NRL REPORT 3797

FR-3797

COMPETITIVE ADSORPTION FROM SOLUTION BETWEEN HYDROPHOBIC AND HYDROPHILIC MOLECULES AND IONS

R. L. Merker and W. A. Zisman

January 1951

Distribution Unlimited

Approved for
Public Release

Approved by:

Dr. P. Borgstrom, Superintendent, Chemistry Division

DEPARTMENT OF THE NAVY ★ OFFICE OF NAVAL RESEARCH ★

NAVAL RESEARCH LABORATORY
CAPTAIN F. R. FURTH, USN, DIRECTOR
WASHINGTON, D.C.

DISTRIBUTION

OpNav	1
ONR	
Attn: Code 425	1
BuAer	5
Attn: Code TD-4	2
BuOrd	5
BuShips	5
CO & Dir., USNEL	2
CDR, USNOTS	
Attn: Reports Unit	2
CO & Dir., USNEES	2
SNLO, USNELO	2
CDR, NAMC	1
Wright-Patterson AFB	
Attn: CADO-D1	1
Attn: CADO-D13	1
Attn: CADO-E1	2
Attn: BAU-CADO	1
Attn: Ch., Electronics Subdiv., MCREEO-2	1
CG, Frankford Arsenal, Philadelphia	
Attn: Mr. Henry Gisser	1
CG, Rock Island Arsenal	
Attn: Mr. F. E. Woodward	1
CG, Army Ground Forces	
Attn: Mr. N. L. Kline, Fuels and Lubrication Section	1

DISTRIBUTION

OCSigO	
Attn: Ch. Eng. & Tech. Div., SIGTM-S	1
CG, SCEL	
Attn: SCEL Liaison Office	3
Chemical Corps	
Attn: Office of the Chief	1
Attn: Technical Command	7
Attn: Med. Div., Army Chemical Center	1
Attn: CO, Naval Unit, Army Chemical Center	1
Attn: CO, Camp Detrick, Frederick, Md.	2
Atomic Energy Commission, Oak Ridge, Tenn.	
Attn: Technical Information Service Documents Control Branch	30
Government Cooperative Committee on Lubrication	
Attn: Mr. C. M. Murphy, Permanent Secretary	15
Office of Tech. Services, Dept. of Commerce	2
Div. of Public Documents, GPO	
Attn: Library	1
Dir., NACA	3
Attn: Subcommittee on Lubrication and Wear	5
RDB	
Attn: Information Requirements Branch	2
Attn: Navy Secretary	1
Attn: Committee on Fuels and Lubricants	15
Naval Res. Sec., Science Div., Library of Congress	
Attn: Mr. J. H. Heald	2

CONTENTS

ABSTRACT

By considering the variation in concentration with *pH* of water-soluble amines and their ions in aqueous solution, it is shown that hydrophobic films on platinum are primarily due to the adsorption of free amine in the more alkaline regions of the *pH* scale. In the less alkaline regions hydrophobicity is due to the adsorption of amine ion. As might be expected the adsorption of amine ion results in hydrophobic films exhibiting lower contact angles than do the films resulting from adsorption of free amine. A similar situation exists in the case of water-soluble carboxylic acids, except that hydrophobic films in the more acid regions are due to undissociated acid molecules, whereas in the more alkaline regions hydrophobicity is due to the adsorption of carboxylate ions.

In the quantitative treatment of the data both hydrophobic and hydrophilic species are taken into consideration. The maximum degree of hydrophobicity occurs at the same *pH* as does the maximum mole fraction of the hydrophobic species present. Other marked changes in the degree of hydrophobicity also occur in the same *pH* regions where corresponding variations in the mole fraction of hydrophobic species are evident. The effect of varying the concentration and dissociation constant on the *pH* at which maximum hydrophobicity occurs is computed. The results are generalized to any weak acid or base or any nonionized compound.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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

COMPETITIVE ADSORPTION FROM SOLUTION BETWEEN HYDROPHOBIC AND HYDROPHILIC MOLECULES AND IONS

INTRODUCTION

Recent reports from this Laboratory have been concerned with the aqueous adsorption of hydrophobic films of primary n-alkyl amines (1) and with a variety of carboxylic acids (2) on platinum foil. Only a qualitative treatment has been given of the effect of the nature of the polar group and concentration of solute on the remarkable curves of contact angle vs. *pH* there reported. This report is concerned with the dissociation equilibria of the hydrophobic molecules and ions present in such experiments and with the effect on the competitive adsorption of the ions and polar molecules caused by varying *pH*, dissociation constant, and concentration. The adsorption equilibria will be considered to be those involving only the dissolved aqueous ions and amphipathic molecules. This is because solutions of the compounds discussed here more dilute than 10^{-2} to 10^{-3} moles/liter do not contain colloidal micelles, according to past published work on critical micellar concentrations and their relation to molecular weight and salt concentration (3, 4, 5).

ADSORPTION OF AMINES

The work of Shafrin and Zisman (1) on the adsorption of primary n-alkyl amines on platinum from aqueous solution has shown how the hydrophobicity of the resulting films, as measured by contact angles, is dependent on the *pH* of the solution. The results obtained for n-octylamine, which was typical of the amines studied, are shown in Figure 1. Variation in *pH* was obtained by the addition of potassium hydroxide or hydrochloric acid. It will be observed that for the higher concentrations the contact angle θ has a peak value at a *pH* of about 10. With increasing *pH* (10-12) the value of θ decreases sharply until complete wetting occurs. With decreasing *pH* (10-8) the value of θ decreases rather sharply to an inflexion point designated as the θ plateau. In the *pH* range of 8 through 5 the contact angle decreases only slightly with decreasing *pH*. However, after a *pH* of 5 is reached, θ decreased sharply with decreasing *pH*. With decreasing concentration it is seen that the width of the plateau or shoulder of the curve becomes smaller. Also, with decreasing concentration the peak value of θ becomes smaller and in general appears to occur at decreasing *pH* values.

Other investigators have also found that organic amines adsorb from aqueous solution most effectively in the more alkaline region of the *pH* scale on such materials as activated charcoal (6) and sphalerite, chalcocite, and galena ores (7, 8, 9).

