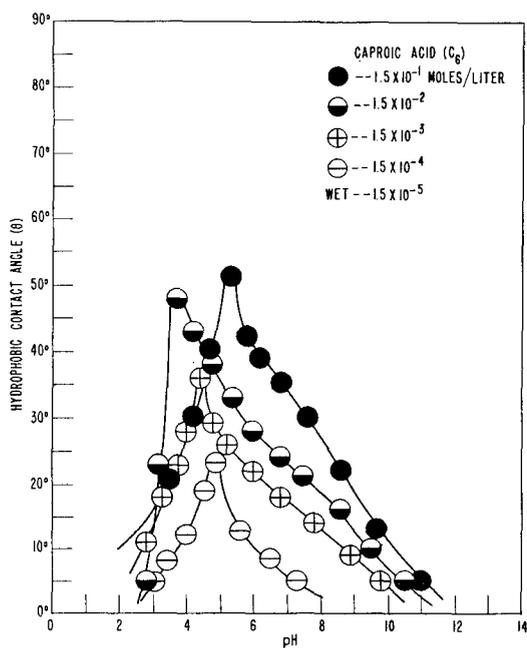
Measurements of the hydrophobic contact angles on films isolated directly from melts of pure compounds were made using drops of distilled water; for the more soluble organic compounds, this may well have resulted in a tendency for the films to dissolve into the test drops. Because of the experimental difficulties involved in transferring a test drop of water onto a highly hydrophobic surface, it was frequently difficult to avoid conditions leading to the existence of a receding contact angle. However, the introduction of additional liquid into the drop following its contact with the monolayer was found to increase the observed contact angle from a somewhat lower initial value to a maximum value equivalent to the advancing contact angle.

## MONOCARBOXYLIC ACIDS

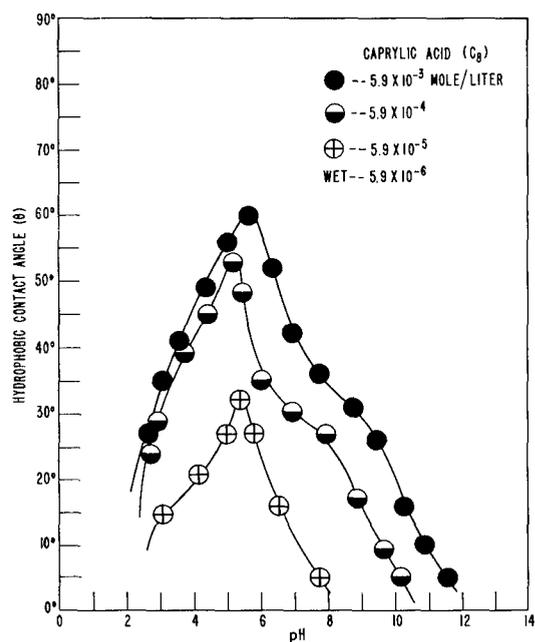
The change of the contact angle ( $\theta$ ) with the pH for each of several concentrations ( $W$ ) of four n-alkyl monocarboxylic acids in aqueous solution is shown in Figures 1a, 1b, 1c, and 1d for caproic ( $C_6$ ), caprylic ( $C_8$ ), capric ( $C_{10}$ ), and lauric acids ( $C_{12}$ ), respectively. At least four different concentrations, representing a 10,000-fold increase in the solutes, were investigated over a pH range of 2 to 13 at intervals of 0.5- to 1.0-pH units. Each curve in the figure is the locus of points obtained from solutions having the same concentration.

The families of curves for the four acids followed the same general pattern: the individual curves rose sharply from some low value between pH 2 and pH 3 to a peak value ( $\theta_p$ ) in the region between pH 3 and pH 6, then slowly declined, dropping to the  $\theta = 0^\circ$  axis between pH 8 and pH 12. Only partial curves have been reproduced for the higher concentrations of lauric acid because of the limitations imposed by the extreme insolubility of this material, particularly at low pH; the presence of precipitate or cloudiness in the solution has been uniformly indicated by dashed lines over the appropriate pH range. The curves for some of the acids exhibited a "shoulder" on the alkaline side of the peak. The curves for successively less concentrated solutions of a given acid covered a smaller span of pH values, extended less into the alkaline pH range, and exhibited lower peak contact angles. Eventually a concentration was reached so dilute that no signs of hydrophobic film formation were obtained at any pH within the allotted immersion period of 30 seconds. The existence of such a critical minimum concentration ( $W_0$ ) necessary for formation of a solution-repellent film had been established in previous studies (1, 2), where  $W_0$  had been shown to be a measure of the total number of molecules available to an adsorbing surface within a given period of time, and thus to be a function of such experimental conditions as concentration, volume, and rate of stirring of the solution. Values of  $W_0$  for different acids are comparable only when all of the experimental conditions have been controlled.

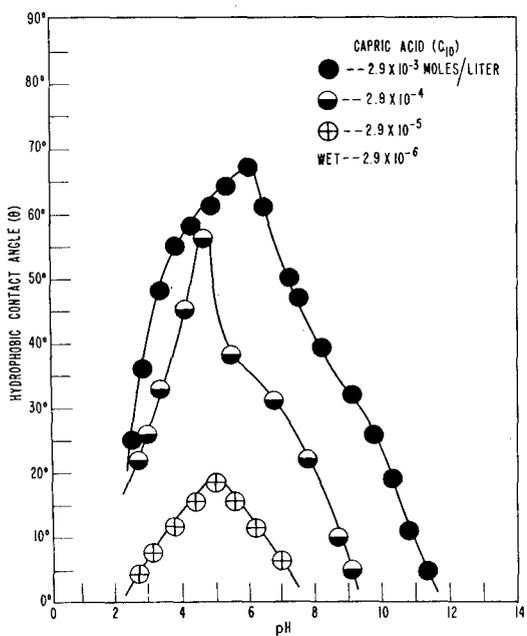
In Figure 2,  $\theta_p$  is plotted as a function of  $W$  for each of these acids. For each compound there is an initial sharp rise in  $\theta_p$  at concentrations just above  $W_0$ , followed by an asymptotic approach (indicated by dashed lines) to some limiting angle ( $\theta_{lim}$ ). The regularity of the change in  $\theta_{lim}$  in the homologous series of acids is evident in the third column of Table 1. In order to demonstrate that  $\theta_{lim}$  is characteristic of the composition of the monolayer and independent of the method of film formation (providing conditions of formation are adjusted to bring about maximum adsorption), monolayers of the saturated straight-chain acids were adsorbed from the molten, pure compound by the thermal-gradient method described later in this report. Contact angles for drops of distilled water resting upon the resultant monolayers are listed in the last two columns of Table 1 (corresponding to conditions of receding and advancing contact angles) for comparison with the values of  $\theta_{lim}$ ; values of  $\theta_{melt}$  (advancing) from the last column in the table have been indicated by bars at the extreme right of Figure 2. Differences in the values are to be expected because of the limitations imposed by the diverse experimental techniques. Since the molecular interstices of a film isolated from aqueous solution are necessarily saturated with water (7),  $\theta_{lim}$  is inherently a receding contact angle. Both receding and advancing contact-angle measurements are possible in determining  $\theta_{melt}$ . The duplication of  $\theta_{melt}$  measurements for the more soluble homologues under conditions corresponding to receding contact angles is complicated, however, by the lack of solution equilibrium between films isolated from the melt and the test drops of distilled water. The tendency for films of the more soluble acids to dissolve into the test drop is eliminated in determining  $\theta_{lim}$  since the films prepared by adsorption from aqueous solution are in equilibrium with the test drops of the generating solution. Nevertheless, Table 1 reveals good agreement between the several values. The same correlation of  $\theta_{lim}$  with  $\theta_{melt}$  has also been observed for monolayers of amines, as shown in Table 2. The effects of homology on  $\theta_{lim}$  and  $\theta_{melt}$  for the monocarboxylic acids (shown in Figure 9a) will be discussed later.



