

**SURFACE TENSION AND ADSORPTION OF SALTS OF FATTY ACIDS
IN THE LIQUID AMMONIA - VAPOR INTERFACE**

by

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INTRODUCTION

Definition of Surface Tension

It is a well known phenomenon that liquids not influenced by external forces assume a shape such that their free surface is a minimum. This suggests the idea that every space filled with liquid acts as if it were enclosed in an elastic membrane, the tension of which tends to cause a reduction in the surface. We thus arrive at a conception of surface tension, a force acting parallel to the surface across a given length of surface, and tending to reduce the area of the surface.

Laplace's Theory of Surface Tension

Laplace explains this phenomenon by assuming that molecules of a liquid attract one another with forces acting over very short distances. The molecules in the bulk of a liquid are subject to an equal attraction from all sides but molecules in the surface are subject to the attraction of many more molecules from the bulk of solution than from the vapor. This unbalanced attraction tending to draw the molecules of the surface into the liquid is the cause of this tension. In Laplace's theory the cause of the molecular attraction is not indicated but the view seems to

have been held at one time that it is gravitational and that the force radiates equally in all directions around the molecules.

Polar Molecule Theory of Surface Tension and Orientation of Molecules

A new theory of surface tension based on the electrical structure of atoms attributes this attraction to electrical and magnetic forces and attributes free surface energy to the stray electrical fields around the molecules within the surface. The pioneers in this theory have been, on the physical side, Debye (1) and Thomson (2); on the chemical side, Hardy (3), Harkins (4) and Langmuir (5). According to this theory some atoms within the molecule may have gained and others lost one or more electrons. Such an exchange would result in one part of the molecule having an excess of negative and the other part an excess of positive electricity, these equal charges being separated by a small distance. Such an arrangement of charges is called a doublet. These doublets, if free to move as they are in solutions, always arrange themselves so that unlike charges are brought together causing attraction. Some other atoms within the molecule may be joined not by a transfer but by a sharing of electrons. In this case the electrical field around the molecule and consequently the attractions will

not be so great as in the former case. Molecules of the first type are termed polar molecules while molecules of the latter type are called non-polar. It has been found that polar molecules attract each other and non-polar molecules attract each other but the attraction between polar and non-polar molecules is very small.

Some molecules, such as the fatty acids, have molecules which are partially polar and partially non-polar. Hardy (3) suggested that if such molecules were placed in a polar solvent, such as water, the molecules of the solvent would have a greater attraction for the polar hydroxyl group than for the non-polar hydrocarbon chain. This would result in the molecules of the acid in the surface of the solution arranging themselves with the hydroxyl group toward the solution and the hydrocarbon chain toward the vapor phase. Since the stray electrical fields around this part of the molecule are small, this would result in a considerable lowering of the surface tension. Hardy presented no experimental evidence to substantiate this idea but such evidence has been furnished by Harkins (4) and by Langmuir (5).

Gibbs' Adsorption Equation

In the surface layers of solutions there may be a decided alteration in concentration of solute compared to the concentration in the bulk of the solution. This change of

concentration in the surface layer is termed adsorption and called positive if there is an increase and negative if there is a decrease. J. Willard Gibbs (6) worked out the following mathematical relation between the surface tension of solutions and the amount of adsorption taking place in the surface.

$$u = - \frac{c}{RT} \frac{d\gamma}{dc} = - \frac{1}{RT} \frac{d\gamma}{d \ln c}$$

In this equation u is the amount of adsorption in moles per square centimeter of surface, c is the concentration of the solution in moles per liter after adsorption has taken place, γ is the surface tension in dynes per centimeter, R is the gas constant (8.316×10^7 ergs), and T is the absolute temperature. To calculate the amount of adsorption it is necessary to determine the surface tension of a series of solutions at various concentrations. If the values of γ are then plotted as ordinates and the values of $\ln c$ plotted as abscissa the slope of the curve at any point is the value of $d\gamma/d \ln c$ for the concentration of solution represented by that point.

Experimental Verification of Gibbs' Equation

Numerous attempts have been made to verify experimentally this equation with rather conflicting results. In the following table experimental determinations of ad-

Table I. A Comparison of Calculated and Observed Adsorption

Worker	Solute	Comparison of observed and calc. adsorption
W. C. McLewis	Non-Electrolytes	Obs. 15-70 times calcd.
	Inorganic Electrolytes	Obs. 6-30 times calcd.
	Aniline, Caffeine	Obs. 3-25 times calcd.
	Sodium glycocholate	
Donnan and Barker	Honylic Acid	Agreement claimed.
	Saponine	
Scheffield	Mercurous salts	Agreement claimed.
	p-toluidine	
McBain and Davies	Amyl Alcohol	Obs. 2 times calcd.
	Camphor	Obs. 4 times calcd.
		Obs. 3 times calcd.
Lang, McBain, and Harrison	Sodium oleate	Obs. 2 times calcd. Approximate agreement. Obs. 3 times calcd.
	Honylic Acid	
	Amyl Alcohol	
McBain and Dubois	Iso-amyl Alcohol	Obs. 2 to 8 times Calcd.
	Acetic Acid	
	Butyric Acid	
	Caproic Acid	
	Honylic Acid	
	Phenol p-toluidine	

Worker	Solute	Comparison of observed and calc. adsorption
McBain and DuBois	Resorcinol Thymol Camphor Sodium Chloride	
Taber (a)	Saponins	Agreement with Solns ranging from 00001 to .00003 molar. Obs. 2 times calcd. with solns 0001 to .0006 molar.

sorption made by various workers is compared with the values calculated using Gibbs' equation. (7).