Consideration is needed of the concentrations of the ions and molecular species present in the aqueous solutions from which adsorption occurred. These are H^+, OH^-, K^+, Cl^-, and B and BH^+, where the last two symbols refer to the amine molecule and

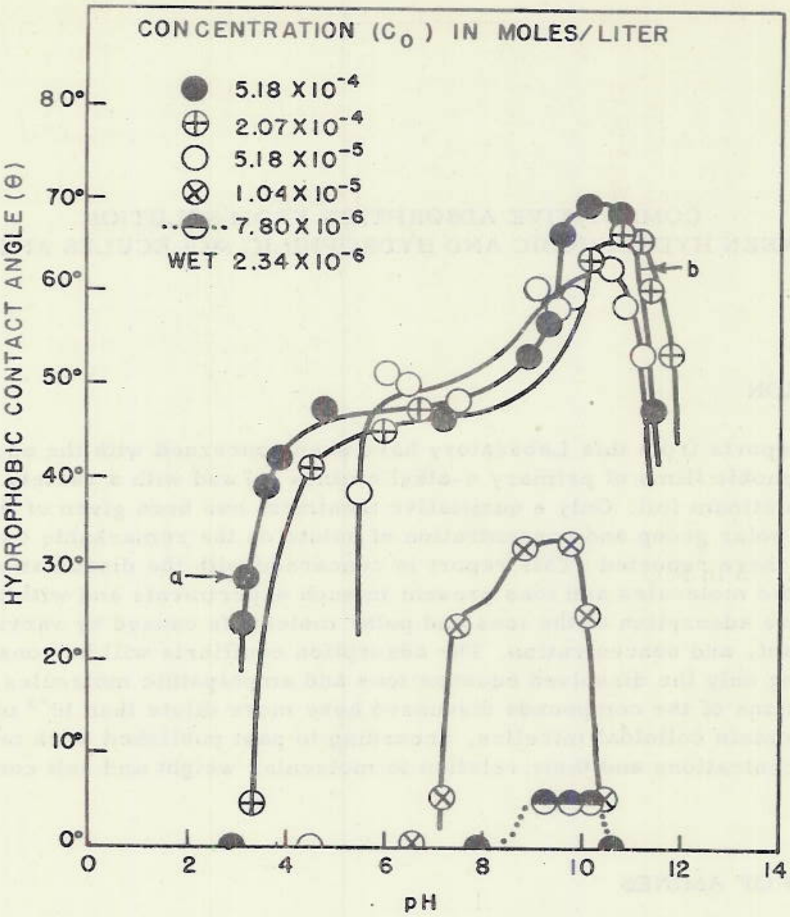

Figure 1 - Adsorption of *n*-octylamine on platinum from aqueous solution

the amine ion derived from it. A calculation of the equilibrium concentrations of these ions and molecules can be based on the mass action law and the assumed dissociation equilibrium using concentrations rather than activities, since the solutions are so dilute. The reaction assumed is

$$B + H_2O \rightleftharpoons BH^+ + OH^- \qquad \text{(i)}$$

Letting the dissociation constant of the amine be K_b, the molar concentrations be C_{OH^-}, C_{BH^+}, and C_B, and the concentration of the amine originally added to the water be C_0, then

$$\frac{(C_{BH^+})(C_{OH^-})}{C_B} = K_b \qquad \text{(ii)}$$

where

$$C_{BH^+} + C_B = C_0 \qquad \text{(iii)}$$

and

$$(C_{H^+})(C_{OH^-}) = 10^{-14} \qquad \text{(iv)}$$

In these experiments K_b and C_o were of the order of magnitude of 10^{-4} ; hence we will assume $K_b = 10^{-4}$ and $C_o = 10^{-4}$ moles/liter to simplify the calculations. Since K_b varies from 10^{-3} to 10^{-4} for nearly all aliphatic primary amines, this is a reasonable assumption. Now since by using Equation (iv) the concentration of hydroxyl ion is known for any particular pH , it is possible to calculate the corresponding concentrations of BH^+ and B utilizing Equation (ii) and (iii). The concentrations of K^+ and $C\ell^-$ are easily calculable from the respective amounts of potassium hydroxide or hydrochloric acid necessary to produce a given pH in the presence of the particular concentration of amine added (C_o) .

If the hydrophobic behavior is assumed to be solely dependent on the solution concentration of free amine (C_B) and independent of the other species present, and since to a first approximation the amount adsorbed and hence the contact angle is directly proportional to some function of the concentration, a plot of C_B , or for convenience log C_B , versus pH should be comparable with respect to the location of points of inflexion with the experimental plot of θ vs. pH . Such a plot is shown in Figure 2, where log C_B is the ordinate and the negative logarithm of the hydrogen ion concentration (pH) is the abscissa. It is seen that the concentration of free amine is essentially constant over the pH range of 10 to 12, and consequently the contact angle θ could be expected to be fairly constant. However, as seen in Figure 1, θ decreases sharply in this pH range. Since in this pH region C_{BH^+} , $C_{C\ell^-}$, and C_{H^+} are negligible in comparison with C_B , C_{K^+} , and C_{OH^-} and since C_B remains constant while C_{K^+} and C_{OH^-} are increasing, it can be concluded that either the K^+ or OH^- ion or both are adsorbed in preference to the free amine (B) . Thus since adsorption of K^+ or OH^- ions would lead to hydrophilic behavior, the contact angle would decrease in this region of the pH scale.

The absence of a plateau region in the plot of log C_B versus pH is also significant, for the data in Figure 1 lead one to conclude that the adsorbable species maintains a more or less constant concentration over the plateau segment of the curve. Since as shown in Figure 2 the concentration of free amine is decreasing rapidly over this portion of the curve, it is apparent that one of the ion species in the system is adsorbing to yield hydrophobic films. Further evidence for such a belief is furnished through a consideration from Figures 1 and 2 of the actual concentration of free amine at pH 8 (ca. 1×10^{-6}) and a comparison of this with the concentration of free amine at which complete wetting occurred (2.34×10^{-6}).

