

ADSORPTION OF ACETIC, BUTYRIC, VALERIC AND CAPROIC
ACIDS AT AMMONIA LIQUID-VAPOR INTERFACES

by

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B. S., Swing College, Swing, Illinois, 1909

A THESIS

submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

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TABLE OF CONTENTS

	Page
INTRODUCTION	4
LaPlace's Explanation of Surface Tension	5
Kiser's Explanation for Rise of Liquids in a Capillary Tube	7
ORIENTATION THEORY	9
Thompson's Contribution	9
Debye's Contribution	9
The Orientation Theory of Surface Structure	9
Hardy's Contribution	10
Kerkin's and Langmuir's Explanation of Orien- tation and Adsorption	11
J. Willard Gibbs' Contribution	13
Gswaldt's Derivation of Gibbs' Equation	13
Verification of Adsorption by Experimental Results	15
Difference in the Eucken Polanyi Theory and Langmuir's Theory of Adsorption	17
THEORY OF ADMIXTURES	18
King's Work with Adsorption	21
King, Hall and Ware's Work with Admixtures of Ammonia and Water	21
PURPOSE OF THE WORK	22
EXPERIMENTAL PROCEDURE	22
CALIBRATION METHODS	26
Radii of Capillary	28
Volume of Tube	29
Meniscus Corrections	29
MATERIALS USED	30
CALCULATION OF RESULTS	31
DISCUSSION OF RESULTS	33
METHODS OF CALCULATING NORMAL CONCENTRATIONS AND ADSORPTION	33

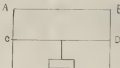
	Page
Discussion of Normal Concentration and Adsorption	53
CONCLUSIONS	56
SUMMARY	58
ACKNOWLEDGMENT	59
LITERATURE CITED	60

INTRODUCTION

A sphere has minimum surface area for a given volume. Liquids assume a spherical shape if no external force acts upon it. Liquids therefore, have a tendency to diminish their surface as much as possible. This suggests the idea that every space filled with a liquid is, as it were, enclosed in an elastic membrane, the tension of which causes the reduction in surface. This tension is called surface tension, and is a force acting across a certain length and tending to reduce the surface. The dimensions of surface tension are therefore, $\frac{\text{total force}}{\text{length}}$ as dynes per cm.

Maxwell's Explanation of Surface Tension

Maxwell's (1) explanation of this phenomenon is as follows:



Imagine a wire ABCD bent into a \cap shape upon which a second wire CD can slide without friction. The arrangement is vertical. In the rectangle ABCD is a film of soap solution which tends to contract and so lift the wire CD. If CD be loaded with weights, it is possible to find a weight at

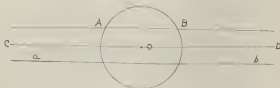
which wire CD will stay at any position corresponding to any size of film, while a smaller weight is pulled upwards and a greater one tears the fully extended film. This particular weight therefore, just balances the surface tension of the film and it corresponds to double the surface tension of one surface, since both surfaces in this case are effective. If we now pull down the movable wire loaded with this weight from a position quite close to AB to the position CD, we do work against the surface tension. This is the free surface energy. Surface tension therefore, may be regarded as the free surface energy per unit of surface, in other words, it is numerically equal to the mechanical work which must be done in generating unit surface.

A case in which the properties of a liquid determine its shape appears very noticeably in the rise of water in a capillary. Harkbee (2) showed that the capillary rise with equal diameters is independent of the thickness of the walls. This idea suggested itself that the attraction between particles of the wall and those of the liquid is only active over very short distances.

LaPlace's Explanation of Surface Tension

LaPlace (3) assumes that molecules of a liquid attract one another with forces acting over very small distances.

This distance beyond which this attraction becomes imperceptible is known as the radius of molecular action. This radius is 5×10^{-7} cm. or $5 \mu\mu$. The mutual attraction between molecules would cause liquids to contract if there was no other opposing force. In gases, as well as in liquids, forces oppose compression owing to the heat motion of its molecules. A liquid also possesses tensile strength, a force which opposes any tendency to enlarge the volume. As long as a molecule is in the interior of the liquid, the forces acting on it are equal in all directions, but when the molecule approaches the surface nearer than the radius of molecular attraction, the case is different.



Let O be a molecule, and the circle represent a sphere with the radius C of molecular attraction. Then, only the liquid in the sphere will have any influence on the molecule. In the position shown, the molecule is attracted downward by the liquid contained in the segment ab, equal to the upward pull in the segment AB, as the downward attraction of the slab abcd is balanced by the upward pull of the slab ABCD. This

This downward pull increases until O is in the surface, and decreases as O rises above the surface to become zero when the distance O from the surface becomes C . So the molecules in the interior of a liquid will have balanced forces acting on them, but the condition is different in the layer at the surface, the thickness of which is smaller than the radius of molecular action. In this layer, the molecules are subject to unbalanced attraction from the adjoining molecules in the interior, in other words, to an inward pull which keeps the surface in a state of tension, therefore, this state of tension or surface tension is tangent to the surface. The surface tension or free surface energy decreases as temperature rises, and becomes equal to 0 at 6° below critical temperature. $\sigma_0 = \sigma (1 - \theta)$. θ equals the temperature, σ_θ the surface tension at that temperature, and σ_0 the surface tension at 0.

Edser's Explanation for Rise of Liquids in a Capillary Tube

A liquid will wet the walls of a capillary if the force of adhesion of liquid to glass is greater than the force of cohesion of liquid to liquid. This force will cause the liquid to spread upon the walls of the capillary forming a surface with its center of curvature in the air phase, thus forming a concave surface between the air and water. Since

surface tension will attempt to contract this surface to a minimum, it becomes an effective force for lifting the liquid into the capillary. This force will act until an equilibrium is established between the surface tension and weight of liquid lifted. Edser (4) assumes that if the liquid wets the inside of the capillary tube, the surface which comes in contact with the inside of the tube forms part of a cylinder of radius r , where r is the internal radius of the tube. The circumference then of this cylinder will be $2\pi r$, and a force γ acts vertically across each centimeter of this circumference giving a resultant force equal to $2\pi r \gamma$. If the meniscus made a contact angle θ , then the effective force upward would be $\gamma \cos \theta$, and the resultant force would equal $2\pi r \gamma \cos \theta$.

