# SURFACE TENSION OF LIQUID AMMONIA AND ADSORPTION STUDIES AT ITS LIQUID VAPOR INTERFACE

bу

### GLEN CHASE WARE

B. S., Kansas State Agricultural College, 1918

### A THESIS

submitted in partial fulfillment of the requirements

for the degree of

MASTER OF SCIENCE

KANSAS STATE AGRICULTURAL COLLEGE

1928

## TABLE OF CONTENTS

																		Page
Introduction	on .	•	•	•	٠	•	•	•	•	•	•	•	•	•	•	•	•	1
Acknowledge	ment	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	3
Experiments	al Pi	ro	cec	du	re	•	•	•	•	•	•	•	•	•			•	4
Apparatus	•	•	•	•			•	•	•		•	•		•	•	•	•	18
Discussion	of I	Res	su:	lt	3	•	•	•	•	•		•	•		•		•	19
Summary		•	•	•	•	•	•			•		•	•				•	37
Literature	Cite	эđ	•		•													39

# SURFACE TENSION OF LIQUID AMMONIA AND ADSORPTION STUDIES AT ITS LIQUID VAPOR INTERFACE

#### INTRODUCTION

Harkins (1917) and Langmuir (1917) independently have developed the theory of orientation of molecules in surfaces. Polar groups of molecules are attracted by polar liquids and present their non-polar end to the surface. Surface energy, therefore, should be largely determined by the character of the non-polar end of adsorbed molecules in polar liquids and by the amount of adsorption in the surface.

Wampler and King (1922) of this department have studied the effect of certain organic acids and esters upon the surface energy of water. They conclude that the polar groups do orient to the body of the liquid with the least active portion of the molecule in the surface.

It is now proposed to use liquid ammonia as the solvent and to determine if it behaves as a polar liquid

toward adsorbed substances containing polar groups. It would seem in light of the orientation theory that to the polar portion of the molecule would be due its solubility in ammonia and that if progressively longer carbon chains were attached, 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 carbon chain increases in length. Due to the properties of liquid ammonia and the paucity of data concerning these properties, a great number of difficulties had to be met to develop a technique which would give reliable data. It was first considered advisable to make a study of surface tension of the system, waterammonia, in order to compare the properties of ammonia to water.

Surface tension in liquid ammonia has been investigated by Berthoud (1918) but the range of his work was not sufficient nor determined at convenient temperatures for laboratory procedure with solutions. Rice (1928) recently has made determinations upon solutions up to a concentration

of 14 moles per liter. The density of pure liquid ammonia is given by Drewes (6), Andreef (6), and Lange (6). It was necessary to develop a method for determining the density of solutions, for no data upon the density of ammonia-water solution at 20° could be found in the literature for concentration above 50 per cent ammonia. A new determination was made at these concentrations and used in all calculations.

#### ACKNOWLEDGMENT

The writer wishes to acknowledge his indebtedness to Dr. H. H. King who has suggested this problem for research and has given his hearty cooperation in guiding the work and providing necessary materials. The writer wishes also to express his appreciation for the aid of Dr. J. Lowe Hall in designing apparatus, and assisting in the solution of the problems involved.

#### EXPERIMENTAL PROCEDURE

The capillary height method was used to determine the surface tension. The apparatus consisted of a heavy grade pyrex tube. (Fig.1 - A). The large bowl was used to provide a surface of such size that its center portion could not be appreciably lifted by the surface tension at its perimeter. A capillary side arm was attached to the bowl below and to the stem above with a goose neck at its juncture with the stem. This design permitted 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 pyonometer. The lower part could not serve this purpose for if the bowl were large enough to offer a flat space on the surface of the contained liquid it would be too

large to measure accurately for volume. The barrel and the small tube attached were of such size that the volume of the pycnometer measured from the tip of the small tube to the middle of the stem was about equal to the volume of the bowl and side-arm up to the middle ring on 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.

Gaseous ammonia was condensed into the tube by carbon dioxide snow. Figure 1 shows how the apparatus was connected to fill the tube. Off to the left not shown in the sketch was a steel tank of gaseous ammonia. The gas was led first to a drying train consisting of freshly fused soda lime. A "T" tube through which protruded a long small-bore tube which reached down into the top part of the bowl was used to introduce the gas into the tube. The top tube of the "T" placed vertically served as a jacket for the

small-bore tube. The stem served as an outlet for excess gas.