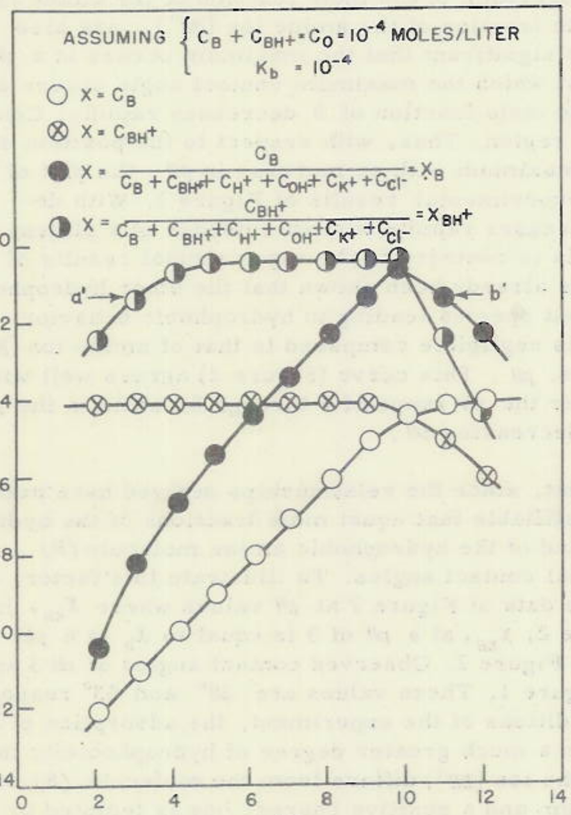

Figure 2 - The effect of pH on the concentration of free amine (B) and amine ion (BH^+)

Thus if the free amine (B) were the only species leading to hydrophobic behavior, complete wetting should have occurred around pH 8. Actually, as seen in Figure 1, a contact angle of approximately 46° was evidenced at pH 8. Therefore it is concluded that the hydrophobic behavior in the pH range of 8 to 3 is due to the adsorption of some species other than free amine.

Of the inorganic ions present (H^+, K^+, OH^-, and $C\ell^-$) none would yield hydrophobic films when adsorbed on platinum. Thus the only ion present which could lead to hydrophobic film formation is the amine (BH^+) ion. Others have also reported the adsorption of amine ions on films adsorbed at the oil-water interface (10), on negatively charged monomolecular films (11), on colloidal silver iodide (12), on various minerals (7, 9), and on steel in numerous pickling inhibitors (13).

A plot of log C_{BH^+} versus pH is also shown in Figure 2. By comparison of this curve with those of Figure 1, and using arguments analogous to those presented concerning the free amine, it can be shown that the BH^+ ion is not the only adsorbable species leading to hydrophobic film formation, nor is the adsorption of BH^+ ions independent of the concentrations of the other species present. Thus it has been shown that the hydrophobic films obtained from aqueous solutions of amines at varying pH are due to the adsorption of free amine (B) and amine ion (BH^+) and that the adsorption of these species decreases as the concentration of hydrophilic species increases.

The variation with pH of log X_B, the logarithm of the mole fraction of the amine (B), and of log X_{BH^+}, the logarithm of the mole fraction of the amine ion (BH^+), are also shown in Figure 2. Considering X_B, it is significant that the maximum occurs at a pH of approximately 10, about the same pH at which the maximum contact angle occurs as seen in Figure 1. With increasing pH, the mole fraction of B decreases rapidly. Contact angles also decreased rapidly in this region. Thus, with respect to the position of the maximum and the decrease from the maximum with an increase in pH, the plot of log X_B versus pH agrees very well with the experimental results of Figure 1. With decreasing pH, i.e., below 10, log X_B decreases rapidly without evidence of a plateau region in the pH range of 8 through 5. This is contrary to the experimental results of Figure 1, but since in this pH range it has already been shown that the other hydrophobic species, the BH^+ ion, must be the significant species leading to hydrophobic behavior, and since the concentration of free amine (B) is negligible compared to that of amine ion (BH^+), we will now consider the plot of log X_{BH^+} vs. pH. This curve (Figure 2) agrees well with Figure 1 in that it possesses a plateau over the pH range of 8 through 5, while in the pH range of 5 to 2 it decreases rapidly with decreasing pH.

At this point it is worth mentioning that, since the relationships derived have been purely qualitative, the inference is not justifiable that equal mole fractions of the hydrophobic ion (BH^+), where C_B is negligible, and of the hydrophobic amine molecule (B), where C_{BH^+} is negligible, would yield equal contact angles. To illustrate this factor, observed contact angles were taken from the data of Figure 1 at pH values where X_{BH^+} is equal to X_B in Figure 2. As seen in Figure 2, X_{BH^+} at a pH of 3 is equal to X_B at a pH of 11. These points are shown as a' and b' in Figure 2. Observed contact angles at pH 3 and pH 11 are shown as points *a and b* in Figure 1. These values are 28° and 63° respectively. Thus it is seen that, under the conditions of the experiment, the adsorption of free amine (B) to the platinum surface results in a much greater degree of hydrophobicity than the adsorption of amine ion (BH^+). Since the ion (BH^+) differs from the molecule (B) only in that it possesses one more hydrogen atom and a positive charge, one is tempted to conclude that a more closely packed film results upon adsorption of free amine than from the adsorption of the amine ion. This appears reasonable since the repulsive forces

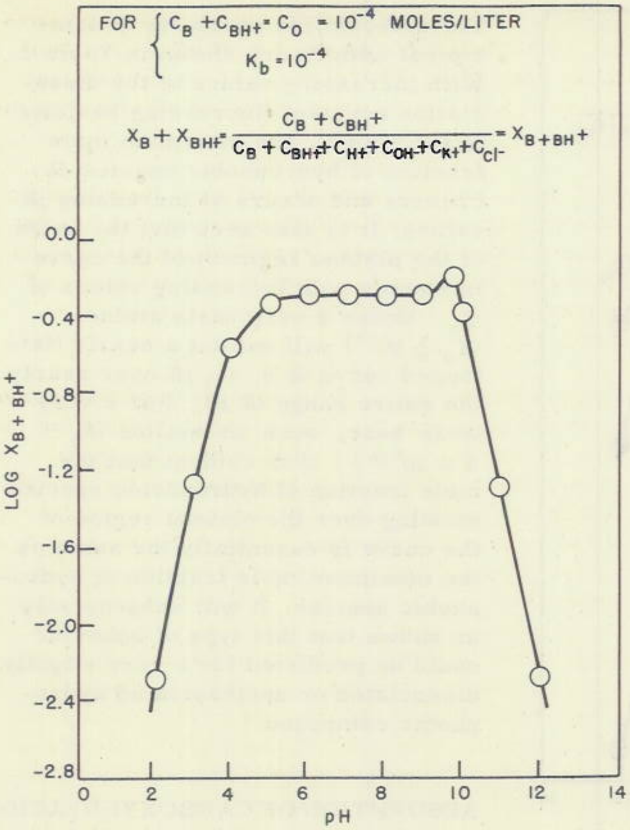

Figure 3 - The effect of *pH* on the mole fraction of hydrophobic species for an amine