As can be seen from the tabulated results, the evidence seems to be rather contradictory but the preponderance of evidence seems to indicate that except for very dilute solutions, more adsorption takes place than is predicted by the equation. A partial explanation may be that the equation was derived for dilute solutions by assuming that $V = \frac{RT}{C}$. If activities were used instead of concentrations any error due to deviation from this law would be eliminated. The variations are too great in many cases to be explained by this argument. McBain attempts to explain this by assuming that the mono-molecular surface layer in which adsorption takes place acts as a support for chains of oriented molecules which extend relatively far into the solution. The results obtained by Tabor seemed to substantiate this theory.

Purpose of this Investigation

It would seem in the light of the orientation theory and the theory of adsorption that the surface energy of solutions of the fatty acids in polar solvents would be due to the non-polar end of the adsorbed molecule and the amount of adsorption which has taken place. The solubility of the

acid should be due to the polar portion of the molecule. If progressively longer carbon chains were attached to this polar group the molecules would become less soluble and more highly adsorbed in the surface. The concentration in the bulk of the solution at which the surface becomes saturated should become lower as the chain increases in length.

H. H. King (9) made a study of the adsorption of the normal paraffin acids with carbon chains of one to ten carbons in water solutions. His data verifies the above predictions. It is now proposed to make a similar study of the same series of acids using liquid ammonia as the solvent. In this investigation solutions of the ammonium salts of formic, propionic, and pelargonic acids were studied. W. P. Harris at the present time is completing a similar study of the ammonium salts of acetic, butyric, valeric, and caproic acids.

THE SURFACE TENSION OF MIXTURES

The solubility in liquid ammonia of the ammonium salts of the shorter hydrocarbon chain fatty acids is quite high. For example four and one-half grams of ammonia were sufficient to dissolve 15 gms of ammonium propionate. In such systems it may be possible to explain the results obtained by the theory of admixtures. According to Whatmough's rule

for binary-mixtures (10) the surface tension of the mixture is represented by the formula $\gamma = R (V_1 \gamma_1 - V_2 \gamma_2)$, R being the ratio of the calculated to the observed density, V_1 and V_2 are the volume fractions of the components, and γ_1 and γ_2 are the surface tensions of the pure components. Worley (11) in his study of water aniline mixtures has shown that decrease in solubility caused by addition of sodium chloride caused a decrease in the surface tension not predicted by Whatmough's rule. This could be explained by the polar theory of surface tension by saying that positive adsorption of aniline had increased causing a decrease in the surface tension with a decrease in the solubility of the solute. Therefore, whenever the molecules of one component in a mixture have very unsymmetrical electrical fields we would expect the surface tension of the mixture to deviate from the surface tension calculated from Whatmough's rule. It would be possible to get a series of mixtures in which the surface tension increases with the increase in concentration and yet have positive adsorption taking place if the solvent has a lower surface tension than the solute. Adsorption in this case would cause the observed values to be lower than the values calculated from Whatmough's rule. The character and amount of adsorption can therefore be estimated more reliably from the deviation from the rule of admixtures than

by attempting to apply Gibb's equation directly to the solution.

CAPILLARY HEIGHT METHOD OF DETERMINING SURFACE TENSION

The capillary height method was used to determine the surface tension. When a capillary tube is placed in a liquid which wets the tube, the surface of the liquid becomes concave upward. In order for equilibrium to exist between a concave and a convex or flat surface, the pressure on the concave surface must be increased. Since the pressure on the flat surface of the bulk of the solution and on the capillary meniscus is equal, the liquid rises in the tube until the hydrostatic pressure becomes great enough to make up the necessary difference in pressure. At equilibrium the weight of the liquid is $r^2 \pi h (D-d) g$ where r is the radius of the tube, h is the height the liquid rises in the tube, D and d are the densities of the liquid and the vapor above the liquid, and g the acceleration due to gravity. This weight is supported by the vertical component of the surface tension acting around the circumference of the capillary, $2 \pi r \gamma \cos \theta$. θ is the angle of contact the liquid makes with the glass and γ is the surface tension of the liquid. By equating these two quantities, we obtain the formula for calculating surface tension from capillary height measurements.

$$2\pi r \gamma \cos \theta = r^2 h (D-d) g$$

$$\text{or } \gamma = \frac{h (D-d) g r}{2 \cos \theta}$$

Richards and Carver (12) have shown that the angle of contact is zero for several liquids which wet glass and they draw the conclusion that this is probably true for all liquids which wet glass. Using this assumption the equation for calculating surface tension becomes:

$$\gamma = \frac{h (D-d) g r}{2}$$

MATERIALS USED

The ammonium formate used was purchased from the Eastmann Kodak Company and was the purest obtainable. It was not deemed necessary to further attempt to purify it other than drying it in a vacuum desiccator over sulfuric acid to remove moisture.

The ammonium propionate and ammonium pelargonate used were made in the apparatus by neutralizing the acids with gaseous ammonia just before filling the tubes. The acids used were purchased from the Eastmann Kodak Company and were the purest obtainable. The propionic was distilled from sulfuric acid to remove moisture, redistilled, and the mid portion used. No further attempt was made to purify the

pelargonic acid. The density and surface tension of samples of the pure acids were determined at 20°C. and the results are given below (Table II). A 25 cc. vacuum walled pycnometer was used for the density determination.

Table II. Density and Surface Tension of Propionic and Pelargonic Acids.

Acid	Density $\frac{20^{\circ}}{4^{\circ}}$	Surface Tension dynes/cm.
Propionic	.9937	26.63
Pelargonic	.9033	24.82

EXPERIMENTAL PROCEDURE AND APPARATUS.