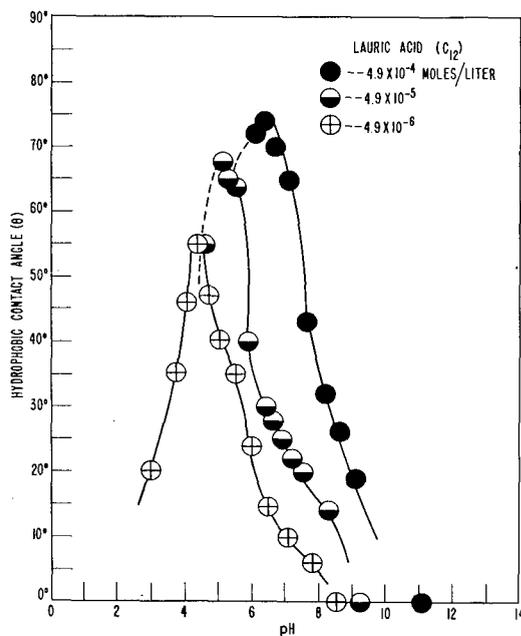
(a)



(b)



(c)



(d)

Figure 1 - Effect of pH on hydrophobicity of n-alkyl monocarboxylic acids

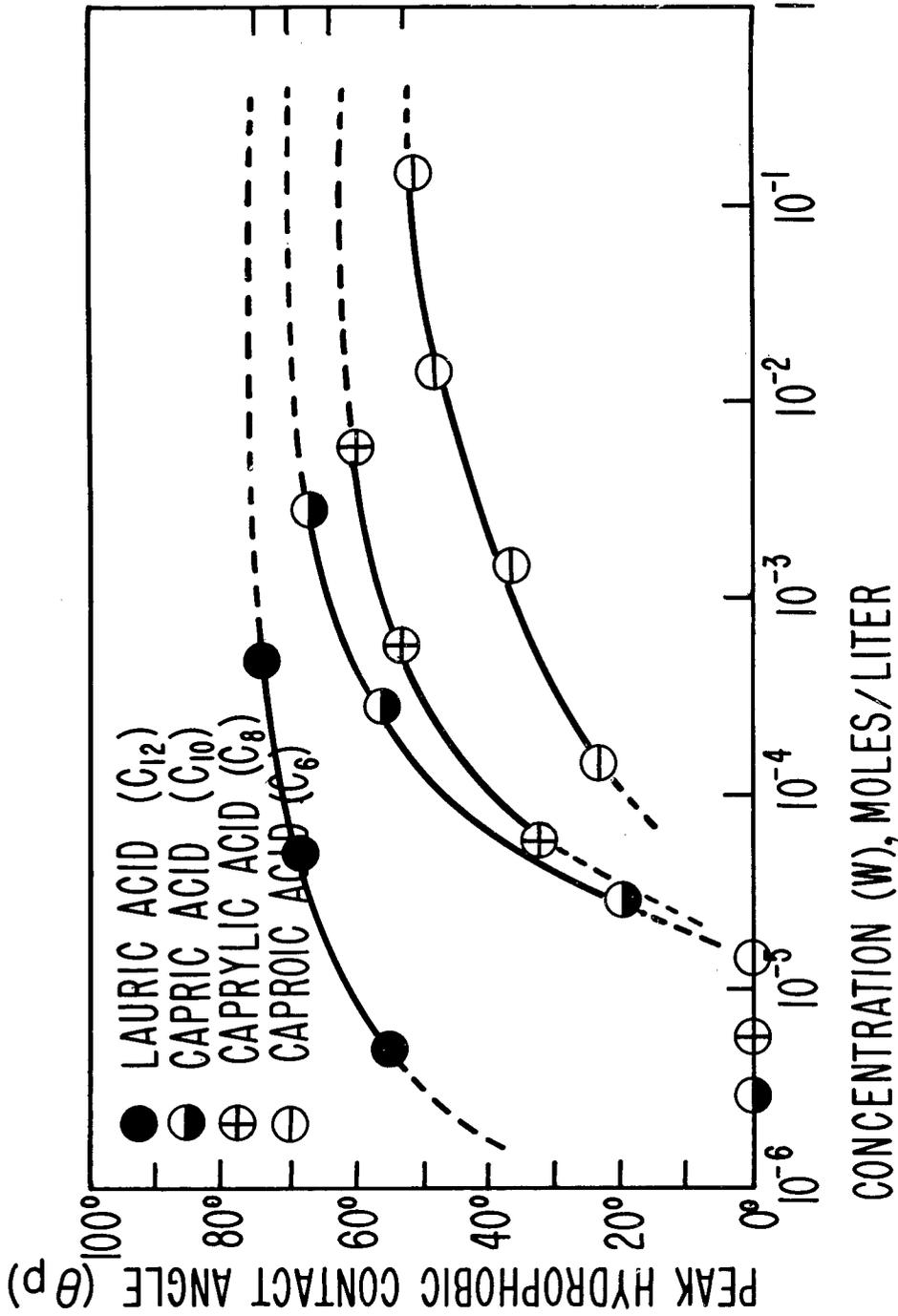


Figure 2 - Correlation of peak contact angle ( $\theta_p$ ) with concentration for n-alkyl monocarboxylic acids

TABLE 1

Hydrophobic Contact Angles * for Monolayers of Carboxylic Acids Adsorbed on Platinum				
Acid	N**	Films Prepared from Aqueous Solution	Films Prepared from Molten Compound by Thermal-Gradient Method	
		$\theta_{lim}$	$\theta_{melt}$ Receding Drop	$\theta_{melt}$ Advancing Drop
<u>n-Alkyl Monoacids</u>				
Caproic	6	52°	49°	53°
Caprylic	8	62	59	64
Capric	10	70	66	70
Lauric	12	76	71	75
Myristic	14	--	75	78
Palmitic	16	--	79	83
Stearic	18	--	81	88
Behenic	22	--	89	96
<u>Cycloalkyl Monoacids</u>				
Cyclohexylcarboxylic	7	53	44	52
Cyclohexylacetic	8	--	65	76
Cyclohexylpropionic	9	64	66	76
Cyclohexylbutyric	10	--	64	74
Cyclohexylcaproic	12	66	64	75
<u>Aromatic Monoacids</u>				
Benzoic	7	53	46	48
Phenylbutyric	10	--	45	49
<u><math>\alpha, \omega</math>-Alkane Dicarboxylic Acids</u>				
Succinic	4	29	24	26
Adipic	6	40	35	40
Sebacic	10	54	52	56
Dodecanedioic	12	--	62	65
Tetradecanedioic	14	--	72	76
<u>n-Alkyl Succinic Acids</u>				
Octylsuccinic	12	71	69	73
Decylsuccinic	14	72	71	76
Octadecylsuccinic	22	77	72	79

\* Contact angle measurements made at  $20.0^\circ \pm 0.1^\circ\text{C}$   
\*\* N = Total number of carbon atoms per molecule

TABLE 2

Comparison of Hydrophobic Films of Amines								
n-Alkyl Amine	N*	Films Prepared from						
		Molten Compound				Cetane Solution		Water Solution
		Thermal-Gradient Method **		Isothermal Method **		Oleophobic Method **		Hydrophobic Method
		Advancing	Receding	Advancing	Receding	Advancing	Receding	$\theta_{lim}$
Butylamine	4	55°	48°	55°	51°	--	--	52° ***
Octylamine	8	81	67	74	69	73	68	69 ***
Dodecylamine	12	90	83	89	83	89	83	85 ***
Tetradecylamine	14	91	84	92	87	90	86	86 ***
Hexadecylamine	16	96	87	96	89	96	89	89 ***
Octadecylamine	18	102	89	102	91	101	90	90 **

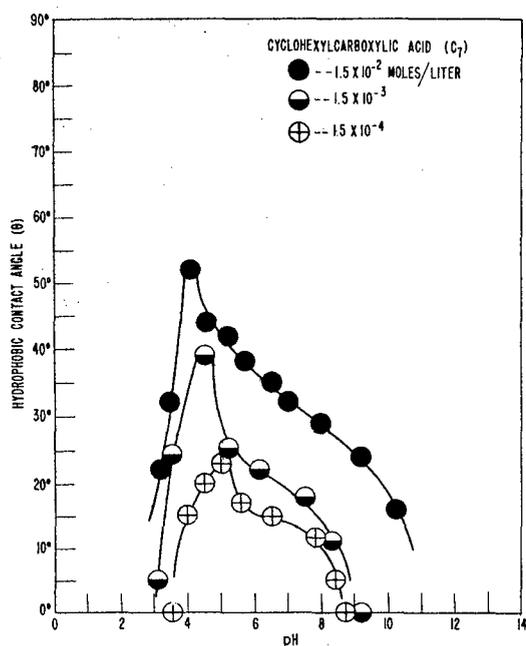
\* N = Total number of carbon atoms per molecule  
\*\* Measurements were made at temperature  $20.0^\circ \pm 0.1^\circ\text{C}$   
\*\*\* Measurements were made at temperature  $25^\circ \pm 1^\circ\text{C}$ . These data are reproduced from Table 2 in Reference (1).