between positively charged BH^+ ions would be expected to lead to a more loosely packed film structure.

Since the free amine (B) and the amine ion (BH^+) are both capable of hydrophobic film formation, the total mole fraction X_{B+BH^+} of hydrophobic species is the subject of interest, and evidently

$$X_{B+BH^+} = X_B + X_{BH^+} = \frac{C_B + C_{BH^+}}{C_B + C_{BH^+} + C_{H^+} + C_{OH^-} + C_{K^+} + C_{Cl^-}} . \quad (v)$$

The plot of log X_{B+BH^+} vs. *pH* is shown in Figure 3 for an amine $(K_b = 10^{-4}$ and $C_0 = 10^{-4}$ moles/liter). It will be noted that this quantity reaches a maximum value at a *pH* of about 10, the same *pH* at which X_B reaches a maximum in Figure 2 and approximately the same *pH* where θ has a peak value in Figure 1. Since it has already been shown that adsorption of free amine results in films exhibiting higher contact angles than films arising from BH^+ ion, it is significant that the maximum mole fraction of free amine (B) occurs at about *pH* 10. Figure 3 is also qualitatively comparable with Figure 1 for the two curves plotted for higher concentrations of amine than $C_0 = 10^{-4}$, i.e., the location of maximum, the plateau region, and the regions of numerically large slope. Clearly the mole fraction of hydrophobic species, X_{B+BH^+} is one of the most significant quantities we can calculate for interpreting such adsorption experiments.

EFFECT OF VARYING CONCENTRATION AND DISSOCIATION CONSTANT OF AMINE

It is interesting to determine the effect of variation in concentration (C_0) on the position of maximum, width of the plateau segment, etc. The calculations were carried out utilizing Equations (ii), (iii), and (iv) for an amine $(K_b = 10^{-5})$ at values of C_0 of 10^{-1}, 10^{-2}, 10^{-3}, 10^{-5}, and 10^{-7} moles/liter. A plot of log X_{B+BH^+} vs. *pH* for each concentration is shown in Figure 4. With decreasing concentration, the maximum mole fraction of hydrophobic species becomes smaller, and also the maximum occurs at decreasing *pH* values. It is also evident that the breadth of the plateau segment of the curve becomes smaller with decreasing concentration. Thus, the effect of concentration on the mole fraction of hydrophobic species is in agreement with the effect of concentration on the contact angle data shown in Figure 1.

The effect on the log X_{B+BH^+} vs. *pH* curves of varying the dissociation constant (K_b) of the amine is shown in Figure 5 for a concentration (C_0) of 10^{-3} moles/liter.

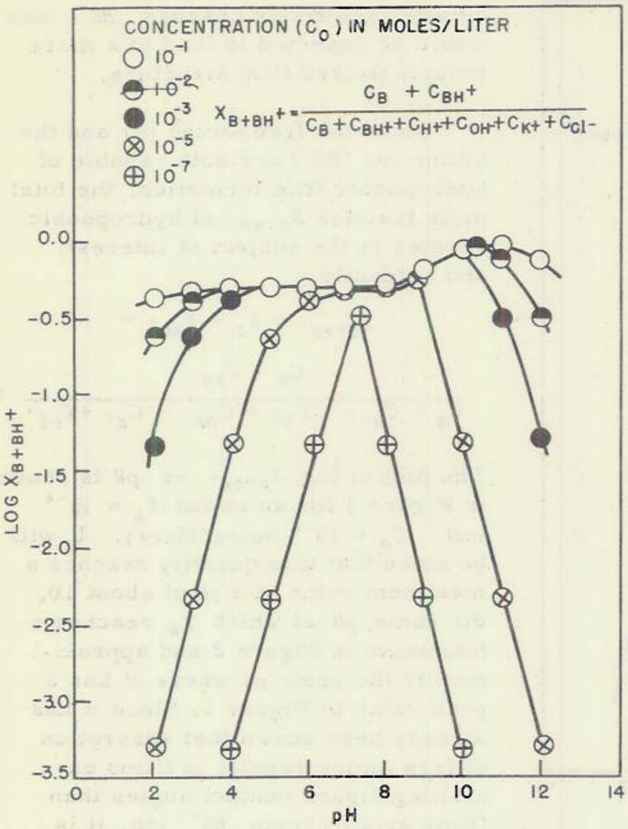

Figure 4 - The effect of concentration on the relation of X_{B+BH^+} to *pH* for an amine ($K_b = 10^{-5}$)

The dissociation constants of some typical amines are shown in Table 1. With increasing values of the dissociation constant (increasing basicity of the amine), the maximum mole fraction of hydrophobic species decreases and occurs at increasing *pH* values. It is also seen that the width of the plateau segment of the curve increases with increasing values of K_b. Hence a very basic amine ($K_b \geqq 10^{-2}$) will exhibit a nearly flat-topped curve of θ vs. *pH* over nearly the entire range of *pH*. For a very weak base, such as aniline ($K_b = 5 \times 10^{-10}$), it is evident that the mole fraction of hydrophobic species existing over the plateau region of the curve is essentially the same as the maximum mole fraction of hydrophobic species. It will subsequently be shown that this type of behavior could be predicted for a very slightly dissociated or undissociated hydrophobic compound.