The weight of the liquid column supported by the surface tension will be $\pi r^2 h d g$. This upward force due to surface tension and the downward force due to gravity or weight of the liquid column are equal or $2\pi r \gamma \cos \theta = \pi r^2 h d g$. $\gamma = \frac{hr d g}{2 \cos \theta}$. If θ is 0, as it is in case the tube is wetted by the liquid and $\cos \theta = 1$, $\gamma = \frac{hr d g}{2}$.

ORIENTATION THEORY

Thompson's Contribution

Thompson's (5) theory of intra-molecular ionization states that some of the atoms in the liquid molecule have lost electrons and some have gained electrons. Positive rays and modern work with X-ray on crystal structures point to the same thing.

Debye's Contribution

Debye (6) shows that an electrically neutral atom will possess a strong field just beyond its outer electrons and this acting on neighboring molecules will polarize them, i.e., will cause a relative shift of their positive and negative charges. Hardy (7) in 1912, arrived at the conclusion, that surface tension effects are due to a polarity of the molecules.

The Orientation Theory of Surface Structure

All crystalline solids possess an internal molecular structure, which consists of an orderly and symmetrical arrangement of the molecules. This structure was made apparent by the symmetrical distribution and orientation of the surface molecules of crystals by X-ray analysis. The

interior symmetry was made evident through the effects of crystals upon X-rays by Laue. The passage of X-rays through liquids give no such evidence of any such internal structure. The most fundamental characteristic of a liquid surface is the unlikeness of its two sides and resultant dissymmetry of the molecular forces involved. If the molecules in the surface are not entirely symmetrical, this lack of balance in the forces must result in their orientation to a smaller or greater degree.

The molecules in the surface are vibrating with extreme rapidity but their orientation is also disturbed by the escape of molecules from the surface.

Hardy's Contribution

Hardy (7) in 1912 and 1913, established the idea of orientation.

The corpuscular theory of matter traces all material forces to the attraction and repulsion of foci of strain of two opposite types.

If the stray field of a molecule be unsymmetrical, the surface layer of fluids and solids must differ from the interior mass in orientation of the axes of the fields with respect to the normal to the surface, and so form a skin on the surface of a pure substance having all the molecules oriented in the same way instead of purely in random way.

The inwardly directed attractive force along the normal to the surface will orientate the molecules there.

Harkins's and Langmuir's Explanation of Orientation and Adsorption

Harkins's (8) and Langmuir's (8) ideas of orientation are given as follows:

1. Organic liquids arrange themselves in the surface layer in such a way that their active portions are drawn inwards leaving the least active portions to form the surface.

2. Surface tension or surface energy is a measure of the potential energy of the electromagnetic stray field which extends out from the surface layer of the molecules. The molecules arrange themselves so that this field is a minimum.

3. Surface energy of a liquid depends upon the least active portion of the molecules and on the manner in which they arrange themselves in the surface layer. Liquid hydrocarbons of the paraffin series arrange themselves so that CH_3 at the ends of the hydrocarbon chains form the surface layer. The surface is thus the same no matter how long the hydrocarbon chain may be, all having from 46 to 48 dynes per cm. surface tension.

4. Best evidence in support of this theory is derived

from experiments on thin films of fatty acids on water or mercury. The hydrocarbon chain stands vertically on the water surface with the COOH group of the fatty acid in contact with water. "Like dissolves like."

5. Acetic acid is soluble in water. Oleic acid is not, so it spreads because by so doing, the COOH can dissolve in the water without separating the hydrocarbon chains from each other.

6. Oils which do not contain active groups, do not spread upon the surface of water. Molecules of the type of those of the paraffin group may be styled homo-polar, while groups like COOH may be styled polar.



The idea of orientation came from the idea of logs floating in water. Ordinarily, they do not arrange themselves symmetrically, but if the logs are weighted on one end with heavy enough weights, that end will be pulled under the surface of the liquid and the other end will be tilted into the air, or in other words, they will be oriented in a definite way.

So in the surface of liquids, if a polar homo-polar molecule is present, it will orient itself in such a way as

to bring the polar end toward the bulk and the other end, the homo-polar or non-polar end, into the air and surface tension then becomes a measure of this homo-polar end. Surface tension therefore, is actually a measure of the potential energy due to slightly polar groups and accordingly the molecules will be arranged in the surface so that the stray magnetic fields will be a minimum. Surface tension would also depend upon the character of the slightly polar groups and their arrangement in the surface layer.

J. Willard Gibbs' Contribution

The difference in concentration between the surface layer and the bulk of the solution is called adsorption. It is called positive adsorption when the concentration in the surface layer is greater than the bulk, and negative adsorption when it is smaller. J. Willard Gibbs (9) in 1876, was the first to formulate this idea of adsorption, deriving it from thermodynamic considerations.

Oswaldt's Derivation of Gibbs' Equation

There are several modifications of Gibbs' equation, one of the simplest derivations of the equation is due to Oswaldt (10). Let S be the surface of a solution whose surface tension is γ and let it be assumed that the surface contains one mol of the solute. If a very small por-

tion of the solute enters the surface layer from the solution, causing a change d in the surface tension, the corresponding change in energy will be Sd . But this amount of energy set free must be equal to the osmotic work absorbed in effecting the removal of the same weight of solute from the solution. Let V be the volume of solution containing unit weight of solute and let dp be the difference in the osmotic pressures of the solution before and after its removal. The osmotic work will be $-Vdp$, since the gain in surface energy and osmotic work are equal.

$Sd = -Vdp$. The solutions being dilute, we may assume that the gas laws hold, and since $V = \frac{RT}{p}$, we may write

$Sd = -\frac{RT}{p} dp$ or $\frac{dS}{dp} = -\frac{RT}{Sp}$. Since pressure is directly proportional to concentration $\frac{dY}{dp} = -\frac{RT}{US}$. But S is the

surface which contains one mol of solute in excess, therefore the excess of solute in unit surface is $1/S$ or U .