The surface tension was determined for a series of ammonia solutions of ammonium formate and ammonium propionate ranging in concentration from 0.5 molar to near the saturation point and for solutions of ammonium pelargonate ranging in concentration from .015 molar to .12 molar which is very near the saturation point. The method and apparatus used are the same as described by King, Hall, and Ware (13). The apparatus, a modification of the Richards and Coombs type, was constructed of heavy grade pyrex tubing (Fig.1). The cylindrical bowl, 35 m.m. in diameter, was used to provide a surface of such size that its center portion would provide a flat surface. A capillary side arm was attached to the bowl below and to the stem above with a gooseneck at its juncture with the stem. The design permitted thorough ir-

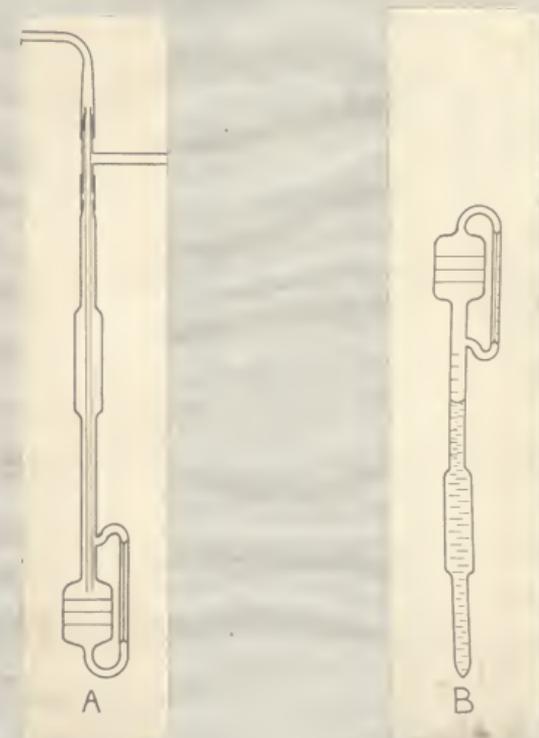


Fig. 1. A, showing method of introducing ammonia vapor into apparatus where it is condensed; B, showing method of measuring volume of vapor phase in density determination.

rigation of the capillary at will and yet prevented the liquid which drained down the walls from draining into the capillary after agitation of the contents. The bowl was banded by three rings 1 cm. apart etched into the glass. These served only as a guide when filling the tube so that the quantity of liquid could be approximated quickly and controlled.

The portion of the tube above the juncture of the side arm to the stem was designed to serve as a pycnometer. This allowed density determinations to be made in the same apparatus in which surface tensions determinations were made thus eliminating any possibility of error due to the escape of gaseous substances. The barrel and the small tube attached were of such size that when the tube was inverted the volume of liquid necessary to fill the bowl to the center mark was sufficient to fill the pycnometer to near the center of the stem as shown in Fig. 1B. The fact that the volume of the pycnometer changed each fill was met by determining the volume of the other end of the tube to each of several lines etched on the stem and the volume per m.m. of length of the stem. The volume of the vapor could then be determined by measuring the distance of the meniscus from the nearest calibration mark. After each fill the total volume of the tube was determined and the volume of liquid found by difference. To correct for the volume of liquid

in the meniscus the length of stem (H_0) equal in volume to the meniscus was added or subtracted from the measured distance of the meniscus from the volume mark. The values of H_0 were determined by calculating from the Bashforth and Adams data (14) values of H_0 for each value of density/surface tension. These were plotted and a curve drawn so that values of H_0 could be read for any desired value of density/surface tension. This method necessitated a preliminary estimation of H_0 for calculation of approximate values of density and surface tension. These gave a correct value of H_0 with which correct values of density and surface tension were calculated.

In the calibration of the capillaries used, no attempt was made to determine the radius of the tubes by weighing measured lengths of mercury since this method depends on the capillary being a perfect cylinder. Much better results can be obtained by measuring the capillary rise for liquids of known surface tension and density, substituting these values into the surface tension formula, and solving for the radius. Since the capillaries were not uniform the radius was determined at intervals of one-half centimeter and these values of the radius plotted on graph paper against the position in the capillary. The radii of the tubes for any point in the capillary could then be read directly from the graph.

Benzene was used in calibrating the lower part of the capillary and conductivity water in the upper part. Water and benzene were both used at the same point near the center of each capillary and found to give the same value for the radius.

Pure thiophene free benzene, purchased from the Eastmann Kodak Company, was used. It was allowed to stand over sodium to remove moisture and distilled, boiling at 80°C. at 740 m.m. of pressure. The density at 25 was determined in a 25 cc. vacuum walled pycnometer and found to be .87875. This checks with the value (.8787) obtained from the International Critical Tables. The value used for the surface tension, 28.88 dynes per centimeter, is the value given in the International Critical Tables.

The surface tension of the water used was determined by the drop weight method and found to be 72.6 dynes per centimeter.

The ammonium formate to be used was dried by placing it in clean glass tubes about six millimeters in diameter and of such length that each tube held about two grams of salt. These were allowed to stand in a vacuum desiccator over sulfuric acid to remove moisture. From these tubes the amount of salt desired could be quickly charged into the apparatus without allowing it to come into contact with the air long enough to take up moisture. The apparatus, which

had been previously weighed, was stoppered and again weighed to get the exact weight of salt. Gaseous ammonia from a tank of anhydrous liquid ammonia was then condensed into the tube with carbon dioxide ice. Figure 1A shows how the apparatus was connected to fill the tube. The ammonia was led first to a drying train consisting of freshly ignited aluminum oxide. A T-tube with rubber connections through which protruded a small bore tube which reached down into the top part of the bowl was used to introduce the gas into the tube. The stem served as an outlet for uncondensed gas. This outlet was connected to a mercury trap which served to control and increase the pressure and condensation.