ADSORPTION OF CARBOXYLIC ACIDS

Recent research by Baker, Shafrin, and Zisman (2) on the adsorption of water-soluble carboxylic acids on platinum has yielded results analogous to those for the n-alkyl amines. The results obtained for cyclohexyl carboxylic acid are shown in Figure 6. The location of the points of inflexion on this curve can be derived by the same method of calculation used for the amines. The dissociation equilibrium involved is,

$$HA = H^+ + A^- \tag{vi}$$

where

$$\frac{(C_{H^+})\ (C_{A^-})}{C_{HA}} = K_a \tag{vii}$$

and

$$C_{H^+} + C_{A^-} = C_O. \tag{viii}$$

In Figure 7 log C_{HA} and log C_{A^-} are plotted against the *pH* for a carboxylic acid having a dissociation constant $K_a = 10^{-5}$ for a concentration of $C_O = 10^{-3}$ moles/liter. Using exactly the same procedure as that previously described for an amine, it can be shown that both free acid (HA) and acid ion (A^-) are capable of adsorbing to a platinum surface to yield films exhibiting hydrophobic behavior.

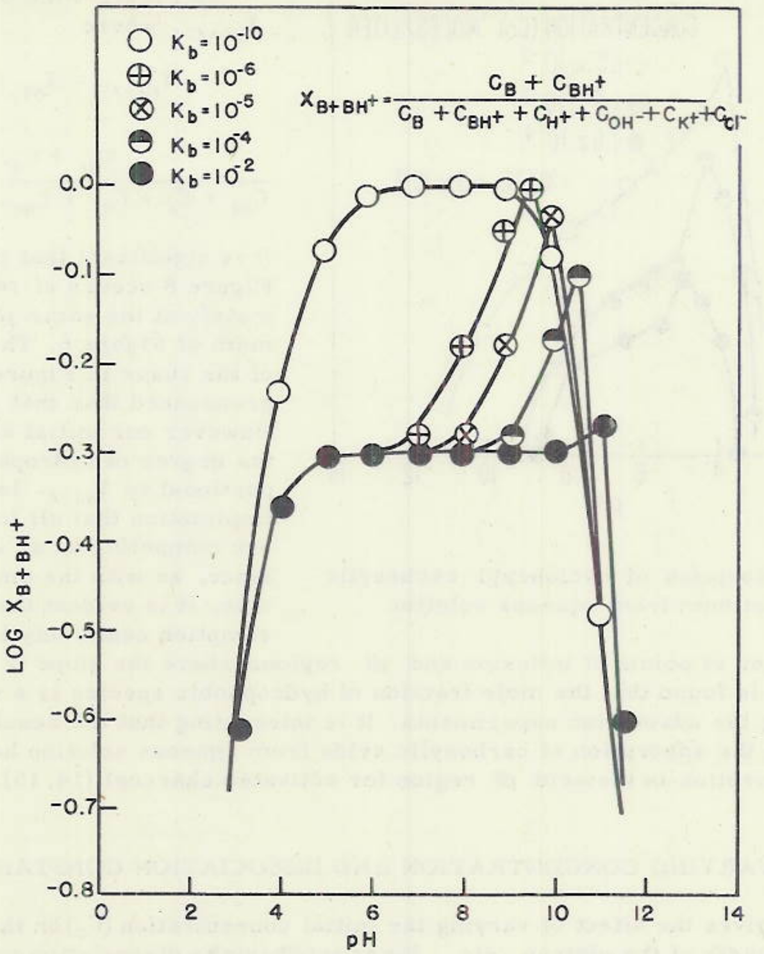

Figure 5 - The effect of varying the dissociation constant (K_b) on the X_{B+BH^+} vs. *pH* curves for an amine ($C_o = 10^{-3}$ moles/liter)

TABLE 1

Dissociation Constants of Some Typical Amines

BASES	K_b 25°*	ACIDS	K_a 25°*
Diethylamine	1.3×10^{-3}	Dichloroacetic	5.1×10^{-2}
Ethylamine	5.4×10^{-4}	Chloroacetic	1.52×10^{-3}
Trimethylamine	5.9×10^{-5}	Lactic	1.36×10^{-4}
p-Phenetidine	2×10^{-9}	Caprylic	1.41×10^{-5}
Aniline	5×10^{-10}	Trimethylacetic	9.6×10^{-6}
		Guaiacol	1×10^{-7}
		m-Nitrophenol	1×10^{-8}
		Phenol	1×10^{-10}

*From "Organic Chemistry" by Fieser and Fieser

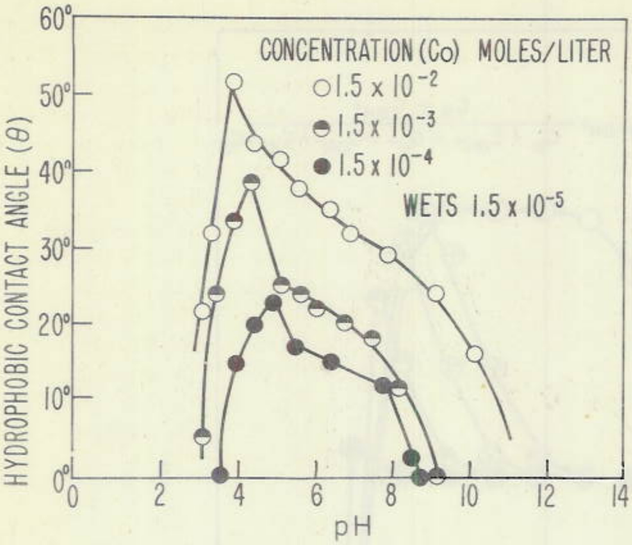

Figure 6 - Adsorption of cyclohexyl carboxylic acid on platinum from aqueous solution

In Figure 8 the ordinate is log X_{HA+A^-}, where

$$X_{HA+A^-} = X_{HA} + X_{A^-} = \frac{C_{HA} + C_{A^-}}{C_{HA} + C_{A^-} + C_{H^+} + C_{OH^-} + C_{K^+} + C_{C\ell^-}} \quad (ix)$$

It is significant that the maximum of Figure 8 occurs at *pH* 4, approximately at the same *pH* for the maximum of Figure 6. The plateau region of the curve in Figure 8 is more pronounced than that in Figure 6. However our initial assumption that the degree of hydrophobicity is proportional to X_{HA+A^-} leads to the implication that all ions and molecules are competing on an equal basis. Since, as with the amines, this is not true, it is evident that our initial assumption could only lead to an approximate prediction of points of inflexion and *pH* regions where the slope is large in magnitude. Again it is found that the mole fraction of hydrophobic species is a valuable quantity in interpreting the adsorption experiments. It is interesting that the results of other investigators on the adsorption of carboxylic acids from aqueous solution have reported a maximum adsorption in the acid *pH* region for activated charcoal (14, 15).