Short sections of rubber tubing connected the small-bore tube to the jacket and the jacket to the tube to be filled. The stem of the "T" tube was connected to a second drying train so that fluctuations in pressure could not draw moisture back into the tube with the returning gases. Last in the train of apparatus was a mercury trap which to a certain limit increased the pressure on the gaseous ammonia when condensation lessened and decreased it when condensation was more rapid. This increased the rate of condensation of gas for a small head of mercury was maintained by regulating the influx of ammonia with the valve on the tank.

The tubes, when not in use, were filled with cleaning solution and allowed to stand until the next fill.

They were then thoroughly rinsed with surface tension water and dried only when to be filled with pure ammonia. For aqueous solutions drying would serve no purpose, after the tubes had been weighed empty, and was omitted.

Tubes to be filled with pure ammonia were placed in an insulated container and connected in the train as shown by figure 1. The U tubes containing freshly fused soda lime were immersed in salt-ice mixture. The ammonia gas was admitted and the tube thoroughly swept out. Carbon dioxide snow was then packed around the tube. As the gas began to liquefy, the control valve was opened until a small pressure was maintained at the mercury trap. When sufficient ammonia was condensed, the tube was removed from the filling train and while still packed in carbon dioxide snow its tip was sealed with an oxygen blow torch. Removed from its snow packing, the tube was deposited in a well padded piece of iron pipe for safety where it might slowly warm to room temperature.

After a period of several hours the tube was placed in a thermostat. After about an hour in which the temperature of the tube and its contents came to the temperature of the thermostat, the tube was thoroughly agitated and the capillary repeatedly rinsed with the liquid. The tube was then aligned before the window of the thermostat with

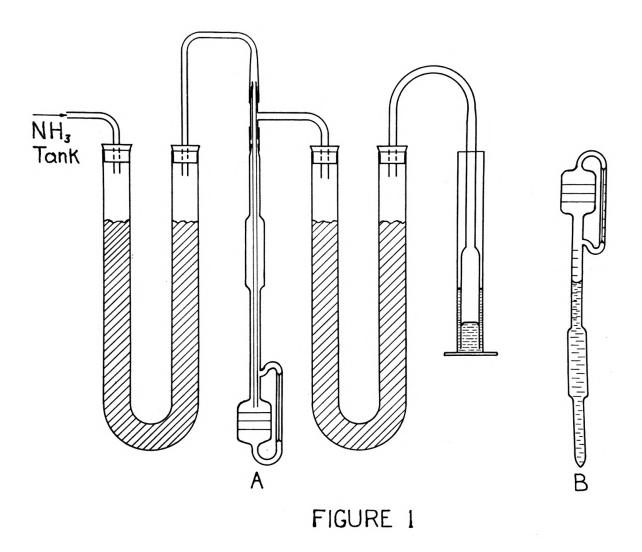
the capillary vertical and allowed to stand until the system came to equilibrium. Capillary height readings were taken with a William Gaertner traveling microscope. To empty the contents, the tube was first chilled with carbon dioxide snow to relieve the pressure and its tip was heated with a fine pointed oxygen flame until a small pin hole blew out. The contents were discharged through this hole.

Density for solutions above 50 per cent at 20° was determined by weighing the tube before and after filling and measuring the volume in the pycnometer, the tube being in the inverted position shown in figure 1 (B) while volume readings were taken. The fact that the volume of the pycnometer was changed each fill introduced considerable difficulty. This was met by calibrating a volume scale on the stem to be read with the microscope. After reading the capillary height the tube was inverted and allowed to stand until all the contents drained into the pyconometer and equilibrium between the gaseous and liquid phases became established. It was then plumbed and the position of the meniscus read with the microscope. From this reading the

volume of the gas phase above the liquid could be calculated. Since the calibration of the stem was made relative to the bowl, changes in volume of the pycnometer did not affect the volume of the calibrated portion. The volume of the liquid was determined by difference after the total volume of the tube had been measured.

When the tubes were opened, as mentioned before, a small pin hole was blown through the tip. The sharp edges were melted back so that no weight would be lost by this breaking off. The minute bulb raised with the pin hole was shrunk back to its former position. When the glass at the tip cooled, the tube was inverted and the contents expelled through the pin hole by the vapor pressure of the liquid.