$U = -\frac{1}{RT} \frac{dS}{dC}$ or $U = -\frac{1}{RT} \frac{dY}{d \ln C}$. All adsorption values

were calculated from this formula. From this equation, it is evident that if the surface tension increases with the concentration, then U is negative, and the surface concentration is less than the concentration of the bulk of the solution. On the other hand, if decreases as the con-

centration increases, the adsorption is positive. If the surface tension is independent of the concentration, then the concentration of the solute in both the surface layer and the bulk of the solution will be the same.

Verification of Adsorption by Experimental Results

A number of attempts have been made to verify Gibbs' theory experimentally with variable success, as indicated below according to McBain (11):

Worker	Interface	Solutes Studied	Comparison of Observed and Calculated Gibbs' Adsorption
Milner	Air-water	Sodium Oleate	No comparison made
Lewis	Oil-water	Non-electrolytes Inorganic electrolytes	Observed 15 to 70 times calculated Observed 6 to 30 times calculated
	Hg-water	Aniline Caffeine Sodium Glycocholate $Hg_2 SO_4$	Observed 3 to 25 times calculated
Donnan & Barker	Air-water	Novyllic acid Saponins	Agreement claimed
Griffin Van der Neulen, Pieman & Harkins	Oil-water	Soaps	No comparison made
Oliphant & Burdon	Hg - H ₂ or Hg - A	Carbon dioxide	No comparison made
Schofield	Hg-H ₂ O	Mercurous salt	Agreement claimed
McBain & Davies	Air-water	p-Tolindine Amyl alcohol Camphor	Observed 2 times calculated Observed 4 times calculated Observed 3 times calculated

Author	Interface	Solutes Studied	Comparison of Observed and Calculated Gibbs' Adsorption
Loing, McBain & Harrison	Air-water	Sodium oleate	Observed greater than calculated and twice mono- molecular adsorption
Harkins & Gaus	Air-water	Benzoic acid Amyl alcohol	Approximate agreement Observed 3 times calculated

Difference in the Eucken Polanyi Theory and
Langmuir's Theory of Adsorption

Whenever the same substance is dissolved in one or both phases of a heterogeneous system, there is usually a difference between the concentration on the bounding surface and in the interior. These changes in the concentration at the surface are termed adsorption. A substance becomes concentrated on the surface if it reduces the surface tension (positive adsorption). On the other hand, if it increases the surface tension, it becomes less concentrated on the surface (negative adsorption).

Present-day investigators consider that adsorption is due to the attractive force exerted outwards at the surface of the colloid particle or molecule by the free or unsatisfied valences of the particle. As a rule, the valences causing adsorption seem to be weaker than the ones causing chemical combination, although there are a few instances wherein the forces of adhesion seem to approximate the forces of chemical combination in strength.

From the modern conception of the atom, the atomic forces seem to be developed from the deviations of the orbits of the outer electrons in the atoms. The forces acting in chemical compounds would be due to very strong deviations of these orbits, while in adsorption phenomena the

forces acting should be due to comparatively small deviations.

There are two theories which have been advanced to explain adsorption known as the: 1. Langmuir Theory (12), and 2. The Eucken Polanyi Theory (12).

In accounting for adsorption, the Langmuir (12) theory assumes that on the surface of a particle, there are certain number of points or spaces where there is residual valence. The forces acting in adsorption are concentrated at these points and adsorption consists in a fixation of the adsorbed atoms in these spaces or points. Langmuir's theory considers the surface layer as only one molecule thick, thus the forces between the atoms of the surface and the atoms of the adsorbed substance will act only when very close together. In the Eucken Polanyi theory the adsorbed layer consists of more than a single layer of atoms or molecules, with a density of charges varying continually from the adsorbing surface out into the free gas or liquid.

THEORY OF ADMIXTURES

DuClaux (13) in 1878, carried out experiments with a series of alcohols and fatty acids. He pointed out that a considerable drop in surface tension occurred on passing from pure water to a weak alcoholic solution, and that this drop increased in magnitude as the molecular weights of the

alcohols increased.

J. Traube (14) in 1884 determined the capillary heights of mixtures of the alcohols, fatty acids, and isomeric esters with water. He noticed the decreasing value of the surface tension of a solution of given strength with increasing molecular weights.

Worley (15) observed that there is a marked fall in the surface tension of a solution of given strength on passing from the members of a homologous series which are miscible with water in all proportions to those members which are only partly miscible at the ordinary temperatures. Worley in 1914, in his study of these mixtures says that neither of these investigators pointed out what was the most marked peculiarities of surface tension of mixtures, as, first, the lowness of the surface tension of an aqueous solution of liquids which are only partly miscible with water, and second, the divergence of the surface tension composition curves in cases of liquids, which are perfectly miscible, from the straight line that would express the relationship between surface tension and composition, if the former were merely an additive property. In perfect mixtures, the surface tension volume composition diagram of the two components is a straight line, commonly called the admixture rule. But, with solutions where one component is only slightly soluble, there is a divergence in this diagram from

a straight line.

Zawidski (16) found in his work with benzene and ethylene dichloride, acetone and carbon disulphide, pyridine and acetic acid solutions three characteristic and very different types of vapour pressure volume composition diagrams.

1. Benzene and ethylene dichloride. The vapor pressure curve composition corresponds with the theoretical straight line.

2. Acetone and carbon disulphide. The vapor pressure composition curve lies above the theoretical straight line and passes through a maximum value.

3. Pyridine and acetic acid. The vapor pressure composition curve lies below the theoretical straight line and passes through a minimum value.

Worley (17) determined the surface tensions of the same three sets of solutions. In comparing the surface tension volume composition diagram with the vapor pressure volume composition curve, he found them to be antitatic in each case.

According to Volkmann (18) the surface tension of a binary mixture is represented by the formula:

$S = V_1 S_1 + V_2 S_2$, where V_1 and V_2 are the volumes of the liquids in the mixtures expressed fractionally, and S_1 and

S_2 their surface tensions when unmixed.

Whitnough (19) modified this formula to take into account the change in volume which takes place on mixing, $S = R (V_1 S_1 - V_2 S_2)$, R being the ratio of the calculated to the observed density.