EFFECT OF VARYING CONCENTRATION AND DISSOCIATION CONSTANT OF ACID

Figure 9 gives the effect of varying the initial concentration (C_0) on the position of the maximum, breadth of the plateau, etc., for an acid having a dissociation constant $K_a = 10^{-5}$ at concentrations of 10^{-1}, 10^{-2}, 10^{-3}, 10^{-5}, and 10^{-7} moles/liter. With decreasing concentration, the maximum mole fraction of hydrophobic species becomes smaller and occurs at increasing *pH* values. The plateau segment as in the case of the amines contracts with decreasing concentration. These results on the effects of decreasing the concentration agree well with the contact angle vs. *pH* curves of Figure 6.

In Figure 10 is shown the effect of varying the dissociation constant (K_a) of the carboxylic acid while maintaining a concentration (C_0) of 10^{-3} moles/liter. The dissociation constants of some typical acids are shown in Table 1. With increasing K_a, the maximum value of X_{HA+A^-} decreases, and the *pH* at which the maximum occurs decreases. The breadth of the plateau segment of the curve increases with increasing values of K_a. Hence for the stronger acids ($K_a \geqq 10^{-2}$), the maximum practically has disappeared.

EXTENSION TO ORGANIC BASES, ACIDS, AND NONIONIZED COMPOUNDS

Although the arguments presented have been concerned with amines and carboxylic acids, they apply equally well to any organic base or acid for which the law of mass action holds over the concentration range of 10^{-6} to 10^{-2} moles/liter. They also can be

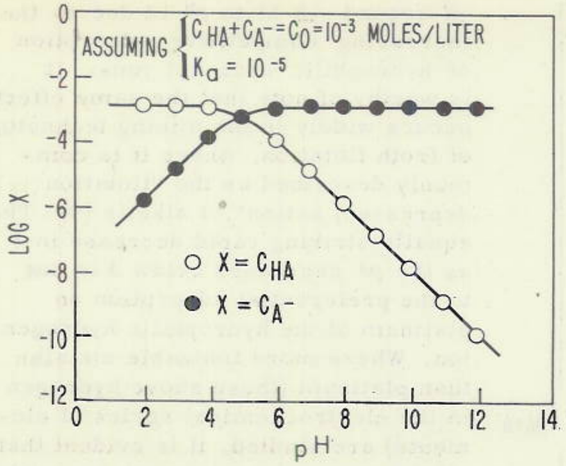

Figure 7 - The effect of *pH* on the concentration of a carboxylic acid (HA) and carboxylic acid ion (A^-)

extended to nonionized molecules in either of two ways: (a) by considering the limiting case where either $K_a = 0$ or $K_b = 0$, or (b) by calculating the mole fraction of the hydrophobic species for a system consisting of undissociated molecules and the H^+ ions, Cl^- ions, K^+ ions, and OH^- ions which are necessary to adjust the *pH* to each value of interest. Case (a) has already been covered in Figure 5 by the limiting envelope of maxima of the curves shown as K_b progressively decreased from 10^{-2} to 10^{-10}. A similar treatment with acids produces the same envelope in Figure 10 as K_a is varied from 10^{-2} to 10^{-10}.

It is interesting to work out case (b). In Figure 11 is given the result obtained by plotting against the *pH* the mole fraction X_U of the hydrophobic species present for an undissociated hydrophobic compound (U) assuming values of C_0 of 10^{-1}, 10^{-2}, 10^{-3}, and 10^{-4} moles/liter. The results show that cases (a) and (b) are in agreement. Hence, it is concluded that, for the highest concentration of hydrophobic material, the mole fraction of hydrophobic species X_U is essentially constant over a wide range of the *pH* scale and only commences to decrease significantly from this constant value in the very acid and very alkaline regions. With decreasing concentration of hydrophobic compound, X_U remains constant over a shortening range of *pH* values. A dilute aqueous solution of a nonionized hydrophobic compound, therefore, would be expected to manifest the greatest hydrophobicity at *pH* 7.

A simpler method for visualizing both the effect of dissociation constant and concentration on the contact angle vs. *pH* curves is shown in Figure 12. There the logarithm of the dissociation constant (pK) is plotted as ordinate, and the abscissa is the *pH* of the peak of the curve of the mole fraction of the hydrophobic species vs. *pH*. Curves for concentrations (C_0) of either acid or base of 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, and 10^{-6} moles/liter are plotted. This is a useful summary of the effect of both concentration and dissociation constant on the contact angle vs. *pH* curves. It is evident from Figure 12 that water-soluble organic acids and organic bases are always distinguished by the fact that the peak of the θ vs. *pH* curve occurs below *pH* 7 for acids and above *pH* 7 for bases.

DISCUSSION

Throughout these calculations it has been assumed that the physical condition and chemical nature of the adsorbing solid surface was not affected by the changes in *pH* and in concentrations of molecules or ions present. This was entirely reasonable as far as platinum foil was concerned. As the results are entirely concerned with physical adsorption, they should apply equally well to other unreactive metals like gold, silver, nickel, molybdenum, chromium and stainless steel, and even to many nonmetallic and unreactive solids.