When the tube was empty of liquid, the tip was immersed in distilled water. The familiar ammonia fountain immediately filled the tube. This water was used only for rinsing. It was immediately removed with an aspirator. The tip of the tube was pushed up through a rubber stopper into the bottom of a water container. The top of the container was connected to an aspirator. Within it was a quantity of boiled distilled water.



The aspirator removed the air from the tube while the container was tilted to expose the tip so that air would not be bubbled through the water. When the tube was exhausted, water was allowed to flood over the tip and the air line broken. Atmospheric pressure forced the water into the tube. When filled, the tube and water container, the tip still covered with water, were connected to a vacuum pump and exhausted until vigorous boiling removed the last traces of air which high temperature boiling had not previously expelled.

The whole filling assembly was then immersed in the thermostat and brought to 20°. The tube was disconnected from the water container and quickly dried and weighed. From the weight of water the volume of the tube could be accurately determined.

To calibrate the volume scale on the stem, rings one centimeter apart were etched on it. The tube was filled with air free water to a point near the lowest ring and the weight of water determined. Three more additions of water were made at higher points on the tube. The volume of the

tube to each of these points was calculated. The cubic centimeters of volume per centimeter of length of the stem was determined and tabulated for use in figuring volumes from microscope readings.

To correct these volumes for the volume of the water in the meniscus, a short piece of glass tubing from the same stock as the stem was ground smooth and a flat bottom cemented to it. It was weighed empty then with a small amount of water in it. With a traveling microscope the depth of water was measured. Another small portion of water was added and the process repeated. The data obtained yielded the weight per unit height, the total weight of water, the diameter of the tube and the total height of water. From these was calculated the weight of water which the tube contained to the bottom of the meniscus. value subtracted from the actual weight of water in the tube gave the weight of water in the meniscus. Duplicate determinations checked to four significant figures. This value was subtracted from the weight of water in the tube when volume calibrations were made.

To find the weight of liquid in the meniscus formed by solutions of various concentrations proved a more difficult task. According to Gould (1926), the volume of liquid in any meniscus depends upon the density of the solution and to the surface tension. Using the formula

$$V_1 = \frac{D_w}{D_1} \cdot \frac{\gamma_1}{\gamma_w} \cdot V_w$$

where  $V_l$ ,  $D_l$ ,  $V_l$  represent respectively meniscus volume, density, and surface tension of the liquid and  $V_w$ ,  $D_w$ , and  $\gamma_w$  represent respectively meniscus volume, density, and surface tension of water. The volume of the liquid in the meniscus of each solution was calculated and subtracted from the measured volume of the gas. The values obtained agreed closely with meniscus volumes calculated by formulae in international Critical Tables. It should be noted that the vapor is in the calibrated end of the tube. Its volume is subtracted from the total volume of the tube to obtain the volume of the liquid.

$$v_1 = v_t - v_v$$

When the determinations were to be made on solutions of ammonia and water the tube was first carefully dried and

weighed. It was then washed with cleaning solution, and rinsed with surface tension water. The desired quantity of water was weighed in the tube and the tube was connected in the filling train and packed with carbon dioxide snow before being swept out with ammonia gas. After a short time a small pressure was built up by means of the mercury trap until approximately the desired amount of ammonia had collected as indicated by the rings on the bowl. The tube was disconnected from the filling train with a small flow of gas maintained to blow out any liquid which condensed in the small-bore tube. Properly adjusted, the small-bore tube showed little tendency to collect liquid. The top of the tube was immediately sealed and the portion of glass removed was labeled and weighed with each subsequent weighing of the tube and its contents. Subsequent manipulation of the tube was the same as for pure ammonia.