If no external forces act on the surface tension, it is an additive property. The divergence in the surface tension volume composition curve from a straight line is probably due to not having perfect solutions or due to adsorption.

King's Work with Adsorption

King (20) in 1923, working with the fatty acids and water solutions, found that the surface tension was nearly the same for all the solutions, about 27-36 dynes per cm. His results showed positive adsorption, and a decrease in the surface tension with an increased concentration.

King, Hall and Ware's Work with Admixtures of Ammonia and Water

King, Hall and Ware (21) in 1930, found that "surface tensions of water ammonia mixtures follow closely values to be expected from the rule of admixtures except in the middle region where a divergence of less than six dynes occurs.

Assuming divergence to be due to adsorption, it is shown that adsorption of ammonia in the surface is small, amounting from one to five per cent of the normal surface concentration." In the previous work just cited, liquid ammonia and water are shown as similar liquids.

PURPOSE OF THE WORK

It is the purpose of this work to verify or disprove that the fatty acid solutions in liquid ammonia behave in a similar manner to the solutions of the fatty acids in water, i.e., they should show positive adsorption, and a decrease in surface tension with an increase in concentration and be rather soluble in liquid ammonia. Similar work has been recently completed by Mundell on the formic, propionic and pelargonic acid with liquid ammonia.

EXPERIMENTAL PROCEDURE

The capillary height method was used to determine the surface tension. The apparatus, a modification of the Richards and Coombe type, was constructed of a heavy grade pyrex tubing. The cylindrical bowl, 35 mm. in diameter, was used to provide a surface of such size that its central 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. This design per-

mitted thorough irrigation of the capillary at will and yet prevented the liquid which drained down from the walls after agitation of the contents from draining into the capillary.

The bowl was banded by three rings etched into the glass. These served only as a guide when filling the tube so that the quantity of liquid introduced 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. The barrel and the small tube attached were of such size that the volume of the pycnometer measured from the upper end down to the upper end of the graduated scale in the stem, was about equal to the volume of the bowl and side arm up to the middle ring of the bowl. This provided an apparatus easily handled in which the density and surface tension of a given solution could be determined without the necessity of transferring it to other apparatus or even unsealing the tube. Errors in transference of solutions or escape of gaseous substances were entirely eliminated.

A measured amount of the acid was first placed in the tube. This acid was neutralized by dry ammonia vapor forming the salts needed. Careful attention was given that none of the neutralized salt formed in the capillary, as this salt in the capillary is very hard to dissolve in liquid ammonia due to its small surface exposed to the liquid

ammonia. Gaseous ammonia then was introduced into the tube and condensed into the liquid state by carbon dioxide snow. Plate I shows how the apparatus was connected to fill the tube. The gas 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.

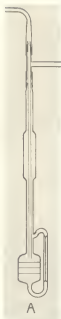
Last in the train of apparatus was a mercury trap which served to control and increase pressure and condensation. The tube was dried, weighed and then filled with sulfuric acid and dichromate cleaning solution, and allowed to stand until the next fill. They were then thoroughly rinsed with surface tension water, dried, and weighed.

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 of the tube until the apparatus was sealed. In this manner, air was excluded while the tube was being sealed; the tip or sealed-off piece was retained to be included in further weighings. Capillary height readings were taken with a William Gaertner calibrated traveling microscope. Densities for the solutions at 20°C. were determined by weighing the tube before and after filling and measuring the volume of the pycnometer on

Explanation of Plate I.

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. The total volume is determined subsequently.



the calibrated volume scale, the tube being in the inverted position shown in Plate I B, while volume readings were taken. The acid sample was weighed in, ammonia introduced, and the tube was sealed off and weighed. After reading the capillary height, the tube was inverted and the volume of the vapor was read on the calibrated scale on the stem of the pycnometer. All measurements were made in a thermostat at $20^{\circ}\text{C} \pm 0.1$. The volume of the liquid was determined by difference after the total volume of the tube was measured. The tube was opened by heating at the tip with a needle flame after the pressure had been greatly reduced in carbon dioxide snow. When tubes were opened, a small pin hole was blown 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.

Meniscus volume corrections were made by means of the Bashforth and Adams data in the "International Critical Tables" Vol. 1, page 73. Corrections for air buoyancy were made on all weighings.

Obviously, the vapour, especially at high pressures would contain enough ammonia to effect the calculated value of the density. Raoult's law was used to determine this amount of vapor weight. The density of saturated ammonia vapor at 20°C . was taken as .00669 from the International

Critical Tables, and the weight of the vapor determined by this formula: $W = Vd \frac{n_1}{n_1 - n_2}$, where n_1 is the mols of the salt, and d , the density of the pure ammonia vapor at 20°C. Raoult's law is, $\frac{p_1 - p_2}{p_1} = \frac{n_1}{n_1 - n_2}$.

CALIBRATION METHODS

Radius of Capillary

The radii of the capillaries were carefully determined by the use of the surface tension of pure benzene. Pure benzene was dried over sodium and distilled. The boiling point corrected for pressure corresponded exactly as given in the International Critical Tables. The density observed was .8787 in vacuo. The capillary tubes selected were as near uniform in bore as possible. The radius of this bore was determined at several different points on the capillary tube and a diagram drawn, with the dimensions of r as the ordinate and the capillary gradations as the abscissa. The radius of the capillary was then easily read from this diagram, the height of the liquid being known.

Volume of Tube

The tube was calibrated for volume with reference to the pycnometer scale by filling the tube with water to four different points on the scale, and measuring to the nearest line. Meniscus volume corrections were made, and the weighings were calculated in vacuo. The radius of the pycnometer was determined by dividing the difference between



two of these partial volumes by 2 h and extracting the square root.