One of the striking features of all the graphs of contact angle vs. *pH*, or of mole fraction of hydrophobic species (X) vs. *pH*, is the rapid drop of θ (or log X) with rising

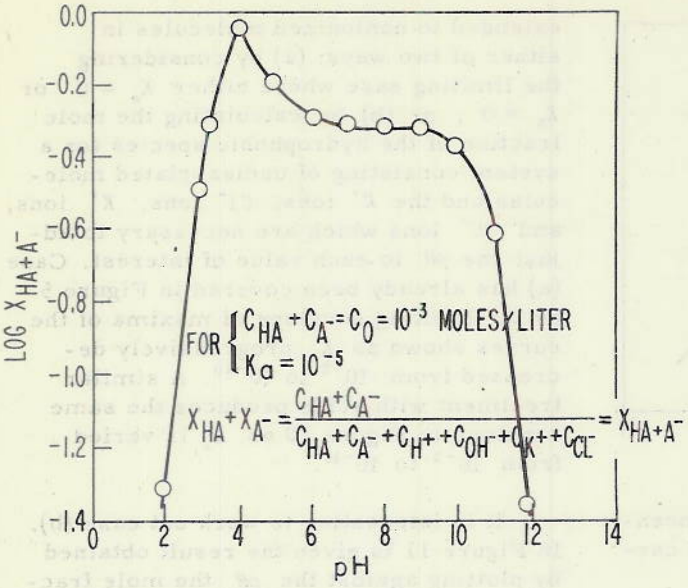

Figure 8 - The effect of *pH* on the mole fraction of hydrophobic species for a carboxylic acid

pH around *pH* 11 to *pH* 12 due to the increasing competitive adsorption of hydrophilic hydroxyl ions. It is worthy of note that the same effect occurs widely in the mining technology of froth flotation, where it is commonly described as the "flotation depressant action" of alkalis (9). The equally striking rapid decrease in θ as the *pH* decreases below 3 is due to the preferential adsorption on platinum of the hydrophilic hydrogen ion. Where more ionizable metals than platinum (those above hydrogen in the electrochemical series of elements) are studied, it is evident that affairs cannot be so simply described because they become complicated by the evolution of hydrogen gas or by other chemical changes.

The conclusions reached here should be of interest in connection with research on (a) the inhibition of corrosion by organic-type compounds, (b) electrode phenonema in the field of electrochemistry, and (c) wear prevention in aqueous lubricants, for they make more understandable the role played by physical adsorption and the effect of the competition between the hydrophobic and hydrophilic ions and molecules. Where the surface chemical reaction occurs slowly, or after a series of preliminary steps, the entire process cannot be understood without proper recognition being given to the initiating physical adsorption mechanism and the variables influencing it.

CONCLUSIONS

Several useful and important conclusions can be drawn. Not only are amines and organic acids capable of hydrophobic film formation on platinum from aqueous solution, but the ions arising from such amphipathic molecules are also capable of yielding hydrophobic films. Competitive adsorption between hydrophobic ions and/or molecules and hydrophilic ions undoubtedly occurs in the systems studied. Since the maximum degree of hydrophobicity occurs in the same *pH* region as does the maximum mole fraction of hydrophobic species, a method is available for predicting the *pH* at which a peak contact angle occurs.

The calculations made here have made it possible to generalize the results of past work on the effect of *pH* on the adsorption of carboxylic acids and amines and to permit predicting the results of similar experiments on any weak acid, any weak base, and any nonionized compound. However, the results may not necessarily apply where any of the adsorbing compounds can react chemically with the surface of the solid.

ACKNOWLEDGMENTS

The authors wish to express their appreciation of the interest and cooperation of Elaine G. Shafrin and H. R. Baker, both of NRL.

* * *

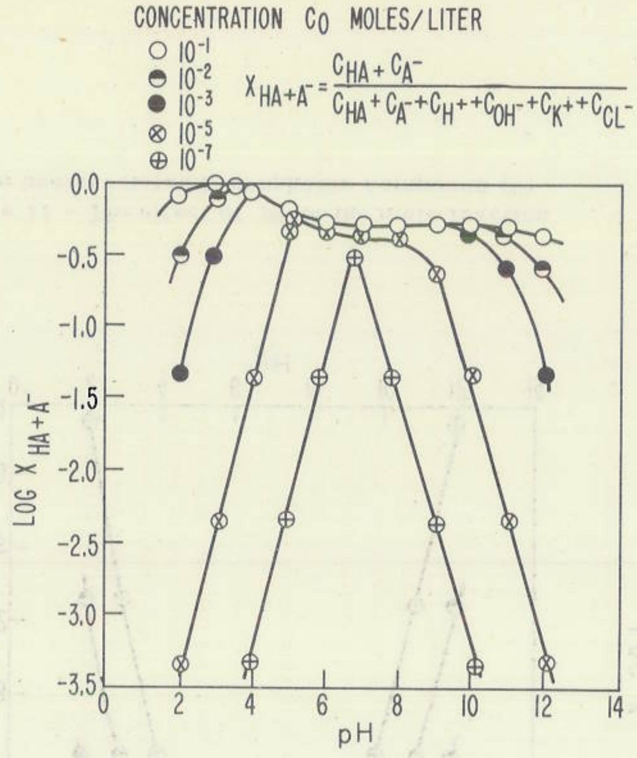

Figure 9 - The effect of concentration on the mole fraction of hydrophobic species vs. *pH* curves for a carboxylic acid (K_a = 10^{-5})

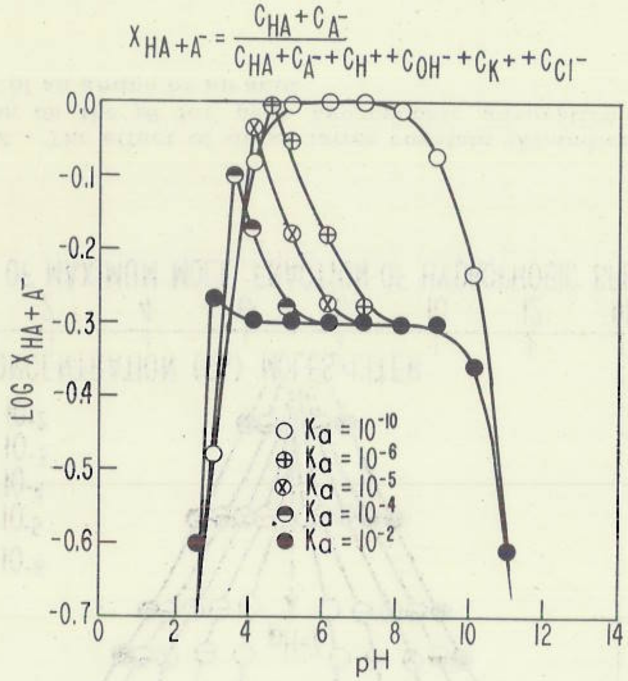

Figure 10 - The effect of varying the dissociation constant K_a on the X_{HA+A^-} vs. *pH* curves for a carboxylic acid(C_o = 10^{-3}moles/liter)