It should be noted that the tube now contained a system with a known weight of water and a known weight of ammonia but to determine the density it was necessary to know just how much water and how much ammonia were in the

vapor, for obviously the vapor, especially at high pressures, would contain enough ammonia to affect the calculated value of the density. The tables of Wilson (1925) were used to give the total vapor pressure of ammonia water solutions and the composition of the vapor phase corresponding to each solution composition studied. His tables for total vapor pressure were plotted and values read from the curves. The density of the vapor present was assumed to be directly proportional to the pressure and the mean weight of the molecules of the vapor.

$$D = D_a \cdot \frac{P}{P} \cdot \frac{M}{M}$$

in which Da, Pa, and Ma refer respectively to the density, pressure, and molecular weight of the vapor above pure ammonia and D, P, and M refer respectively to the density, pressure, and mean molecular weight of the vapor above the solution. Since the vapor over the solutions, whose densities were determined in no case, contained greater than a few tenths of 1 per cent water vapor, no objectional error was introduced by omitting the second proportionality factor from density calculations.

The volume of the vapor was measured as previously stated. Subtracting the weight of the vapor from the total contents of the tube gives the weight of the solution. This with the volume of solution determined as explained previously completes the necessary data for the density calculations. If the weight of water is subtracted from the weight of solution, we have the weight of ammonia in solution since at the concentration used for density studies no appreciable weight of water is found in the vapor. With this item added to our data, it is possible to calculate the concentration in per cent by weight, mol per cent, and moles per liter. The density of saturated ammonia vapor was taken from Drewes (1905) values. Sufficient density determinations were made to determine the curve plotted in figure 2. These were plotted on sufficiently large scale to be read to the fourth significant figure. Densities for calculating surface tension values were read from this curve.

Table I

Density determinations from which curve was constructed

Per cent NH3 by weight	:	Density
47.237		0.83516
	•	
54.200	:	0.81010
60.990	:	0.78404
64.350	:	0.76833
72.443	:	0.73427
80.858	:	0.69810
89.754	:	0.65533
96.636	•	0.62447
97.174	•	0.62303
100.000	:	0.60860
	•	
100.000	:	0.60906

#### APPARATUS

The tubes used in this work to contain the liquid whose properties were studied were designed by Dr. J. L. Hall of this department. They were constructed of heavy pyrex tubing. Their ruggedness, accuracy, and ease of manipulation left little to be desired.

All pieces of apparatus were carefully calibrated.

The scale on the traveling microscope was calibrated

against a William Gaertner divided glass slide provided for the purpose and the necessary correction made in all read-The diameter of the capillaries were carefully determined by measuring the length of a weighed pellet of mercury at successive positions in the tube. This was done before the tubes were made. At the end of the experiment, the same capillaries were checked by determining the surface tension of high grade surface tension water whose surface tension had been carefully determined by the drop weight method. An additional check was made with the purest obtainable thiophene-free benzene. These checks showed one capillary to be accurate. The second capillary was shown to have given too high a calculated value for surface tension due probably to a slightly elliptical cross section. These two checks were in excellent agreement with each other. Accordingly from this standardization, the proper correction was made on all data used. All calculations were made with five-place logarithm tables.

Illumination for all microscope readings was provided by a mercury arc lamp. This illumination reduces shadows and reflections and is considered equivalent to two and one-half diameters of magnifications. The thermostat used for readings at 10°, 20°, and 30° was electrically controlled and under ordinary working conditions accurate to about 0.01 degrees.

Owing to the high pressure within the tubes at the higher concentrations of ammonia the density of the gas was subtracted from the density of the liquid in calculating surface tension. If the surface of the meniscus be considered spherical, as small menisci may well be, the volume of the meniscus may be included by adding r/3 to the measured capillary height. The formula for calculating surface tension becomes

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

#### DISCUSSION OF RESULTS

The surface tension of liquid ammonia as determined in this work agrees closely with Berthoud's (1918) value at 11.1 degrees if his data is calculated by the corrected capillary height formula as given above. Since determinations were made at only three temperatures and these far

above the critical temperature of ammonia, it is impossible to draw hard and fast conclusions concerning association; but if this curve is extrapolated to zero surface tension it crosses the temperature axis at about the point predicted by the Ramsay Shields equation if we assume it is unassociated. This leads to the conclusion that ammonia is not greatly if at all associated.

Table II

Temperature coefficient of surface tension of pure ammonia

Temperature	: :Surface tension
0.30	: 26.339
0.3° 0.5° 0.5°	26.197
0.50	: 26.099
10.00°	: 24.166
10.00	: 24.035
10.000	: 21.97

The value at 20° is the average of five determinations.