Meniscus Corrections

It was necessary to determine the r in order to find the meniscus correction for the pycnometer. The method for meniscus correction given by Bashforth and Adams' data taken from the International Critical Tables, Volume 1, page

73 was used. Values for $\frac{H_0}{r}$ and $\frac{gdr^2}{\gamma}$ are given in these tables. R is known, determined by the method above. H_0 can

be found. Also solving for $\frac{d}{\gamma}$ in the expression $\frac{gdr^2}{\gamma}$, where g is 980 dynes and r is known, some 15 points were determined. A diagram was then constructed using $\frac{d}{\gamma}$ as the abscissa and H_0 as the ordinate. In solving for d and γ , H_0 was first approximated for the meniscus correction for volume of the gas. After d and γ were approximately determined, the value for H_0 was determined from the $H_0 \frac{d}{\gamma} 10^4$ diagram, and if the H_0 from the diagram was the same or nearly the same, the d and γ were considered correct. However, if the H_0 assumed was not the same as the H_0 read from the diagram, the H_0 determined by the approximate d and γ was put in the place of the H_0 assumed and d and γ again calculated.

The microscope was calibrated by means of a standard graduated glass slide.

MATERIALS USED

The butyric acid, valeric acid and caproic acid used were chemically pure substances prepared in the Eastman Kodak Company's laboratories and were used as prepared. The acetic acid was 99.5 per cent pure and was obtained from Grasselli. This acid was distilled from sulphuric acid and the middle 2/3 portion used.

CALCULATION OF RESULTS

The formula used for calculating surface tension was,

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

In this formula r is the

radius of the capillary, $(h + r/3)$ the capillary height, d the density of the solution, D the density of the vapor as determined by Raoult's law, and θ the angle of contact.

1. The volume of the tube was determined by dividing the weight of water in the full tube by $(d-D)$ when d is the density of the water at 20°C., 0.99820, as given in the International Critical Tables, and D is the density of air at the temperature and barometric reading at the time of weighing.

2. Calculation of the weight of tube evacuated. Weight of the tube minus the weight of air displaced equals weight of tube evacuated.

3. Calculation of weight of contents. (Weight of sealed tube plus tip and stopper) minus weight of evacuated tube gives weight of contents.

4. Calculation of amount of salt used. Multiply the weight of the acid charge by the salt factor. The salt factor is the molecular weight of salt over molecular weight of acid.

5. Calculation of volume of gas in tube above solution.
 - A. Add approximate meniscus correction to the distance from meniscus to mark of reference.
 - B. Find distance to nearest calibrated line using results of A.
 - C. Multiply distance B by c.c./mm. factor for pycnometer stem. This gives additional volume correction to be either added or subtracted from the volume at the nearest calibrated line. The result gives the volume of gas above the solution.
6. Calculation of volume of solution.
 - A. Volume of gas in tube minus the volume of the liquid in the capillary equals corrected volume of vapor.
 - B. Total volume of tube minus corrected volume of gas equals correct volume of solution.
7. Calculation of weight of vapor.
 - A. Calculate mol fraction of ammonia.
 - B. Density of ammonia gas over liquid ammonia at 20°C . equals .00669.
 - C. Mole fraction of ammonia times .00669 equals the density of ammonia vapor over solution.
 - D. Density of ammonia vapor times correct volume of gas equals the weight of vapor.

6. Calculation of corrected weight of solution.
 - A. Weight of solution. Weight of contents minus the weight of vapor equals corrected weight of solution.
9. Calculate approximate density. Weight of solution divided by the corrected volume of the solution equals the density.
10. Calculate approximate γ where $\gamma = \frac{r(h+r/3)(d-D)g}{2 \cos \theta}$.
 - A. First correct capillary height for microscope reading correction, and meniscus correction.
11. Calculate H_c from the $H_c, \frac{d}{\gamma}$ diagram.
12. Apply H_c corrections and calculate correct density and correct surface tensions.
13. Calculate mols per liter of salt.
 - A.
$$\frac{\text{Grams of salt}}{\text{Molar weight of salt}} \times \frac{1000}{\text{Correct volume of solution}}$$

DISCUSSION OF RESULTS

Concentrations of each salt were run up nearly to the limit of saturation. Surface tension-molal concentration, density-molal concentration and surface tension-log concentration diagrams were made. In the ammonium acetate-ammonia mixtures taken from Table I, the surface tension increased up to 29.37 dynes cm. The density of the solution increased

Table I. Experimental Data for Ammonium Acetates-Ammonia Mixtures at 20°C.

Mols./liter salt	Density of solution	Cap. Height cm. (Corr.)	Radius of Cap. cm.	Surface tension dynes cm.
0.0000*	.6103*			22.03*
1.670	.6867	1.9551	.03458	22.98
1.9374	.6991	2.0640	.03332	23.55
2.6890	.7289	1.9759	.03333	23.72
3.458	.7625	1.9037	.03477	24.54
4.1732	.7250	1.9653	.03335	25.49
4.1980	.7898	1.9266	.03477	25.28
4.4870	.8021	2.0133	.03325	26.12
5.3300	.8430	1.9604	.03477	27.97
5.8940	.8506	2.0562	.03328	28.64
6.0910	.86286	2.0104	.03477	29.37

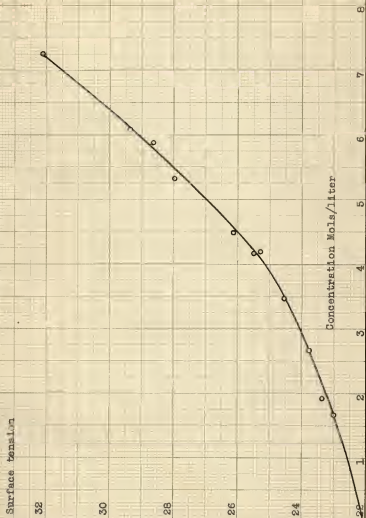
Pure Acetic Acid

Observed	1.0497	27.70
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* Determined by King, Hall and Ware

up to .8628. The surface tension-concentration diagram (Fig.1) shows a downward divergence from a straight line. The density concentration diagram (Fig.2) shows very little divergence from a straight line.

In the ammonium butyrate-ammonia mixtures, Table II, the surface tension increased up to 29.75 dynes cm. The surface tension-concentration diagram (Fig.3) also gives a marked downward divergence from a straight line. The density



Density

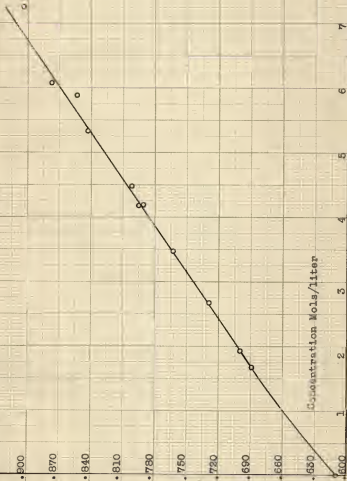


Fig. 2. Density-Concentration Diagram for Ammonium Acetate.