When sufficient ammonia was condensed, the delivery tube was partly removed from the apparatus until the rim of the tube was softened in the flame, then the delivery tube was held just above the opening until the apparatus was sealed. The tip of glass removed in sealing was saved and included in all further weighings.

The tube was placed in an electrically controlled thermostat at 20°C. and capillary height readings were made with a William Gaertner calibrated traveling microscope. Illumination was provided by a mercury arc lamp. The light was reflected horizontally by a mirror through the opposite window of the thermostat. The light was cut off just below the large meniscus by a movable horizontal

screen placed on the mirror. With this illumination the lower contour of the meniscus became clear and sharp. Without the screen the light coming from below was reflected from the meniscus until it was difficult to determine the true boundary. The volume of the vapor was determined as previously described. The tube was opened by heating at the tip with a needle flame after the pressure had been greatly reduced by chilling with carbon dioxide ice. The remaining pressure blew a small pin hole through the tip. The sharp edges were melted back and the minute bulb raised with the pin hole was shrunk back to its former shape. Thus the volume of the tube was not altered. It was then filled with water at 20°C. and weighed to determine the total volume of the tube.

For the solutions of ammonium propionate and ammonium pelargonate the acids were used instead of the salts because they were obtainable in the pure state, were less hygroscopic, and more easily handled. The amount of acid needed was measured into the apparatus with a pipette and weighed accurately. Ammonia gas was then blown slowly into the tube at room temperature until most of the acid was neutralized. The tube was then packed in carbon dioxide ice, and the procedure was then the same as described for ammonium formate.

CALCULATION OF RESULTS

The surface tension of the various solutions was calculated using the following formula:

$$\gamma = \frac{(h + 1/3 r) (D-d) g r}{2}$$

In this equation h is the vertical distance measured from the flat surface of the large meniscus to the bottom of the meniscus in the capillary. D and d are the densities of the liquid and the vapor above the liquid respectively, g was taken as 980, and r is the radius of the capillary. The correction, $1/3 r$ is made to include the liquid in the meniscus of the capillary.

The density of the vapor was calculated from the density of ammonia vapor over liquid ammonia at 20° using the principle of Raoult's law and assuming that the density was proportional to the partial pressure.

$$d = d_a X$$

where d is the density of the vapor over the solution, d_a is the density of the vapor over pure ammonia and X is the mole fraction of ammonia. The value used for d_a , .006694, was taken from the circular of the Bureau of Standards No. 142.

The values of γ as ordinates were plotted against the

values $\log_{10} C$ for each acid. (Fig. 8-10). From the resulting curves the values of $d \sqrt{d \log_{10} C}$ could be read directly for any desired concentration. The adsorption was calculated at various concentrations using Gibbs' formula:

$$u = \frac{1}{2.303 RT} d \sqrt{d \log_{10} C}$$

u is the adsorption in moles per square centimeter of surface, R is 8.316×10^7 ergs, T is the absolute temperature and 2.303 is the conversion factor for changing from Napierian to common logarithms.

The normal concentration in the surface was calculated at each concentration for which the adsorption was calculated. The formula used is:

$$C_s = \frac{(C_1 \times 6.06 \times 10^{23})^{2/3}}{6.06 \times 10^{23}}$$

where C_s is the number of moles of solute per sq.cm. of surface before adsorption takes place, C_1 is the moles per liter of solute in the solution and 6.06×10^{23} is the number of molecules in a mole of substance.

EXPERIMENTAL DATA

Table III. Experimental Data for Ammonium Formate - Ammonia Mixtures at 20°

Moles/Liter Salt	Density of Soln	Cap. Height CM. (Corr)	Radius of Cap. CM.	Surface Tension Dynes/CM
0.0000 (a)	0.6103	2.1798	0.03314	22.03
0.6147	0.6148	2.0669	0.03468	22.49
0.9467	0.6560	2.0080	0.03538	22.94
1.5049	0.6774	2.1103	0.03312	23.36
1.8908	0.6961	1.9600	0.03538	23.59
2.3755	0.7160	2.1663	0.03221	24.12
3.2076	0.7463	2.0985	0.03310	25.27
3.4802	0.7566	1.8733	0.03579	25.36
3.8491	0.7696	1.9991	0.03537	26.24
4.2293	0.7838	2.0747	0.03477	26.93
5.0681	0.8121	2.0206	0.03601	28.50
5.2705	0.8184	2.4252	0.03221	29.18
6.5509	0.8581	2.2365	0.03601	32.65
7.0260	0.8738			34.48

(a) Determined by King, Hall, and Ware (15).

Table IV. Experimental Data for Ammonium Frepionate -
Ammonia Mixtures.