The relations between  $\theta$  and pH for cyclohexylcarboxylic, cyclohexylpropionic, and cyclohexylcaproic acids adsorbed from aqueous solution are shown in Figures 3a, 3b, and 3c, respectively. Some difficulty was encountered in obtaining the complete curves for higher concentrations of cyclohexylcaproic acid in water because of its limited solubility. Since extensive precipitation occurred in the solution before the peak value for the contact angle could be reached, no precise value of  $\theta_{lim}$  was determinable from the plot of  $\theta_p$  as a function of concentration. An indication that the highest value of  $\theta_p$  observed experimentally ( $63^\circ$ ) was close to  $\theta_{lim}$  was obtained however, by noting that a  $64^\circ$  angle was found for  $\theta_{melt}$  under conditions leading to a receding contact angle. Values of  $\theta_{melt}$  for these cyclic compounds were not obtainable by withdrawing a platinum dipper from a pool of the molten polar compound as described in previous papers (1, 3). The values for  $\theta_{melt}$  given for them and their homologues in Table 1 were obtained by the thermal-gradient method which will be described later. Figure 3d summarizes the results obtained with benzoic acid, the value of  $\theta_{lim}$  and the behavior to changes in pH and concentration being nearly the same as that obtained for the corresponding saturated cyclic acid. In Figure 4 is a plot of  $\theta_p$  vs. W for these cyclic acids. As before, the asymptotic approach to  $\theta_{lim}$  is indicated by a dashed line, and the appropriate values of  $\theta_{melt}$  (from the last column in Table 1) are represented by heavy bars at the extreme right of the figure.

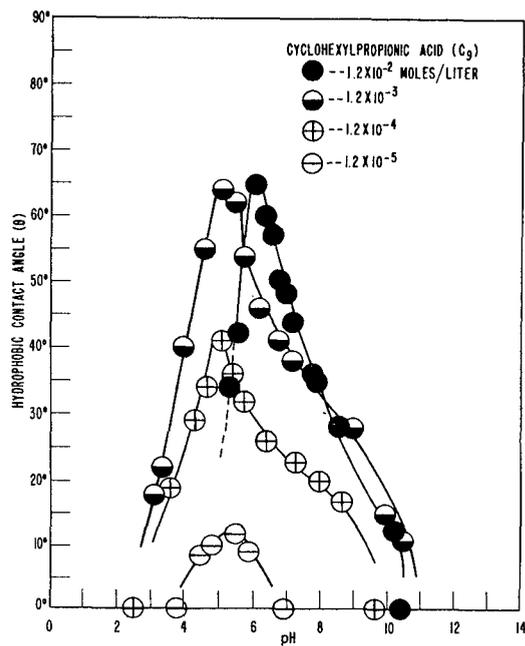
## DICARBOXYLIC ACIDS

The data for three homologous  $\alpha, \omega$ -dicarboxylic acids are presented in Figures 5a, 5b, and 5c for succinic (C<sub>4</sub>), adipic (C<sub>6</sub>) and sebacic acids (C<sub>10</sub>), respectively, and the summary of the  $\theta_p$ -vs.-W data for these compounds is to be found in Figure 6. For the sake of clarity, the curves for one concentration and several additional experimental points have been omitted from Figures 5a and 5b. The appropriate values of  $\theta_p$  have, however, been indicated in Figure 6. The general behavior of the graph of contact angle vs. pH is similar to that previously observed for the monocarboxylic acids. The effects of homology on  $\theta_{lim}$  and  $\theta_{melt}$ , as shown in Table 1 and Curve A of Figure 9b, where the lengthening of the methylene chain in going from succinic acid to tetradecanedioic acid is seen to markedly increase the limiting hydrophobic contact angle, will be discussed later.

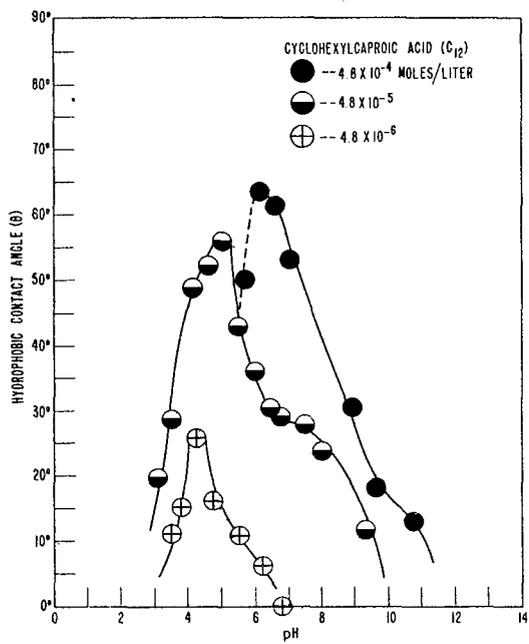
The  $\theta$ -vs.-pH curves for octylsuccinic acid, the most soluble of the three alkyl-substituted succinic acids studied (Figure 7), showed a strong "shoulder" effect on the acidic as well as the alkaline side of the peak, but the curves were not symmetrical. These graphs were reproducible. The low solubility of these alkylsuccinic acids caused precipitation effects which, in the case of the decylsuccinic and octadecylsuccinic acids, prevented the determination of the highly acidic portion of the curves for the higher concentrations. As before, the presence of visible precipitate or cloudiness in the solutions has been indicated by dashed curves over the appropriate pH range. For the most concentrated solution of octadecylsuccinic acid it proved necessary to add ethyl alcohol for all pH values below 7.8 in order to determine the peak of the curve. It is interesting to note that the limiting contact angles ( $\theta_{lim}$ ) obtained (Figure 8) were nearly the same for all three alkylsuccinic acids; the corresponding values in Table 1 for  $\theta_{melt}$  obtained by the thermal-gradient method are in good agreement.



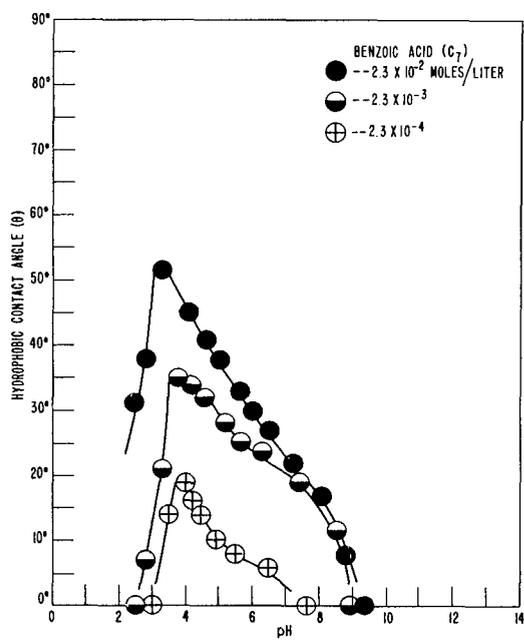
(a)



(b)



(c)



(d)