Table II. Experimental Data for Ammonium Butyrate-Ammonia Mixtures at 20°C.

Mols./liter salt	Density of solution	Cap. Height cm. (Corr.)	Radius of Cap. cm.	Surface tension dynes cm.
0.0000*	.6103*			22.03*
.7069	.6463	2.0180	.03537	22.38
.8844	.6670	2.0235	.03526	22.75
1.5250	.6871	1.9844	.03477	23.01
1.8261	.6944	2.0719	.03331	23.27
2.1490	.7398	1.9734	.03334	23.45
3.5040	.7251	1.8774	.03477	24.92
3.8380	.8151	1.9508	.03334	25.69
4.8810	.8510	1.9515	.03334	26.96
5.3898	.8640	1.8747	.03477	27.32
5.4730	.8661	1.8739	.03477	27.40
6.9070	.9218	1.8889	.03525	29.75

Pure Butyric Acid	.9780			26.80
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International Critical Tables

* Determined by King, Hall and Ware

Surface tension

30

28

26

24

22

20

Concentration Mols/liter

1

2

3

4

5

6

7

8

Fig. 3. Surface Tension-Concentration Diagram for Ammonia butyrate.

concentration diagram (Fig.4) gives very little divergence from a straight line.

In the ammonium valerate-ammonia mixture, (Table III), the surface tension increased up to 28.18 dynes cm. The surface tension-concentration diagram (Fig.5) shows a marked downward divergence from a straight line, much more than the surface tension-concentration diagram of the ammonium acetate ammonia mixtures. The density concentration diagram (Fig.6) shows some divergence from a straight line, but very little.

In the ammonium caproate ammonia mixtures, (Table IV), the surface tension increased up to 34.85 dynes cm. The density increased up to .8934. This surface tension-concentration diagram (Fig.7) shows the most downward divergence from the theoretical straight line of any of the other three mixtures. The density concentration diagram (Fig.8) gives almost a straight line. The surface tension-concentration diagram of ammonium caproate indicates two distinct surface tension values for the same point. In observing the readings of the capillary rise in the ammonium caproate ammonia mixture, the capillary rose to a maximum height, remained there for a short time and then fell abruptly about .5 mm. where another equilibrium seemed to be established. This slipping of the liquid in the capillary is probably due to the fact that as the carbon chain increased from the acetate

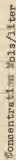
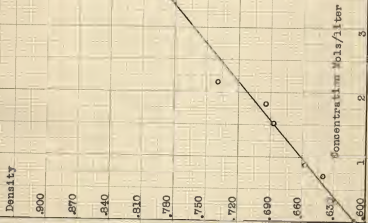


Fig. 4. Density-Concentration Diagram for Ammonium Butyrate.

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

Mols./liter salt	Density of solution	Cap. Height cm. (Corr.)	Radius of Cap. cm.	Surface tension dyne/cm.
0.0000*	.6103*			22.03*
.6088	.6450	2.0646	.03464	22.57
.6149	.6452	2.0307	.03528	22.41
1.5364	.6893	1.9308	.03537	22.85
1.7270	.7078	1.9373	.03480	23.17
3.100	.7739	1.8208	.03529	24.18
4.0140	.8125	1.8032	.03480	24.81
4.7480	.8469	1.7060	.03540	24.92
5.2692	.8671	1.7089	.03526	25.59
5.8210	.8897	1.6800	.03537	25.92
6.1180	.89620	1.7173	.03524	26.45
7.4080	.9478	1.7471	.03480	28.18

Pure Valeric Acid

Observed	.9420			26.68
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* Determined by King, Hall and Ware

Surface tension

28

26

24

22

20

Concentration Moles/liter

1

2

3

4

5

6

7

8

Fig. 5. Surface Tension-Concentration Diagram for Ammonium Valerate.

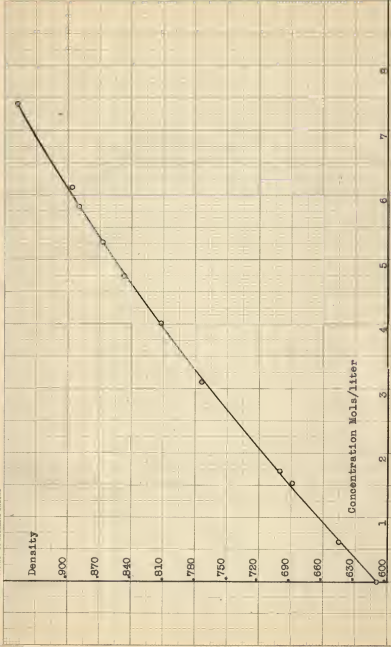


Fig. 6. Density-Concentration Diagram for Ammonium Valerate.

Table IV. Experimental Data for Ammonium Caproates-Ammonia Mixtures at 20°C. for First Curve.

Mols./liter salt	Density of solution	Cap. Height cm. (Corr.)	Radius of Cap. cm.	Surface tension dynes cm.
0.0000*	.6103*			22.03*
.5550	.6374	2.1678	.03310	22.18
1.029	.6689	2.0982	.03310	22.51
2.563	.7510	1.8092	.03531	23.31
3.6120	.8037	1.6476	.03537	23.11
4.1780	.8316	1.7229	.03481	24.28
4.7380	.8610	1.6495	.03577	24.70
5.2271	.8834	1.6343	.03529	24.86

Data for Second Curve

0.0000*	.6103*			22.03*
.4349	.6319	2.0364	.03521	21.97
1.2910	.6695	1.9228	.03521	22.00
2.006	.7184	1.7563	.03590	21.94
2.564	.7488	2.0298	.030200	22.66
3.6120	.8307	1.6920	.03567	23.73

Pure Caproic Acid

Observed	.9220	27.83
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* Determined by King, Hall and Ware

Surface tension

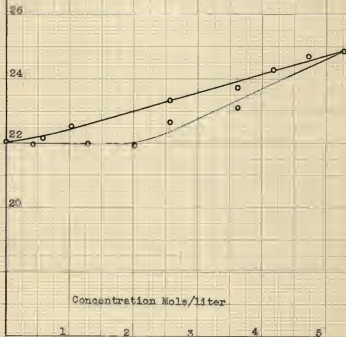


Fig. 7. Surface Tension-Concentration Diagram
for Ammonium Caproate.