Early determinations of surface tension were made in tubes whose bowls were less than 34 millimeters in diameter. The results were uniformly low suggesting that the large meniscus was not flat. No formula was found to

reconcile calculations made from this data with calculations made from data from larger tubes. The correction used by Quinn (1927) was not applicable to data obtained from the type of apparatus employed. This data was not used in any tables or calculations offered in this thesis.

The determined densities of solutions above 50 per cent NH3 are tabulated in Table II and plotted in figure 2 along with data from Mittasch, Kuss, and Schlueter (1926) and with data from the International Critical Tables. The data from all three sources agree very well. The density curve at 15° was included in broken lines for the purpose of comparison. The solid line portion of the upper curve in figure 2 represents the values determined experimentally. The accuracy is indicated from the fact that the density curve joins closely with the points obtained by Mittasch, Kuss, and Schlueter (1926), and that the curve follows closely the character of the 150 density curve. The two density determinations on pure ammonia compared with those of Andreef, Drewes, and Lange (1905) determined independently by each is additional evidence to show the accuracy and dependability of the method used in this work.

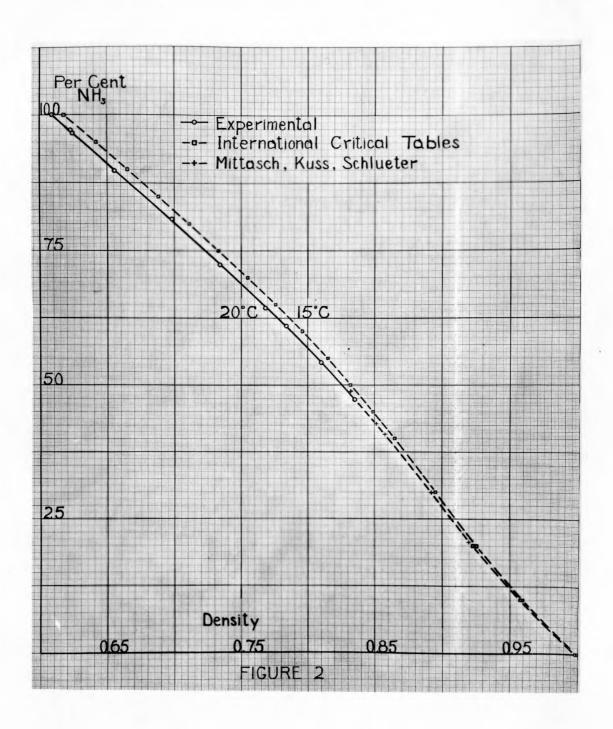


Table III.

Density of pure ammonia at twenty degrees

				:	
Investigat	toı	c		:	Density
Lange .				:	0.6067
Andreef				:	0.6089
Drewes				:	0.6103
Author				:	0.6086
Author				:	0.6090

The surface tension values found in Table IV were calculated from experimental data, the densities being taken from the curve. All surface tension determinations were made under conditions such that the per cent composition of the solution could be determined even though the densities were taken from the curve. It may be significant that the inversion point in the surface tension curve comes at a point where the concentration of the solution is 50 mol per cent of each component. Especially is this so since the adsorption curve of water has a very pronounced break at the same concentration. These results suggest that the ammonia-water system is a three component system.

Rice (1928) has made surface tension determinations of solutions of ammonia in water up to a concentration of 14.08 moles per liter. His values throughout were lower than those obtained in this work with a greater difference at lower concentrations. Since Rice determined density by transferring solutions to a pycnometer and reading the concentration from density-concentration tables, disagreement of results is to be expected. Fluctuations in capillary height ascribed by Rice to the action of ammonia on glass could equally as well be ascribed to a state of unequilibrium because of difficulty to obtain thorough mixing in the system; also to the fact that the apparatus was not enclosed in a thermostat. Distillation of ammonia from the meniscus surface because of unsaturation of the vapor above the liquid, or because of temperature change, would quite obviously cause an increase in the apparent surface tension. Rice does not mention the kind of glass he used.

The pyrex glass apparatus used by the author gave no cause for any suspicion as to its reaction with ammonia. When the system had been given time to come to temperature

equilibrium, the contents had been thoroughly mixed, and the capillary had been irrigated several times, the capillary height became constant within a moderate period of time necessary for the draining of the walls of the apparatus.