Figure 3 - Effect of pH on hydrophobicity of cyclic monocarboxylic acids

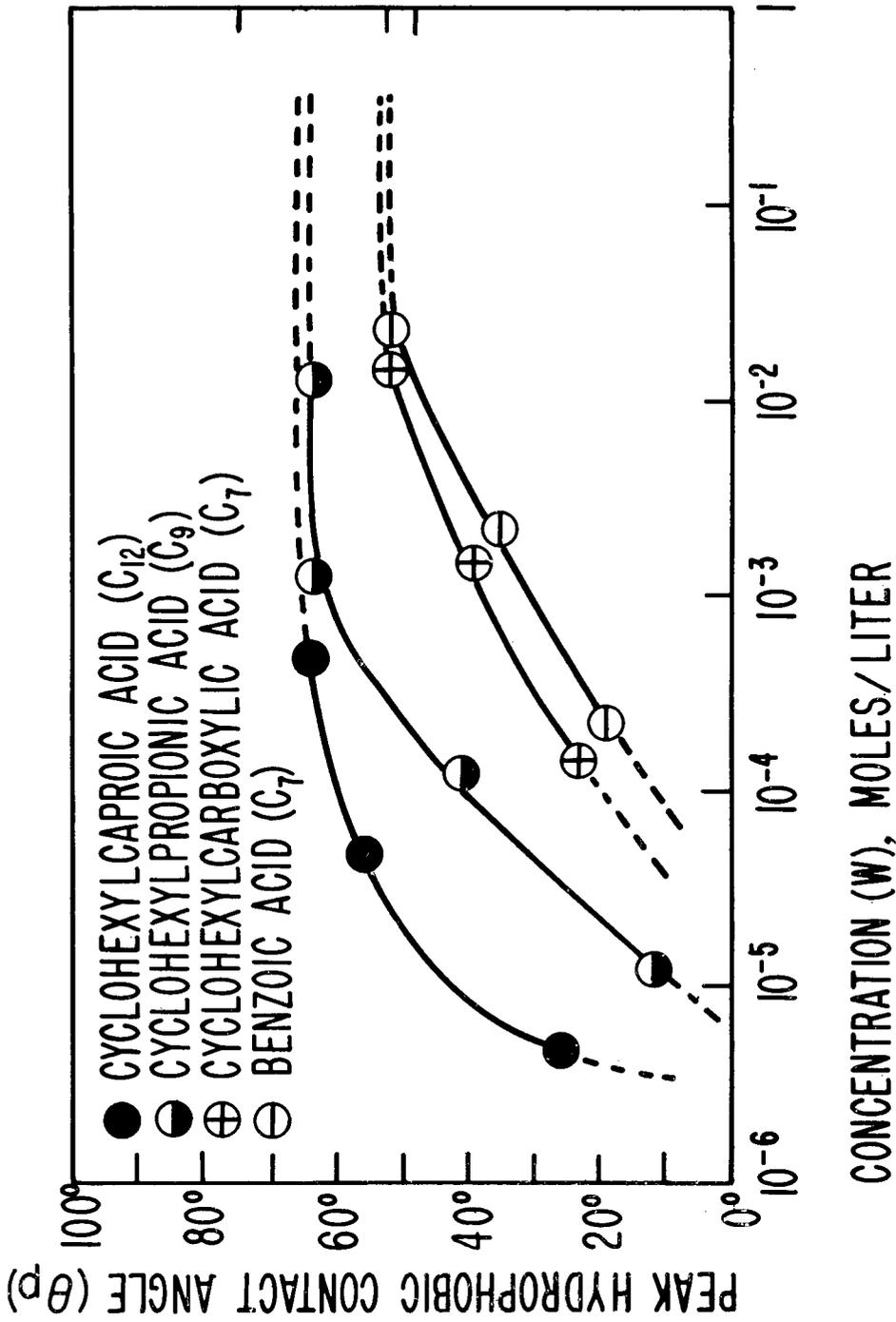


Figure 4 - Correlation of peak contact angle ( $\theta_p$ ) with concentration for cyclic monocarboxylic acids

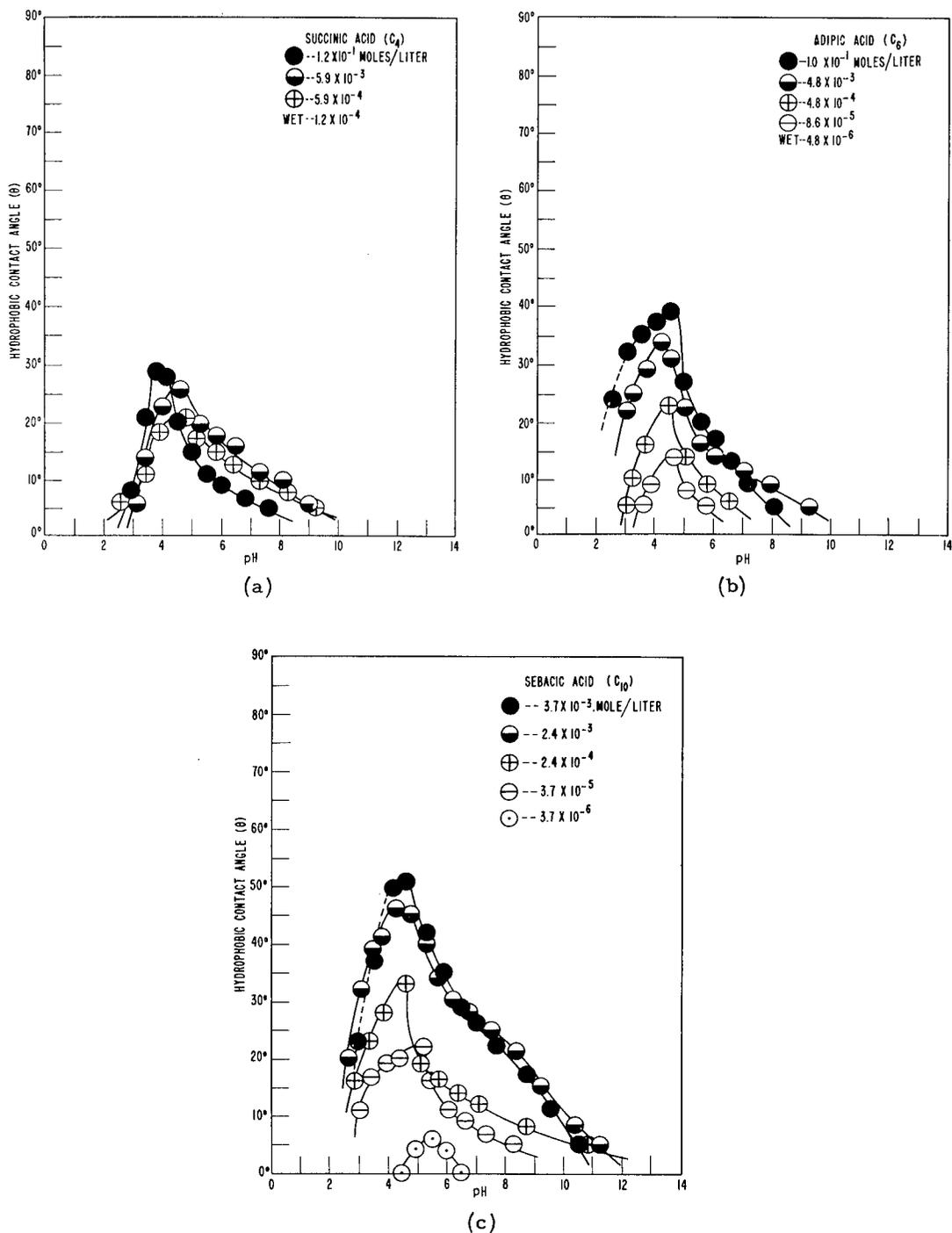


Figure 5 - Effect of pH on hydrophobicity of  $\alpha, \omega$ -alkyl dicarboxylic acids