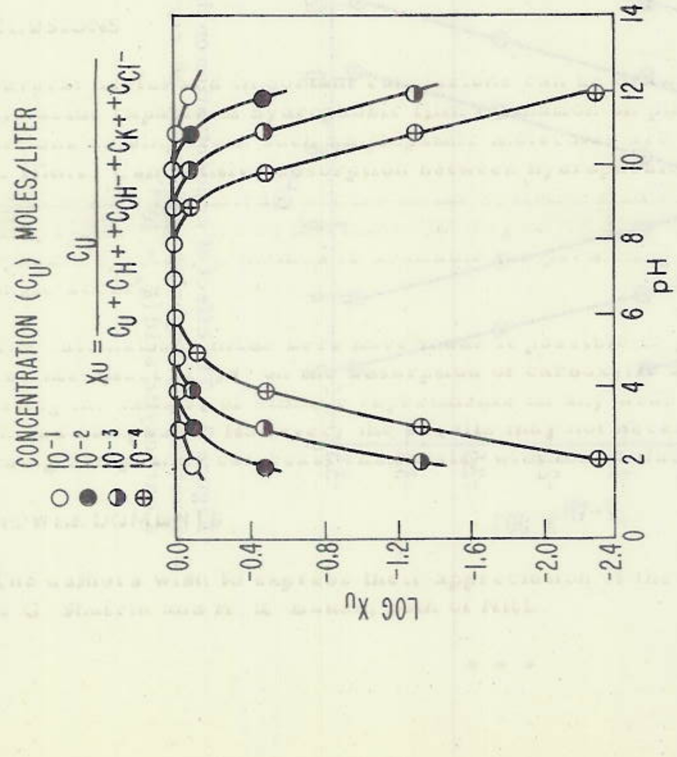

Figure 11 - The effect of *pH* on the mole fraction of an undissociated hydrophobic compound (U)

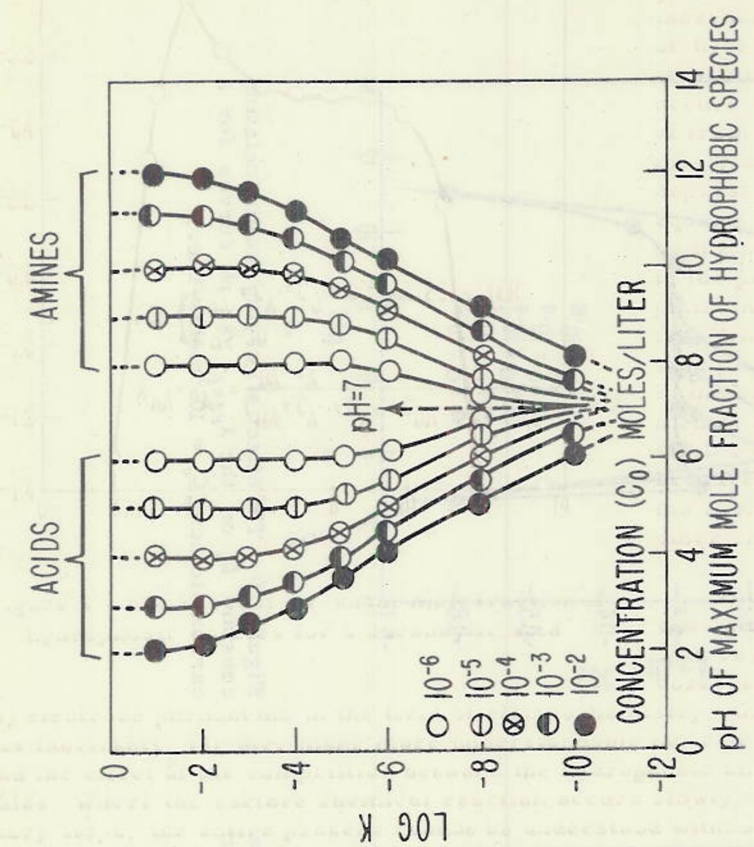

Figure 12 - The effect of dissociation constant (K) and concentration on the *pH* for peak hydrophobic adsorption on platinum of an amine or an acid

REFERENCES

1. Shafrin, Elaine G., and Zisman, W, A., J. Colloid Sci., 4, 571 (1949)
2. Baker, H. R., Shafrin, Elaine G., and Zisman, W, A., Paper in preparation
3. Corrin, M. L., and Harkins, W. D., J. Am. Chem. Soc., 69, 683 (1947)
4. Klevens, H. B., Chem. Rev., 47, 1 (1950)
5. McBain, J. W., "Colloid Science," Chap. 17, D. C. Heath Co., Boston, (1950)
6. Andersen, A. H., Acta Parmacol. Toxicol., 3, 199 (1947)
7. Gaudin, A. N., Mining and Metallurgy, 10, 19 (1929)
8. Kellogg, H. H., and Vásquez-Rosas, H., Mining Technol., 9, 1 (1945)
9. Wark, I. W., "Principles of Flotation," Australasian Inst. Mining & Met., (1938)
10. Zisman, W. A., J. Chem. Phys., 9, 534 (1941)
11. Crisp, D. J., Research (London) Suppl. Surface Chemistry, 65, (1949)
12. Bodforss, S., Kgl. Fysiograf. Sällskrap. Lund. Handl., 52, No. 12 (1943)
13. Mann, C. A., Lauer, B. E., and Hultin, C. T., Ind. Eng. Chem., 28, 159 (1936)
14. Kipling, J. J., J. Chem. Soc., 1483 (1948)
15. Hesse, G., and Sauter, O., Naturwissenschaften, 34, 251 (1947)

* * *

NAVY-DPPO PRNC, WASH., D.C.