The adsorption values in Table IV were calculated by means of the Gibbs adsorption equation

$$u = -\frac{1}{iRT} \cdot \frac{dy}{d \log c}$$

where R is the gas content expressed in ergs -, that is, 8.316 x 10<sup>7</sup> ergs per degree; T is the temperature absolute; dy is taken from the curve of the surface tension d log c plotted against the logarithm of the concentration in moles per liter; u equals the excess of solute in the surface expressed in moles per square centimeter. Since in higher concentrations of ammonia the degree of ionization is quite small, i was taken as unity.

Table IV.

Adsorption of ammonia and water in the liquid-vapor interface of the water-ammonia system

Conc.	:	Adsorption	:	Conc.	:	Adsorption
Per cent	:	moles per	:	Per cent	:	Moles per
NH3	:	sq.cm.	:	H20	:	sq. cm.
10	:	0.226	:	10	:	- 0.131
20	:	0.396	:	20	:	- 0.275
<b>3</b> 0	:	0.685	:	<b>3</b> 0	:	- 0.475
40	:	0.944	:	40	:	- 0.740
45	:	1.140	:	45	:	- 0.740
48.6	:	1.47	:	50	:	- 1.530
50	:	2.10	:	51.4	:	- 1.530
55	:	2.10	:	55	:	- 1.048
60	:	2.10	:	60	:	- 1.048
70	:	2.10	:	70	:	- 1.048
80	:	2.32	:	80	:	- 1.157
90	:	3.25	:	90	:	- 1.481
98	:	4.46	:	98	:	- 2.64

Figure 6 is a graphic study of the adsorption of ammonia and water in the liquid-vapor interface. The evidence here again points to the conclusion that ammonia and water form a three component system, for a sharp break occurs in each curve at the point where the molal concentrations of water and ammonia are equal.

Table VI tabulates the concentration of molecules expected in a unit of normal surface if there were no adsorption together with the number of molecules adsorbed as calculated by the Gibbs' adsorption equation. It will be noted that the number of molecules of water negatively adsorbed at solution concentration near 50 mol per cent exceeds the number that could normally be present in the surface. Obviously this cannot be so but the discrepancy can be explained by considering the system as composed of three components. When the concentration of ammonia is low the solution would contain a small per cent of ammonia, a small per cent of ammonium hydroxide, and a large per cent of water. As the concentration of ammonia increases so does the concentration of ammonium hydroxide, but the concentration of water decreases according to their added value. Consequently, figure 4 has been plotted for too high water and ammonia concentration values and no note has been taken of the ammonium hydroxide concentration.

Table VI.

Ammonia adsorption

Per cent	: Molecules pe	r:square	centimeter	:A	rea/mole	cule
$^{ m NH}$ 3	: Normal	:Adsorbed		_:i	n sq. cm.	
30	:0.0450x10 16	:0.0415x	$\frac{16}{10.0865 \text{x}}$	.00	11.62x10	-10
40	:0.0532	:0.0570	:0.1102	:	9.06	
45	:0.0568	:0.0690	:0.1205	:	8.30	
48.6	:0.0591	:0.0890	:0.1483	:	6.74	
50	:0.0600	:0.1270	:0.1872	:	5.34	
55	:0.0629	:0.1270	:0.1901	:	5.26	
60	:0.0658	:0.1270	:0.1930	:	5.18	
70	:0.0703	:0.1270	:0.1975	:	5.06	

Water adsorption

Per cent	: Molecules pe	r square c	entimeter	:Area/molecul
H2 <b>4</b>	: Normal	:Adsorbed	7.0	16
<b>3</b> 0 40	:0.0385x10 16	:-0.0277x	16:0.0108x	10: 0.925x10
40	:0.0483	:-0.0277	: 0.0206	: 0.486
45	:0.0531	:-0.0448	: 0.0083	: 1.204
50	:0.0578	:-0.0927	:-0.0369	:-0.369
51.4	:0.0592	:-0.0927	:-0.0335	:-0.298
55	:0.0623	:-0.0635	:-0.0012	:-8.330
60	:0.0654	:-0.0635	: 0.0019	: 5,260
70	:0.0760	:-0.0635	: 0.0125	: 0.800