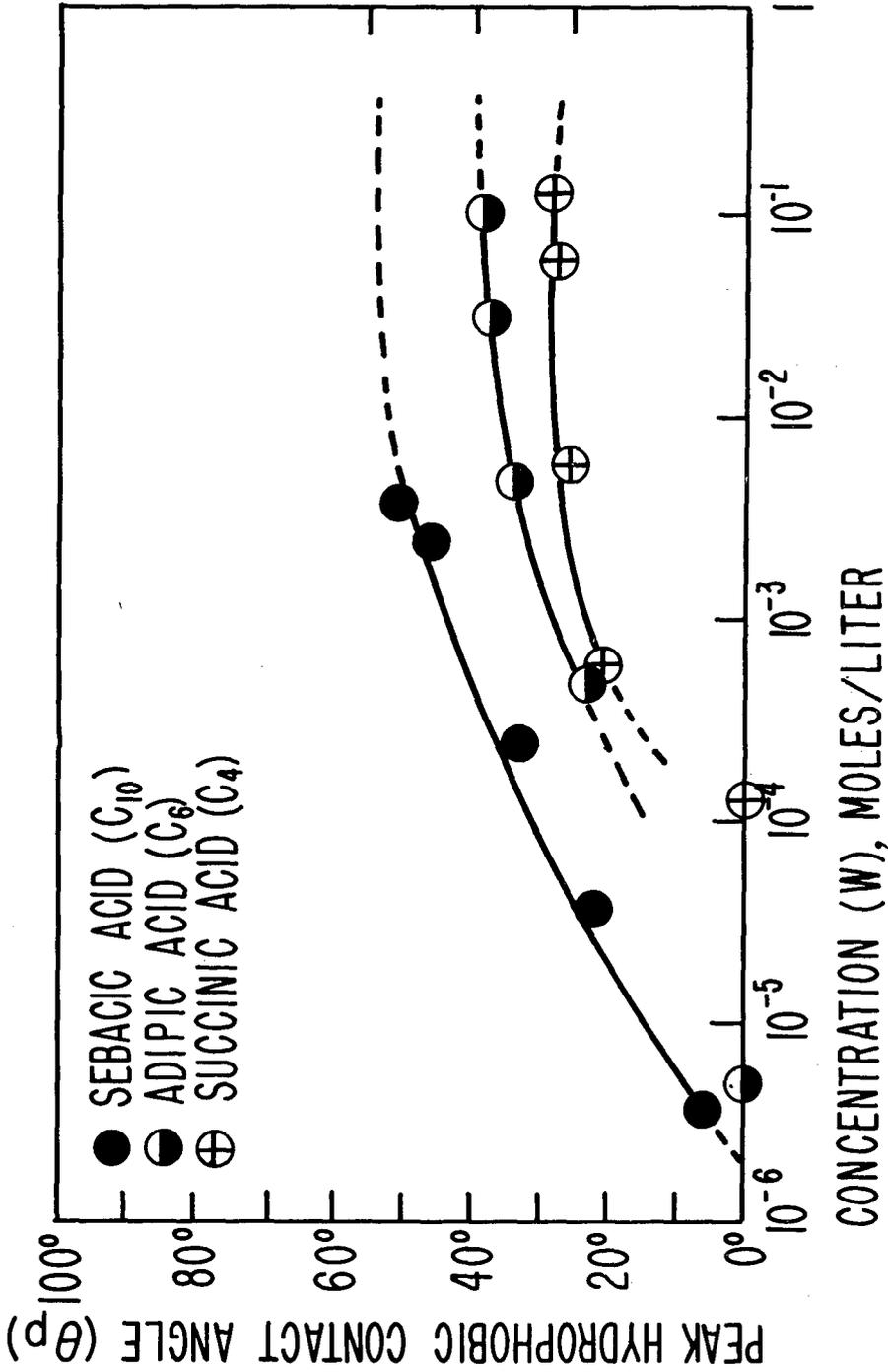


Figure 6 - Correlation of peak contact angle ( $\theta_p$ ) with concentration for  $\alpha, \omega$ -alkyl dicarboxylic acids