Mols./Liter Salt	Density of Soln	Cap. Height CM. (Corr.)	Radius of Cap. CM.	Surface Tension Dynes/CM.
0.5016	0.6376	2.0261	0.03584	22.45
1.2099	0.6691	1.9766	0.03579	22.97
1.8454	0.6995	2.1265	0.03221	23.26
2.1174	0.7091	2.2426	0.03022	23.34
2.5962	0.7291	1.8539	0.03590	23.89
3.1263	0.7556	1.8735	0.03579	24.63
3.5265	0.7741	1.8641	0.03579	25.11
3.9466	0.7915	1.8978	0.03580	25.61
4.4329	0.8091	1.8912	0.03521	26.21
4.6412	0.8227	1.8661	0.03580	26.74
5.0453	0.8367	2.0931	0.03221	27.47
5.4299	0.8496	2.0997	0.03221	27.98
5.6383	0.8559	2.1071	0.03221	28.28
5.9680	0.8729	2.2607	0.03027	29.10
6.2770	0.8832	1.9301	0.03583	29.76
6.5814	0.8947	1.9551	0.03576	30.48
8.0608	0.9477	2.0476	0.03576	33.84

Table V. Experimental Data for Ammonium Pelargonate - Ammonia
Mixtures at 20°.

Mols./Liter Salt	Density of Soln	Cap. Height CM. (Corr)	Radius of Cap. CM.	Surface Tension Dynes/CM.
0.01562	0.6124	2.0625	0.03576	21.89
0.02592	0.6120	2.1065	0.03821	22.00
0.02971	0.6134	2.4525	0.03018	22.00
0.04938	0.6142	2.0893	0.03634	21.98
0.05490	0.6154	2.2923	0.03221	22.03
0.07341	0.6183	2.0862	0.03821	21.90
0.12067	0.6206	1.9675	0.03671	21.14

Table VI. Comparison of Normal Concentration and Adsorption for Ammonium Formate and Ammonium Propionate.

C	Conc. Salt Mols/Liter	Normal Conc. In Surface Mols/Sq.Cm. X 10^{10}	Adsorption of	
			Ammonium Formate Mols/Sq.Cm. X 10^{10}	Ammonium Propionate Mols/Sq.Cm. X 10^{10}
1		1.18	- 0.40	- 0.26
2		1.68	- 0.79	- 0.56
3		2.46	- 1.70	- 1.63
4		2.98	- 2.71	- 2.43
5		3.45	- 4.62	- 3.62
6		3.90	- 7.12	- 5.01
7		4.32	-15.91	- 6.24

Table VII. Normal Concentration and Adsorption of Ammonium Pelargonate.

Mols/Liter Salt	Normal Cons. in Surface Mols/Sq.Cm. X 10^{10}	Adsorption Mols/Sq.Cm. X 10^{10}
0.06	0.18	0.14
0.08	0.22	0.35
0.10	0.25	0.66

DISCUSSION OF RESULTS

In the introduction the prediction was made that the fatty acid molecules should become less soluble in polar solvents with increase in the molecular weight. The ammonium formate and ammonium propionate were both so highly soluble that their limit of solubility was not determined. The ammonium pelargonate was so slightly soluble that several hours of shaking were necessary to get all the salt in the 0.12 Molar solution to dissolve. This is evidence that the solubility of the fatty acids is due to the polar end of the molecule and is therefore evidence in favor of the theory of orientation.

The density - concentration relationships for all three series of solutions are shown graphically in figures 2 to 4. The smoothness of the curves indicates the accuracy of the method used for determining the densities. This is impor-

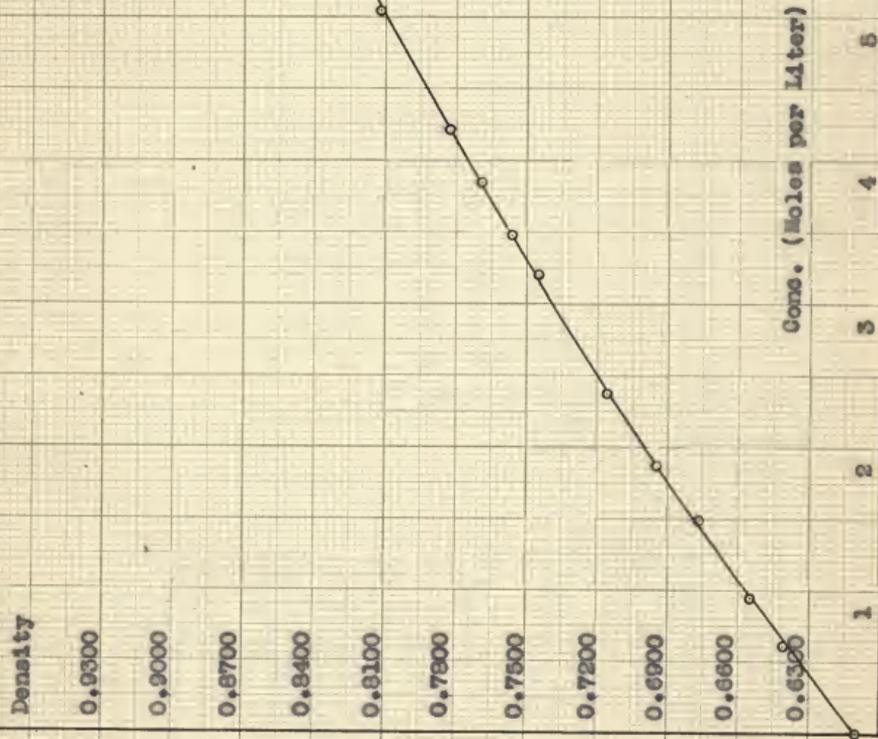


Fig. 2. Density - Concentration Diagram for Ammonium Formate - Ammonia Mixtures.