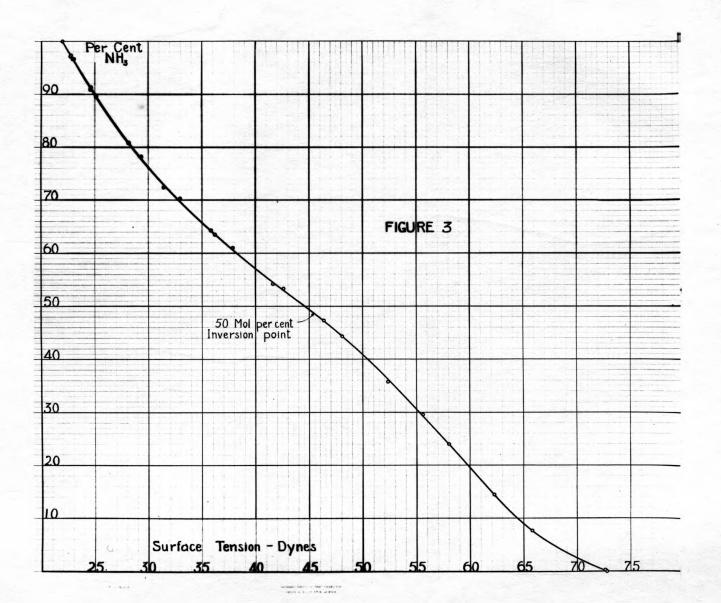
A lowering of the concentration values for water would present a curve from which the computed value of  $\frac{d}{d} = \frac{d}{d} = \frac$ 

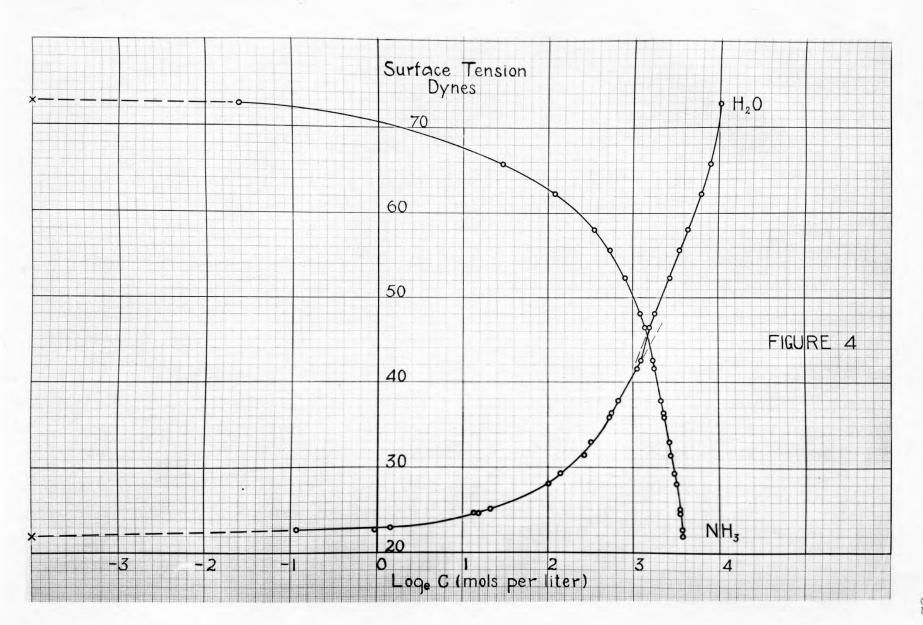
The effect of the presence of ammonium hydroxide upon the calculated adsorption of ammonia is not so obvious because adding the adsorbed molecules to those normally expected in the surface does not so readily show an absurdity.