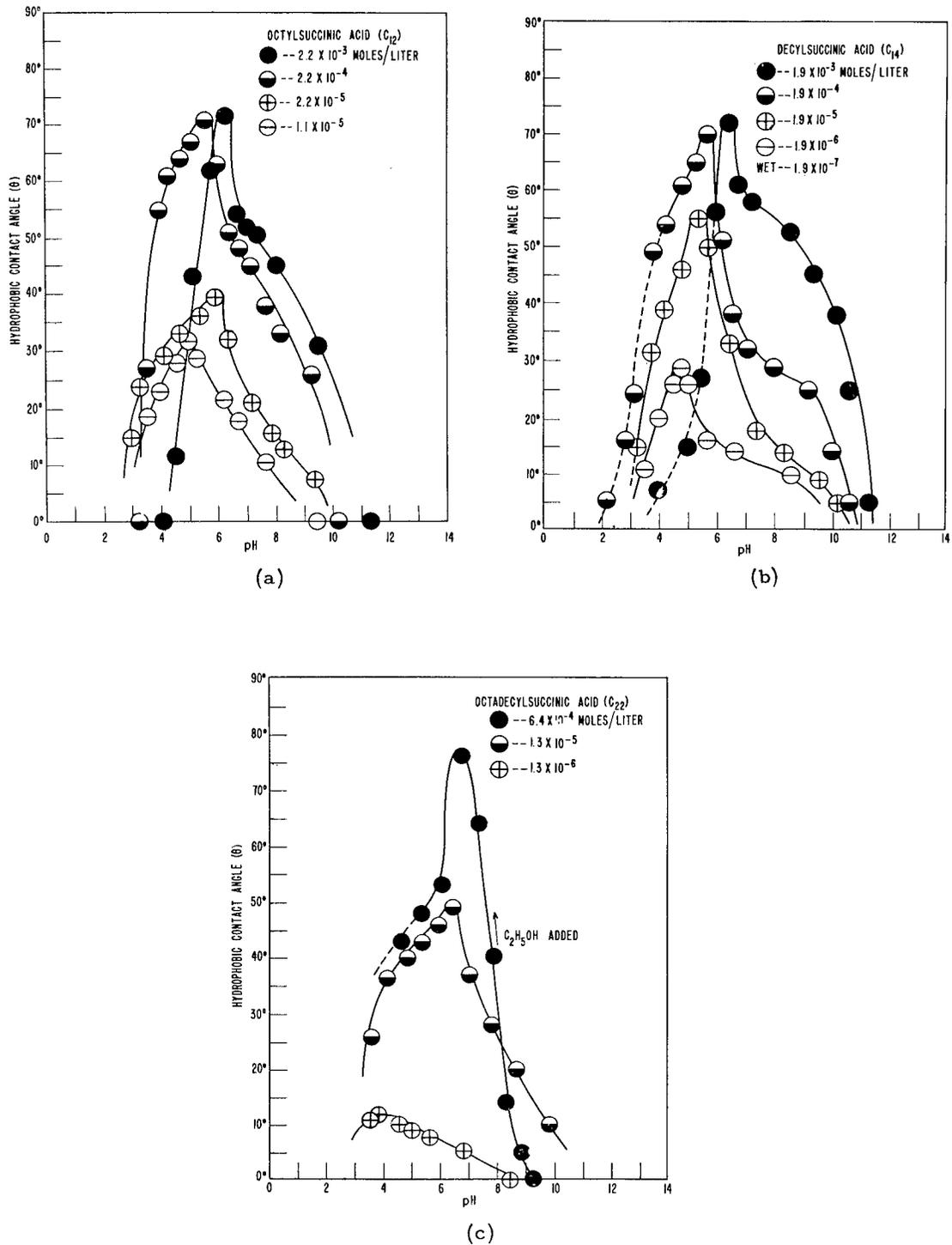


Figure 7 - Effect of pH on hydrophobicity of alkylsuccinic acids

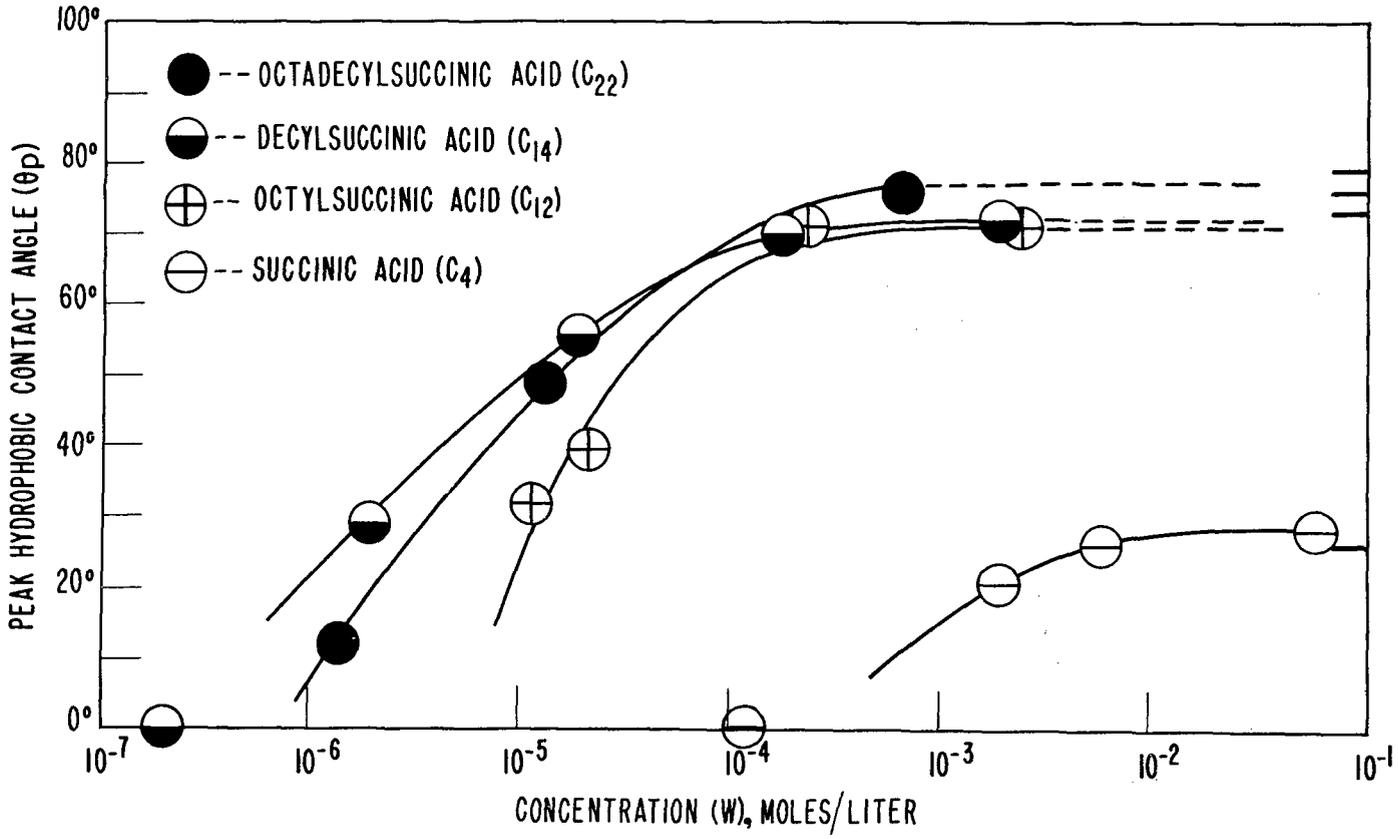


Figure 8 - Correlation of peak contact angle ( $\theta_p$ ) with concentration for alkylsuccinic acids

## THERMAL-GRADIENT METHOD

Previous success in isolating adsorbed monolayers by withdrawing the platinum dipper from a pool of the melted polar compound (3) had been limited to essentially paraffinic or unbranched types of compounds, i.e., those meeting the requirements of structure and orientation for formation of oleophobic films as mentioned in an earlier paper (2). It was even possible, by the use of this "isothermal method," to prepare monolayers of those lower series members which were not sufficiently oleophobic to permit their isolation from oil solution in nonpolar solvents. This method, however, was not effective in isolating monolayers of branched or cyclic compounds. Even for the straight-chain compounds, its effectiveness in preparing monolayers completely free of residual bulk compound was limited by the working range of temperature between the melting point of the compound and the temperature,  $\tau$ , at which the monolayer became wetted by the melt.

The need for a method of preparing, in the absence of solvent, a monolayer of any type of polar compound led to much experimenting with other ways than the isothermal method of separating an adsorbed monolayer from the molten polar material. The result was the "thermal-gradient method." A small amount of the pure compound was placed on a piece of platinum foil held with its plane slightly inclined from the horizontal. After the uppermost edge of the platinum was gently heated, the organic material melted and wet the metal surface. As the heating continued, the molten material suddenly receded to the lower, cooler edge of the platinum, exposing a dry area in a band immediately adjacent to the liquid. The temperature at which this occurred appeared to be slightly below that required for visible vaporization of the organic compound from the hot upper edge of the foil. When the foil was allowed to cool to room temperature while still tilted, the organic material remained at the lower edge where it was either allowed to solidify, or, if a liquid at room temperature, it was drawn off by contact with a filter paper. Hydrophobic contact-angle measurements taken at various positions over the surface of the foil were large and reproducible over the "dry band" immediately adjacent to the bulk material. Lower and erratic contact angles were observed near the uppermost edge of the foil where the higher temperature may well have led to the vaporization of some of the organic film.

Proof that this thermal-gradient method gives rise to films in the "dry band" (mentioned above) which are identical with monolayers prepared by earlier methods is afforded in Table 2 by a comparison of the hydrophobic contact angles observed on monolayers of several homologous n-alkyl pri-amines isolated from the melt by the thermal-gradient method and by the isothermal method with those obtained by adsorbing the monolayer from dilute solution in either cetane or water. The agreement between the several values observed is good considering the differences inherent in the experimental technique. For example,  $\theta_{lim}$ , which is intrinsically a receding contact angle, is measured against a test drop in complete equilibrium with the adsorbed monolayer. Although  $\theta_{melt}$  (by either the thermal-gradient or the isothermal method) is readily reproducible if the test drop of water is placed so as to obtain an advancing angle, the lack of solution equilibrium between the monolayer and the test drop causes difficulties in reproducing receding contact angles for the shorter-chain, more soluble homologues. Such solubility effects become negligible with the longer-chain compounds, and the receding contact angle is then more reproducible.

Because of the greater difficulty of making a test drop adhere to a highly hydrophobic surface (discussed previously), the initial contact angle exhibited by a test drop generally represents a receding contact angle, and only upon continuous buildup of the size of the drop does the advancing angle become manifest. Thus, in the earlier study of amine monolayers (1), the contact angles reported for water on monolayers prepared by adsorption from cetane solutions correspond to the receding contact angles as listed in Table 2 for

the longer-chain, more hydrophobic homologues. A similar qualification is believed applicable to the other contact angles reported for water on highly hydrophobic monolayers (2, 3).

The thermal-gradient method for separating an adsorbed monolayer from the melt involves several factors resulting in one of the following possible mechanisms. The first involves the evaporation, in the "dry band," of all polar molecules present at the heated surface except the more strongly adherent molecules comprising the monolayer in contact with the metal surface. At the upper and hotter edge of the metal, this monolayer is less closely packed because of the evaporation of occasional adsorbed molecules. At the slightly lower temperature prevalent in the area of the "dry band," insufficient thermal energy is imparted to the individual adsorbed molecules to enable them to escape from the close-packed film. At the cooler temperatures near the lower edge, films thicker than a monolayer exist.

A second possible mechanism is that the results observed are due to the combined effects of gravity and thermal agitation. In this instance there is a recession of the liquid phase from the elevated portion of the surface as the result of what may be termed a gravitational diffusion of all molecules except those anchored in the monolayer. The angle of tilt of the metal surface may be necessary to facilitate the slippage of the molecules in the liquid with respect to the external plane of the adsorbed monolayer. The importance of this would be greatest for materials with branched chains or cyclic groups where the greater possibility for the meshing of the molecules in the liquid with those in the adsorbed layer would interfere most seriously with the ease of slippage between these two phases.

A third mechanism could arise if it is assumed that the oleophobic property of the liquid and the adsorbed film does not become operative for some polar substances unless there is an appropriate temperature, encountered in the "dry band," coupled with improved slippage due to the moderate tilt of the plane of the adsorbed monolayer. Definitive experiments are in progress to determine the actual mechanism.

By using the thermal-gradient method it has been possible to obtain, from the melt, monolayers of every type of acid of interest in the present study. Data for the hydrophobic contact angles  $\theta_{\text{melt}}$  have been listed in Table 1 for comparison with the values of  $\theta_{\text{lim}}$  obtained for these several acids from aqueous solution. The maximum hydrophobicity obtainable from an adsorbed close-packed monolayer of any of these acids can evidently be measured quickly with the thermal-gradient method eliminating the evaluation of  $\theta_{\text{lim}}$  by obtaining laboriously all the data needed to graph  $\theta_p$  vs.  $W$ . Moreover, this method of preparing films makes possible the measurement of advancing as well as receding contact angles, whereas receding angles alone are obtainable for films adsorbed from aqueous solution. Moreover, a fuller correlation of hydrophobicity with chain length and acid type becomes possible, since there is no longer the restriction to the lower members of the series because of the required solubility in water. Thus, for the *n*-alkyl monocarboxylic acids, for which  $\theta_{\text{lim}}$  data are available only for the homologues up to  $N = 12$ , it has been possible with the thermal-gradient method to obtain monolayers and to measure the effect of chain length on hydrophobicity for the series through  $N = 22$ , as shown in Figure 9a, Curve A.

In Figures 9a and 9b are presented data showing the effect on hydrophobic contact angle ( $\theta_{\text{melt}}$ ) of the length of the alkyl series studied. Within each series it is possible to represent the data for all but an occasional lowest homologue by a straight line. Changes in the hydrocarbon portion of the molecule or in the number and type of functional groups in going from one homologous series to another are reflected in the slopes and positions of the lines. Table 3 lists the slopes obtained for the various series. In order to indicate the

relative positions of the lines, the intercept of the line with the ordinate  $N = 10$  has been arbitrarily chosen for inclusion in the table. The implications of these data will be more fully developed in the next section.