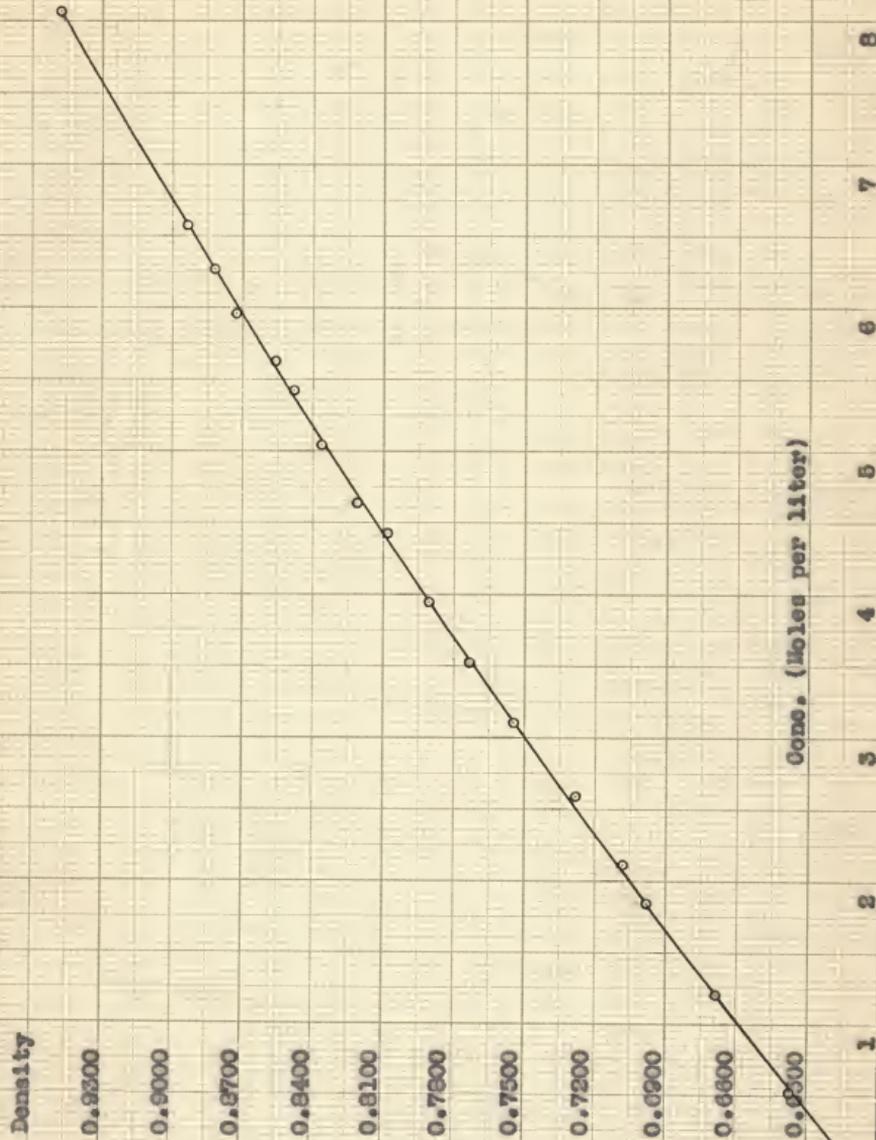


Fig. 3. Density - Concentration Diagram for Ammonium Propionate - Ammonia Mixtures.

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Density

0.6300

0.6700

Conc. (Moles per Liter)

0.02 0.04 0.06 0.08 0.10 0.12

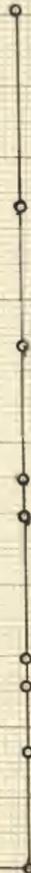


Fig. 4. Density - Concentration Diagram for Ammonium Pelargonate - Ammonia Mixtures.

Surface Tension
Dynes per Cm.

32

30

28

26

24

Conc. (Moles per Liter)

1

2

3

4

5

6

7

8

Fig. 5. Surface Tension - Concentration Diagram for Ammonium Formate-Ammonia Mixture.

Surface Tension
Dynes per CM.

24

22

20

Conc. (Moles per Liter)

0.02

0.04

0.06

0.08

0.10

0.12

Fig. 7. Surface Tension - Concentration Diagram for Ammonium Pelargonate-Ammonia Mixtures.

Surface Tension
Dynes per CM.