Density

.900

.870

.840

.810

.780

.750

.720

.690

.660

.630

.600

Concentration Mols/liter

1

2

3

4

5

6

7

8

Fig. 8. Density-Concentration Diagram for Ammonium Caproate.

to the caproate, the mixture had less tendency to wet the walls of the glass, so evidently there was enough lessening of the force of adhesion between the mixture and the walls of the tube to introduce the factor of a tendency to form a contact angle. As the force of adhesion became less, the effective component of the surface tension became less with the formation of a contact angle.

Rather stable films formed in the tube with high concentrations of the ammonium butyrate, ammonium valerate and ammonium caproate. These rather stable films indicate positive adsorption. Additional evidence of the formation of a contact angle appeared in the higher concentrations of the caproates, wherein after shaking, the liquid appeared to hang up on the walls of the tube in droplets with sharply defined boundaries. Such contact would not be expected if negative adsorption had taken place as indicated by Gibbs' equation, adsorption being negative if surface tension increases with concentration. If negative adsorption had occurred, the surface layer should consist largely of ammonia molecules, which wet glass perfectly as has been shown in the case of pure liquid ammonia. On the other hand, if positive adsorption had occurred with the hydrocarbon chain oriented outward on the surface, the surface would acquire an oil-like character which would not wet glass as readily as pure ammonia does.

Adsorptions were calculated by the Gibbs' equation,

$$U = \frac{1}{2.303 RT} \frac{d\gamma}{d \log c}. \text{ The value } \frac{d\gamma}{d \log c} \text{ was taken from}$$

the surface tension log concentration diagrams. (Figs. 9, 10, 11, 12). The slope in every measurement for $\frac{d\gamma}{d \log c}$

was positive in all the surface tension log concentration diagrams. This indicates an increase in surface tension and negative adsorption. In the equation $U = -\frac{1}{RT} \frac{d\gamma}{d \ln c}$,

R equals 8.316×10^7 ergs, and T equals 293°K , and to change from natural log to base of 10, multiply by 2.303. The ex-

pression $\frac{d\gamma}{d \log c}$ is the slope of the curve found by placing

a straight edge tangent to the point on the surface tension-log of concentration diagram under consideration, and counting up on the γ axis to determine $d\gamma$, and counting on the $\log c$ axis to determine $d \log c$. U in this equation will give the number of mols in each sq. cm. of surface adsorbed. Since U as determined by the surface tension is negative, if there is an increase in surface tension with an increase in concentration, Gibbs' equation would indicate negative adsorption for these salts in solution with liquid ammonia.

Surface tension

32

30

28

26

24

22

Log Concentration

0.2

0.4

0.6

0.8

Fig. 9. Surface Tension-Log Concentration Diagram
for Ammonium Acetate.

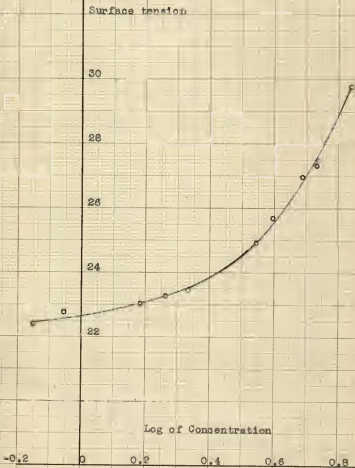


Fig. 10. Surface Tension-Log of Concentration Diagram for Ammonium Butyrate.

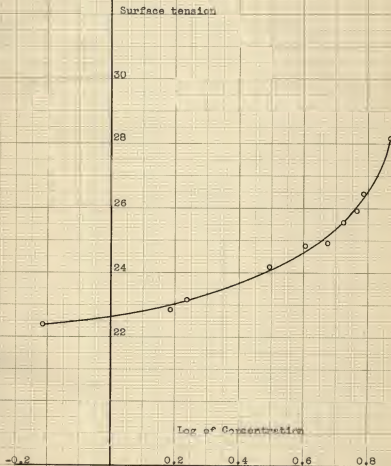


Fig. 11. Surface Tension-Log Concentration Diagram
for Ammonium Valerate.

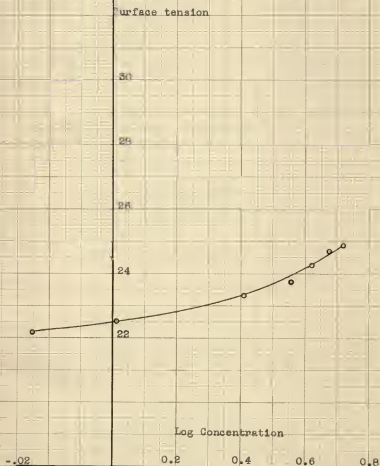


Fig. 12. Surface Tension-Log Concentration for Ammonium Caproates.

METHODS OF CALCULATING NORMAL CONCENTRATIONS AND ADSORPTION

The normal concentration in the surface in moles per sq. cm. was found by the equation, $S_1 = \frac{(6.06 \times 10^{20} \times n)^{\frac{1}{3}}}{6.06 \times 10^{23}}$, where S is the normal concentration. 6.06×10^{23} equals Avogadro's constant or the number of molecules in one gram molecular weight, and since in one mol per liter this number would be contained in one liter, $\frac{6.06 \times 10^{23}}{1000}$ equals the number of molecules in 1 c.c. of 1 mol per liter, or $\frac{6.06 \times 10^{23}}{1000} \times n$ equals the number of molecules in n mole per liter of the mixture. $(6.06 \times 10^{20} \times n)^{\frac{1}{3}}$ equals the number of molecules in 1 sq. cm. of surface. $\frac{(6.06 \times 10^{20} \times n)^{\frac{1}{3}}}{6.06 \times 10^{23}}$ equals the number of moles in a normal concentration.