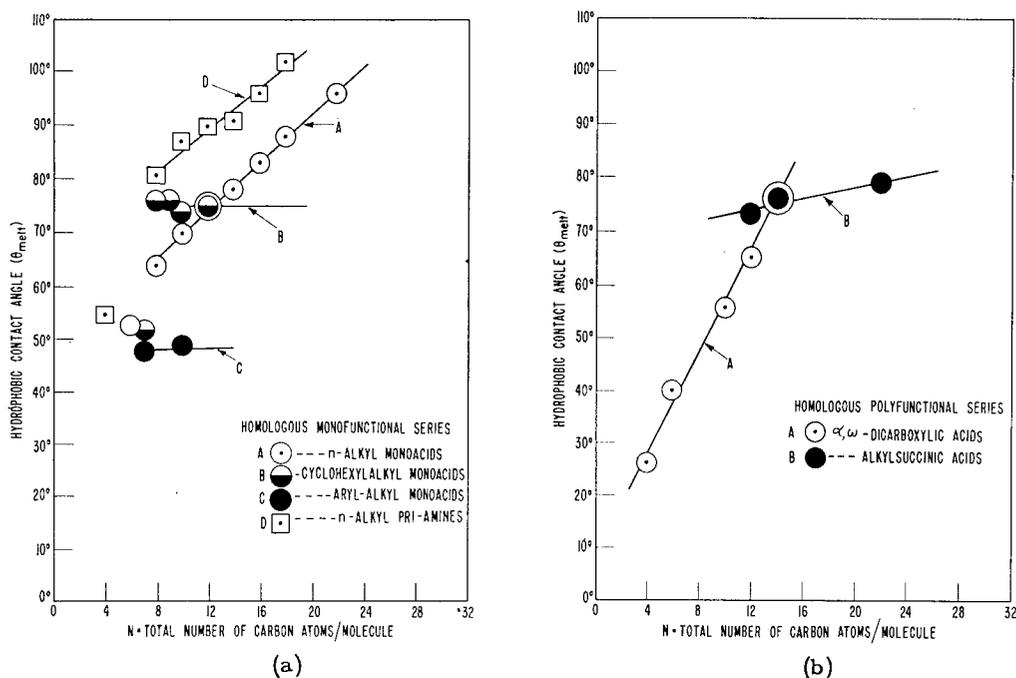


Figure 9 - Effect of chain length on hydrophobic contact angle

TABLE 3

Comparison of Experimental Curves of $\theta_{melt}$ vs. $N$ for Several Homologous Series		
Homologous Series	Slope (degrees/carbon increment)	$\theta$ for $N = 10$
n-Alkyl Pri-Amines	$2.0^{\circ}$	$80^{\circ}$
n-Alkyl Monoacids	2.2	70
Cycloalkyl Monoacids	0	75
Aryl-Alkyl Monoacids	0	49
$\alpha, \omega$ -Alkane Dicarboxylic Acids	4.9	56
n-Alkyl Succinic Acids	0.5	73

## DISCUSSION

Numerous investigators have described the effects of variation of the pH on the surface-chemical properties of aqueous solutions of the carboxylic acids and their salts. This includes the effects on the surface tension and interfacial tension (5, 6, 8, 9, 10), the detergency (11), the flotation of minerals (4, 12), and the stability of foams (13, 14). In most cases the variations observed were attributed to the relative proportions, solubilities, and surface activities of: the carboxylic acid anions, the hydrolytic free acid, the undissociated soap molecules, the acid-soaps, and the colloidal micelles or other aggregates. In general, maximum surface activity was obtained at those pH values which corresponded to partial or complete hydrolysis of the soap, indicating that the molecular form of the acid is the more surface-active species, at least in dilute solutions. The results of research have been recently summarized on the critical micelle concentration (CMC) of various soaps and the effects of salts in decreasing the CMC (15, 16). From these it is concluded that the concentrations of acids and soaps used in this investigation in the more dilute solutions were too low to permit formation of micelles.

The relative importance of the various ions and molecules present in solution and their influence on the adsorption equilibria can best be discussed by an application of the law of mass action and available data on the dissociation constants of the acids present. This has been done and has been reported separately (17). It was shown that at both the extremes of the pH scale the sharp decrease in hydrophobicity is due to the competitive adsorption of nonhydrophobic aqueous ions; in the intermediate range there are adsorbed films made of hydrophobic carboxylate ions and neutral acid molecules, the former being dominant in the alkaline pH and the latter at the acid pH regions, respectively. It was found possible to predict the pH for maximum hydrophobicity from a knowledge of the dissociation constant of the acid.

From its definition it is evident that  $\theta_{\text{lim}}$  is the contact angle for the monolayer in closest-packed arrangement obtainable by adsorption from aqueous solution. Provided the solubility of the organic polar compound is sufficient,  $\theta_{\text{lim}}$  will also correspond to the maximum packing obtainable from solution in any solvent; the only exceptions to be expected would occur under conditions of adsorption of mixed films of solvent and solute. Hence it is not surprising that essentially the same values of  $\theta$  were obtained, in a number of instances already described, by using saturated films prepared by adsorption from water, ethanol-water, benzene, dicyclohexyl, or hexadecane. Since in the limit a solution of increasing concentration will approach in behavior that of the pure molten acid,  $\theta_{\text{lim}}$  should equal  $\theta_{\text{melt}}$ , the exceptions occurring where there are marked effects on the orientation or packing of the adsorbed film due (a) to the higher temperature often needed to produce monolayers from the melt, or (b) to any differences in the films because of mixed film formation. This agreement of  $\theta_{\text{lim}}$  and  $\theta_{\text{melt}}$  is well exhibited in Tables 1 and 2.

The thermal-gradient method is valuable in making available data on the relative hydrophobicity of the closest-packed monolayers not obtainable by adsorption. It can be employed with a wide variety of structural types of compounds with much less experimental difficulty than other methods. With its use it becomes possible to make a rapid survey of the film-packing possibilities of each different class of polar compounds. It should also prove useful in future studies of the adsorption of polar compounds to more reactive metals than platinum. Further research on the mechanism involved is in progress.

In Figure 9a, data for the two most comparable homologous series, the n-alkyl monocarboxylic acids and the n-alkyl pri-amines, are seen to be represented by two straight

lines which are parallel but displaced (Table 3). Inasmuch as molecules of each of these types adsorb on platinum, with the dipoles at the metal surface and the hydrocarbon portion of the molecule extended and oriented approximately normal to the adsorbing surface (18), the lengthening of the aliphatic chain leads to an increase in the van der Waals cohesive forces between adjacent chains and thus to a closer packing of the chains, which is in turn reflected in an increased water-repellency for the films. A saturation effect can be expected for  $\theta$  at or below  $108^\circ$  (a value frequently seen in the literature for water on paraffin) for compounds of longer chain length than those reported here. The identity of the slopes for these two series is indicative of an equivalent effectiveness of increasing chain length on the hydrophobicity of monolayers characterized by this molecular orientation. The displacement of the acid curve some  $10^\circ$  below that for the amines is consistent with the following previously reported relative adsorptive properties of amines and acids: (a) for a given chain length, amines adsorbed from solution in hexadecane or dicyclohexyl have the longer lifetimes of adsorption (2, 3); and (b) for a given chain length, amine monolayers are more resistant than acid monolayers to thermal desorption effects, since the former require approximately an  $80^\circ\text{C}$  increase in  $\tau$ , the temperature characteristic for the wetting of the film by the pure molten compound (3).

A horizontal straight line is found to represent the data for all of the cyclohexylalkyl monoacids with the exception of cyclohexylcarboxylic acid (Curve B in Figure 9a). In the latter case, the absence of a methylene link between the polar group and the cyclic portion of the molecule is reflected by a sharp drop in the hydrophobicity of the monolayer. The existence of a limiting, maximum water-repellency, independent of changes in  $N$  above  $N = 8$ , may be explained if it is assumed that: (a) the cyclic acids are oriented approximately normally to the adsorbing surface, and (b) the maximum hydrophobicity observed corresponds to the closest packing obtainable for molecules containing the cyclohexyl group. Because the effective cross-sectional area of the terminal cyclohexyl group is considerably greater, for saturation packing; than that of the underlying alkyl chain, increases in the length of the alkyl chain should have no effect on the hydrophobic contact angle. This would account for the horizontal straight line observed experimentally for  $\theta$  for values of  $N$  from 8 to 12. The lowered hydrophobicity of monolayers of cyclohexylcarboxylic acid may reflect some basic difference in the orientation of the adsorbed molecules of this type, possibly because of a decrease in the flexibility of the molecule. This problem deserves further investigation, preferably by some more direct method such as electron diffraction.