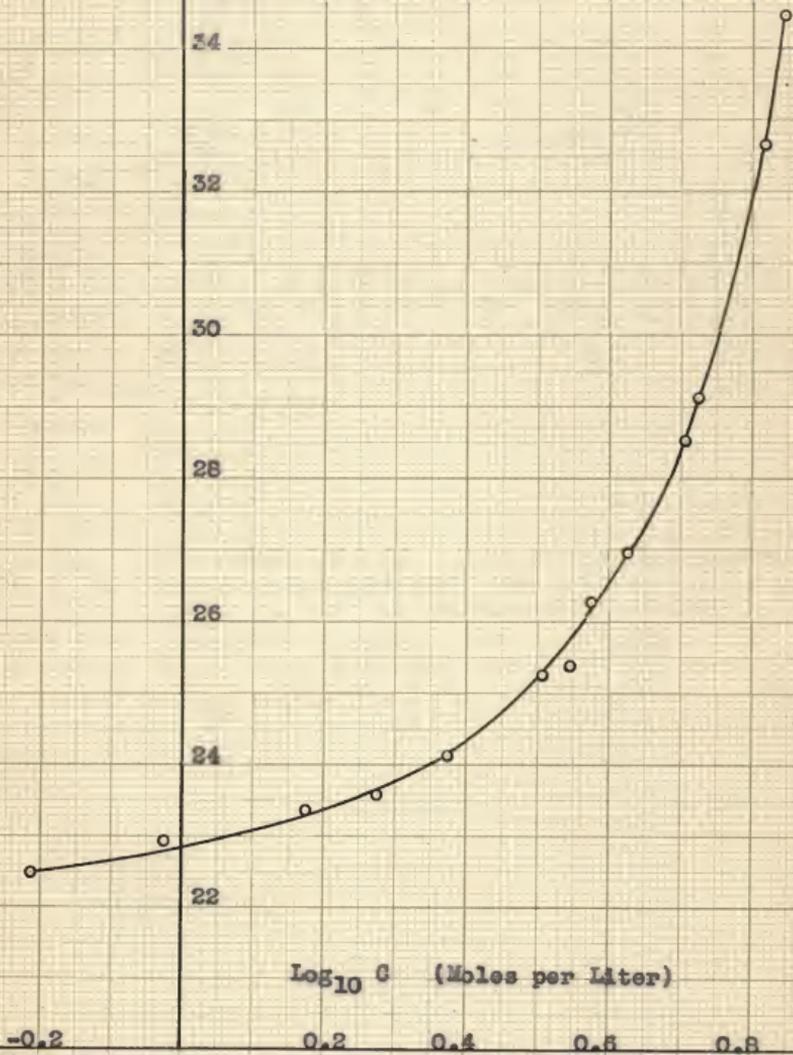


Fig. 8. Surface Tension - Log. Conc. Diagram for Ammonium
Formate - Ammonia Mixtures.

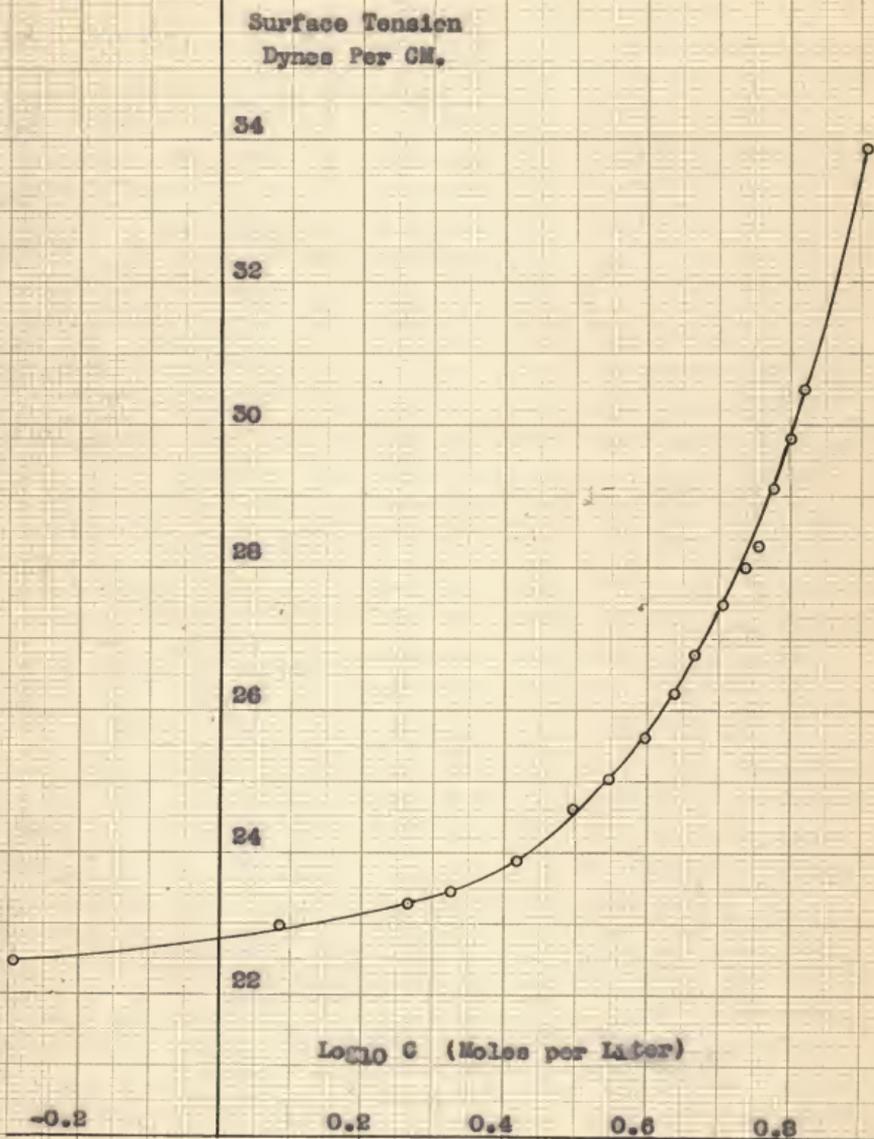


Fig.9. Surface Tension - Log. Conc. Diagram for Ammonium Propionate - Ammonia Mixtures.