Discussion of Normal Concentration and Adsorption

A comparison (Table V) was made of normal surface concentration and adsorption of each salt from 1 to 7 mole per liter. From Table V, it was shown that the normal concentration and adsorption for ammonium acetate from 2 mole per

Table V. Comparison of Normal Concentration and Adsorption for
Ammonium Acetate, Ammonium Butyrate, Ammonium
Valerate and Ammonium Caproate

Conc. salt mols./liter	Normal conc. in surface mols./ sq. cm. $\times 10^3$	Adsorption mols./sq. cm. $\times 10^3$			
		Ammonium Acetate	Ammonium Butyrate	Ammonium Valerate	Ammonium Caproate
1	1.181		.3452	.2979	.2804
2	1.875	.6658	.5870	.3658	.3664
3	2.458	1.3328	1.3142	.6306	.6061
4	2.978	2.2078	2.1723	1.1638	.8236
5	3.456	3.6445	2.6984	1.7838	.9409
6	3.902	4.6257	3.0158	1.8698	
7	4.324	5.6246		3.0483	

liter and up to 7 mols per liter, the adsorption exceeded the normal concentration. This is obviously an impossibility.

In each of the other salts, the normal concentration in surface always exceeded the adsorption. With the amount of adsorption becoming less as the carbon chain increased, the least amount of negative adsorption occurred in the ammonium caproate and the largest amount of negative adsorption occurred in the ammonium acetate.

The surface tensions at the same concentrations, i.e., at about 5 mols per liter was lowered from 27.97 dynes cm. in the acetate mixture to 27.38 dynes cm. in the butyrate to 25.59 in the valerate to 24.85 in the caproate.

The comparison of the densities at the same molality, i.e., 5 mols per liter give ammonium acetate 0.8430, ammonium butyrate 0.8640, ammonium valerate 0.8671, and ammonium caproate 0.8634.

The Gibbs' equation gave negative adsorption in all the salt determinations. The comparison of the amount of adsorption at 5 mols per liter give ammonium acetate 3.6445×10^{-10} mols per sq. cm., ammonium butyrate 2.6984×10^{-10} mols per sq. cm., ammonium valerate 1.7538×10^{-10} mols per sq. cm. and the ammonium caproate 0.9409×10^{-10} mols per sq. cm.

Observation indicates positive adsorption although

surface tension increases. Gibbs' equation does not explain satisfactorily what is indicated by the appearance and behavior of the solutions. Whatmough's rule of admixtures offers an explanation as to how positive adsorption may occur with increasing surface tension in solutions of high concentration. The fatty acid salts are very soluble in liquid ammonia.

CONCLUSIONS

The Gibbs' equation holds for very dilute solutions. These four salts are rather highly soluble in liquid ammonia and large concentrations were used; Gibbs' equation will only partly account for their behavior. Furthermore, by Gibbs' equation, negative adsorption is indicated, and experimental evidence indicates positive adsorption. The five, six and seven mols per liter concentrations of ammonium acetate-ammonia mixtures gave more negative adsorption than the normal surface concentration, an apparent absurdity, or at least a paradox.

Since the salts were quite soluble and constituted the major bulk of the solution in the higher concentrations, the system might better be termed a mixture than a solution in liquid ammonia. If Whatmough's rule for mixtures of liquids may be extended to mixtures of a solid and liquid, which is being investigated at present in this laboratory, the

surface tension-volume concentration diagram for the system should follow in the general direction of a straight line up to the surface tension of the pure salt, if the salt were a liquid at that temperature. From the surface tension of fused salts in general, it would be safe to assume that this hypothetical value for the pure salt would be appreciably higher than the surface tension of any of the mixtures measured. Divergence from the straight line of a perfect mixture might be caused by adsorption of one of the components on the surface. The divergence will be downward or down away from the theoretical straight line if positive adsorption takes place and will curve upward and away from the straight line if negative adsorption occurs. Since in each case here under consideration, the divergence is downward and away from a straight line, and since liquids behave in the above manner, there is reason to believe that the salt-ammonia mixtures behave in a similar manner. If such be the case, this explains the positive adsorption as evidenced in the experiment.

The amount of salt negatively adsorbed according to Gibbs' equation decreases when the carbon chain lengthens. This would indicate by Langmuir's theory that as the carbon chain increased in length from CH_3 in the acetic acid to C_8H_{17} in the caproic, it would become more difficult for the polar end to pull it into solution and the adsorption in the

surface tends to become more positive. This appears to be what happened, the adsorption for these salts being less negative according to the Gibbs' equation in the caproates than in the acetates.

Considering the adsorption from Whatmough's rule since there was a wider and wider divergence from a theoretical straight line in the surface tension-volume concentration diagrams, from the acetate to the caproate, this would indicate an increasing positive adsorption and would indicate that liquid ammonia behaves as a polar solvent.

SUMMARY

1. Surface tensions have been determined for ammonium acetate-, ammonium butyrate-, ammonium valerate-, and ammonium caproate-ammonia mixtures.

2. Densities have been determined for ammonium acetate-ammonium butyrate-, ammonium valerate-, and ammonium caproate-ammonia mixtures.

3. Gibbs' adsorption for 1, 2, 3, 4, 5, 6, and 7 mols per liter have been calculated for each of the salts.

4. The reason for a decreasing adsorption when the carbon chain is lengthened is given.

5. Positive adsorption of ammonium acetate, ammonium butyrate, ammonium valerate and ammonium caproate is explained.

6. Ammonium acetate, ammonium butyrate, ammonium valerate and ammonium caproate are very soluble in liquid ammonia.

ACKNOWLEDGMENT

The work of this paper was undertaken at the suggestion of Dr. H. H. King, head of the Department of Chemistry. All materials were furnished by the department, without cost to the worker. The work was done under the direction of Dr. J. L. Hall.

The author wishes to express his sincere appreciation and gratitude to Dr. King and Dr. Hall for their kindly assistance and many valuable suggestions.

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