Although only two members of the corresponding series of aromatic monoacids were available for study, it is interesting to note that the experimental data lead to a horizontal line (Curve C, Figure 9a), as above. By analogy, the existence of the maximum water-repellency may be attributed to a saturation packing of the phenyl groups. The considerably lower repellency characteristics (a  $25^\circ$  drop in hydrophobic contact angle) for the aromatic compounds as compared with those of the corresponding aliphatic analogues may reflect the differences in the polarity of these two types of hydrocarbons.

Curve A in Figure 9b presents the data for the homologous series of  $\alpha, \omega$ -alkyl dicarboxylic acids. Comparison of this curve with that obtained for the alkyl monocarboxylic acids reveals that the replacement of a methyl end group by a second carboxylic group serves both to depress the hydrophobic contact angle for the lowest homologues (for compounds below  $N = 12$ ) and to increase the effectiveness of lengthening the methylene chain in raising the hydrophobic contact angle (i.e. the slope of the line) by a factor of 2.5.

Several orientations are conceivable for these adsorbed diacids. If only one carboxylic acid group per molecule adsorbs, the remainder of the molecule may be extended normal to the adsorbing plane, presenting an external surface of close-packed carboxylic groups

(Figure 10a). Such an orientation would be expected to result in a  $\theta$ -vs.- $N$  line which, if it exists at all, would certainly be displaced below that for the alkyl monoacids for all values of  $N$ . Moreover, it is inconceivable that the slope of the line would exceed that obtained for the straight-chain monoacids. Other possible configurations would involve the simultaneous adsorption of both acid groups at the metal surface, with the intervening aliphatic chain of methylene groups either looped away from the adsorbing surface (Figure 10b), or extended parallel to it (Figure 10c).

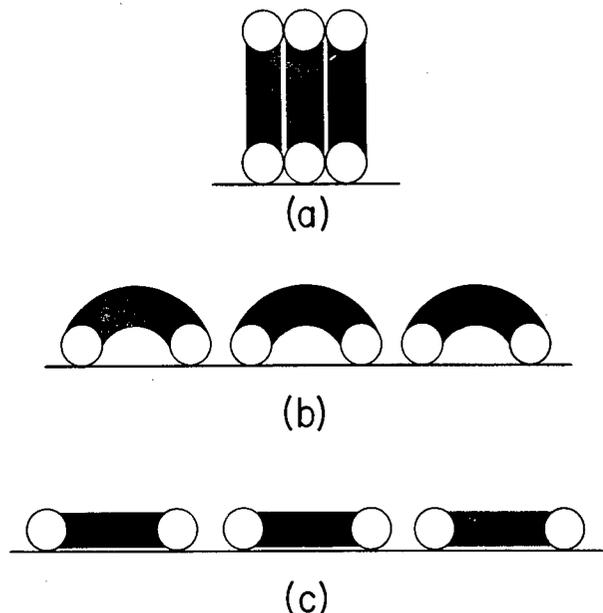


Figure 10 - Molecular configurations possible for adsorbed  $\alpha$ ,  $\omega$ -alkyl dicarboxylic acids

For configuration (b), the longer chain compounds would form taller loops which could pack more closely and, hence, shield the carboxylic groups more effectively from contact with the water drop. In this orientation, the effectiveness of each methylene increment in increasing the hydrophobic contact angle would be expected to be somewhat less than that obtained for a corresponding addition to a normally oriented straight chain.

In the parallel arrangement (c), increasing the chain length would decrease the proportion of exposed carboxylic groups to exposed methylene groups; since the latter are considerably more hydrophobic, this would result in an increase in  $\theta$ . For the lowest homologues, the presence of a high proportion of exposed carboxylic groups would be expected to depress the hydrophobic contact angle considerably below that characteristic of the analogous  $n$ -alkyl monoacid; for the higher homologues, a more favorable ratio exists and the effect of the presence of the exposed carboxylic group might be largely suppressed. Although the curve corresponding to configuration (c) appears somewhat consistent with the experimentally obtained curve, it remains for an independent experimental approach to decide among the several possibilities. Some indication as to probable configuration may be afforded by the comparison of the asymptotic maximum value of  $\theta_{melt}$ , to be expected at high values of  $N$ , with the contact angles characteristic of films of known composition and orientation. A more direct approach, using the electron diffraction method, is now in progress.

In contrast, the curve representing the homologous alkylsuccinic acid derivatives (B in Figure 9b) shows almost no increase in contact angle with increasing chain length in going from octylsuccinic to octadecylsuccinic acid. The approximate constancy of the maximum hydrophobic contact angle obtainable for the three substituted succinic acids with aliphatic side chains differing by ten carbon atoms suggests that the closeness of packing of the aliphatic side chains (assumed to be oriented normal to the adsorbing surface) is limited owing to the presence of the more bulky succinic acid portion of the molecule. Since the effective projected area of the succinic acid group is undoubtedly greater than that of the attached alkyl chain, the lateral forces between chains need not predominate in the packing of the monolayers.

## CONCLUSIONS

The adsorption technique described in an earlier report has been successfully extended to aqueous solutions of typical carboxylic acids. When difficulties with solubility have been encountered, it has been possible to obtain useful data about the limiting contact angle by the use of alcohol-water solutions.

The effects of pH and concentration of acid in the water have been developed and the condition for maximum adsorption found to be at pH between 4 and 6.

The way the limiting contact angle for each polar compound varies with the nature of each acid and with homology has been studied, and it has been found possible to explain the results in terms of orientation and molecular structure.

It has been concluded that the pH effects observed have nothing to do with micelle formation or association and are primarily caused by competitive adsorption between the molecular and ionic species in solution.

A new and convenient "thermal-gradient method" using the pure molten compound has been found by which adsorbed monomolecular films can be prepared and isolated on metal.

The value of  $\theta_{\text{melt}}$  has been shown to be the same by the thermal-gradient method and the isothermal method, and both agree with  $\theta_{\text{lim}}$  from measurements on films adsorbed from aqueous and nonaqueous solutions.

## RECOMMENDATIONS

In order to complete the study of the adsorption of aqueous polar compounds it is desirable to investigate more highly acidic compounds such as alkylsulfonic, phosphonic, and alkyl-substituted phosphonic acids, and more basic compounds like quaternary ammonium hydroxides. Also, representative nonionic surface-active compounds like the alcohols, glycols, and various amides and esters deserve an exploratory examination with respect to pH effects.

The single constant  $\theta_{\text{lim}}$  (or  $\theta_{\text{melt}}$ ) gives a valuable index of the relative hydrophobicity of adsorbed polar compounds, since it indicates the maximum possible effect. Its correlation with the degree of packing and orientation of the molecules in the film is evidently interesting and useful. The work presented here and in the earlier report on

the primary amines needs general extension to cover all types of hydrophobic film structure.

An intensive study of the thermal-gradient method of preparing monolayers on platinum from the molten condition is urgently needed since it has wide application to research on surface chemistry, lubrication, and corrosion prevention. It permits isolation of all types of polar compounds free from the restrictions of the isothermal method.

Eventually a parallel investigation will be desirable for the adsorption on nonnoble metals from aqueous solution and from the pure melt. Especially valuable will be work on iron, steel, and copper because of the obvious relation to research on aqueous corrosion inhibition and the improvement of aqueous lubricants like the hydrolubes and cutting fluids.

#### ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance of Mr. J. G. O'Rear and Mr. N. L. Smith of this Laboratory for the preparation and purification of a number of the compounds studied. The decylsuccinic and octadecylsuccinic acids were prepared from the anhydrides and purified by Mr. O'Rear. The octenylsuccinic anhydride was hydrogenated and converted by Mr. Smith, who was also responsible for the purification of the behenic, dodecanedioic, and tetradecanedioic acids. The decylsuccinic and octadecylsuccinic acids were generously donated by Dr. George von Fuchs. The phenylbutyric acid was kindly supplied by Dr. A. Schneider.

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