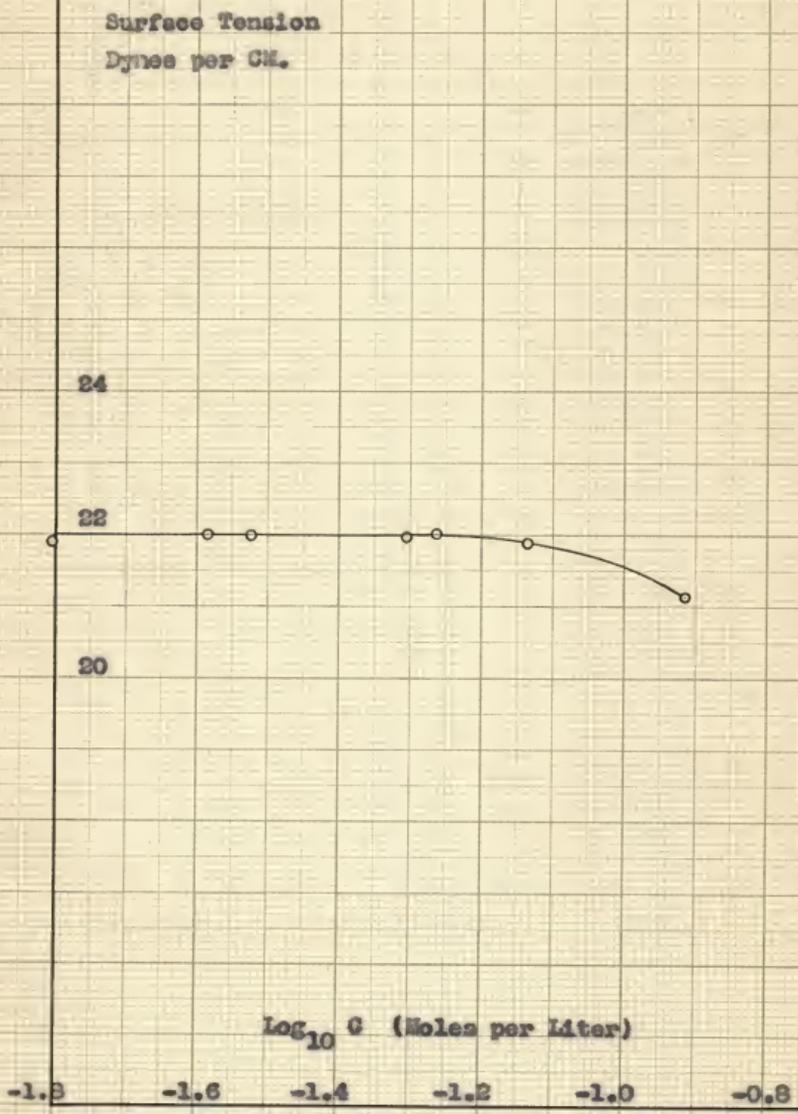


Fig. 10. Surface Tension - Log. Conc. Diagram for Ammonium Felargonate - Ammonia Mixtures.

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tant because the values of the surface tension are dependent on the density values.

The surface tension-concentration graphs for ammonium formate and ammonium propionate (Figs. 5 and 6), if interpreted on the basis of Gibbs' equation, show that negative adsorption has taken place. A comparison of the calculated adsorption with the normal concentration of salt in the surface (Table VI) shows that calculations based on Gibbs' equation give impossible results in the solutions of high concentration. Evidently then some factors other than adsorption influence the surface tension of these solutions. Unfortunately the surface tension of the ammonium salts of these acids in the molten state is not known so that it is impossible to compare the observed surface tensions of these solutions with the values calculated from Whatmough's rule. An attempt is being made in this laboratory to determine the surface tension of these salts in their molten state at various temperatures and by extrapolation to get the value for the surface tension at 20°. If this attempt is successful, the theoretical values for the surface tension of the mixtures can be calculated.

According to the polar molecule theory, positive rather than negative adsorption would be expected to take place in these solutions. This would cause a decrease in the surface tension of the solutions and would cause the experimental

values to be lower than the calculated values.

The behavior of some of the concentrated solutions indicated that there was some positive adsorption. When the apparatus was tipped to allow the solution to run from one end of the tube to the other, thin films of liquid which were quite stable formed across the stem of the tube. This was most noticeable in the concentrated solutions of ammonium caproate in liquid ammonia run by Harris but similar films, not quite so stable, were formed in the concentrated formate and propionate solutions. The stability of these films can be accounted for only by assuming that positive adsorption had taken place resulting in a high concentration of salt in the film.

In some of the solutions, there was evidence of the existence of a contact angle between the liquid and the glass. After the solutions had been agitated the liquid in the capillary became stationary for a short time. Then it suddenly dropped about one-half millimeter and again became stationary. After this had taken place, a sharp definite boundary between the glass and liquid could be observed in the large bowl. Such a boundary cannot be observed with liquids which wet the glass. Also in these tubes the film of liquid left inside the tube broke leaving drops of liquid with definite boundaries hanging to the walls of the tube.

These phenomena can be explained by assuming that immediately after agitation adsorption was not complete in the freshly formed surface. After standing a short time, adsorption and orientation became nearly complete. This resulted in a large excess of salt molecules being collected in the surface with their hydrocarbon chains, which do not wet glass, turned toward the glass or vapor.

Due to the slight solubility of ammonium pelargonate in liquid ammonia the solutions used were very dilute. This is the type of solutions to which Gibbs' equation is supposed to apply. The calculated adsorptions are of the order which would be expected.

SUMMARY

1. The slight solubility of ammonium pelargonate indicates that the solubility of the fatty acids in liquid ammonia decreases as the length of the carbon chain increases. This is evidence that the solubility is due to the polar end of the molecule and therefore that the molecules will be oriented in the surface with the polar group toward the bulk of the solution and the hydrocarbon chain toward the vapor.

2. Comparison of the calculated adsorption with the normal concentration in the surface shows that Gibbs' equation does not apply for concentrated solutions.

3. There is not sufficient data available to calculate the values of the surface tension of the mixtures predicted by Whatmough's rule. An attempt is being made at the present time to secure the needed data. On the basis of the polar molecule theory of surface tension, positive adsorption of salts molecules into the surface would be expected. This would cause the experimental values for the surface tension of the mixtures studied to be lower than the values calculated from Whatmough's rule.

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