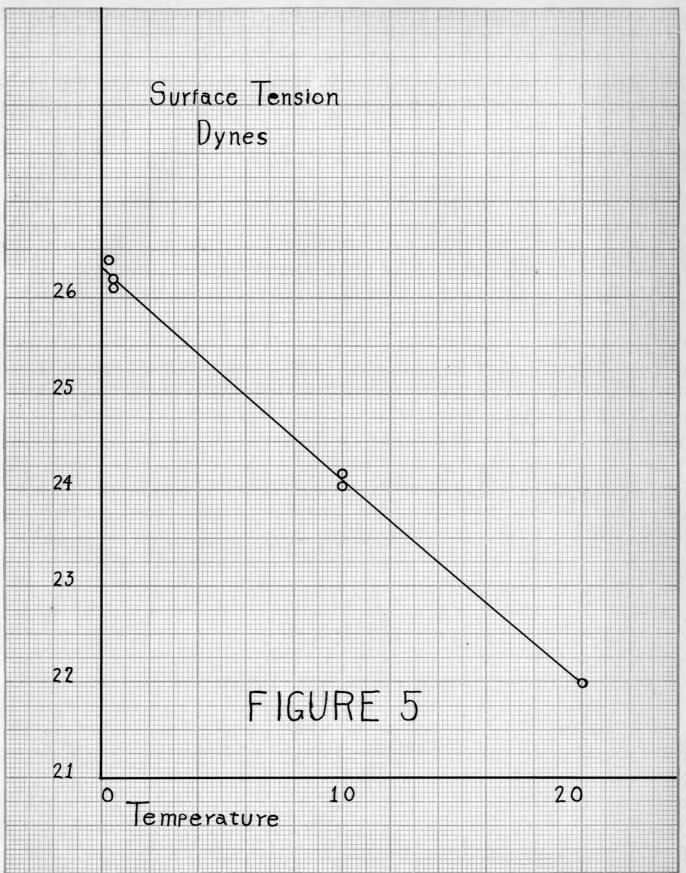
Table VII.

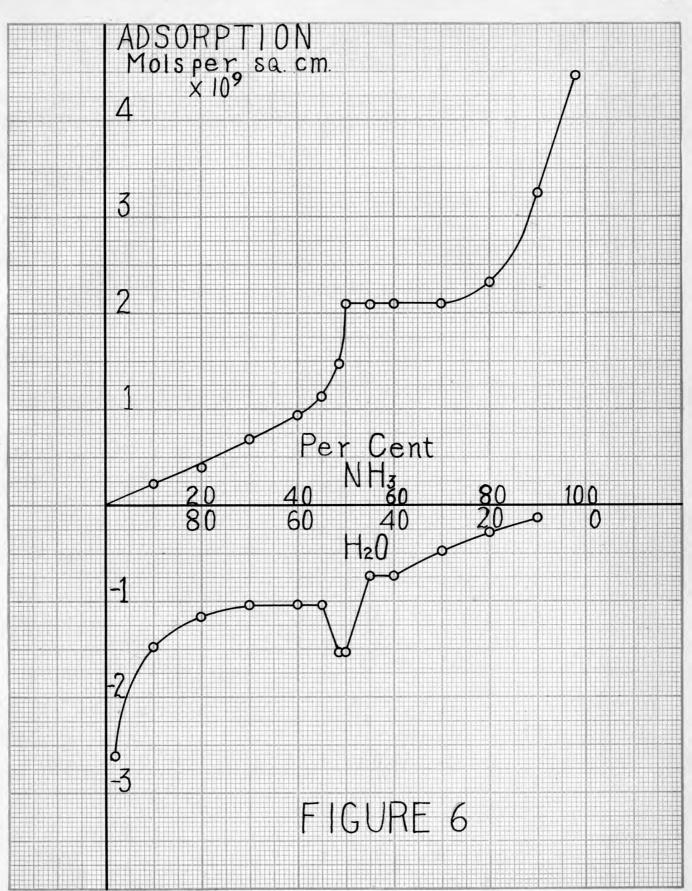
Density and surface tension of ammonia-water Solutions in five per cent steps

Per cent NH	3:		:	Surface
by weight	:	Density	:	tension
5	:	0.9771	:	65.70
10	:	0.9576	:	64.38
15	:	0.9396	:	61.98
20	:	0.9228	:	59.76
25	:	0.9070	:	57.52
30	:	0.8919	:	55.25
35	:	0.8763	:	52.90
40	1	0.8601	:	50.45
45	•	0.8432	•	47.65
50	•	0.8258		44.55
5 <b>5</b>		0.8074	•	41.25
<b>6</b> 0	:	0.7877	:	38.20
65	:	0.7667	:	35.40
70	:	0.7451	:	32.80
	•			
75	•	0.7230	•	30.50
80	:	0.7006	:	28.48
85	:	0.6781	:	26.62
90	:	0.6551	:	25.00
95	:	0.6320	:	23.42
100	:	0.6088	:	21.973









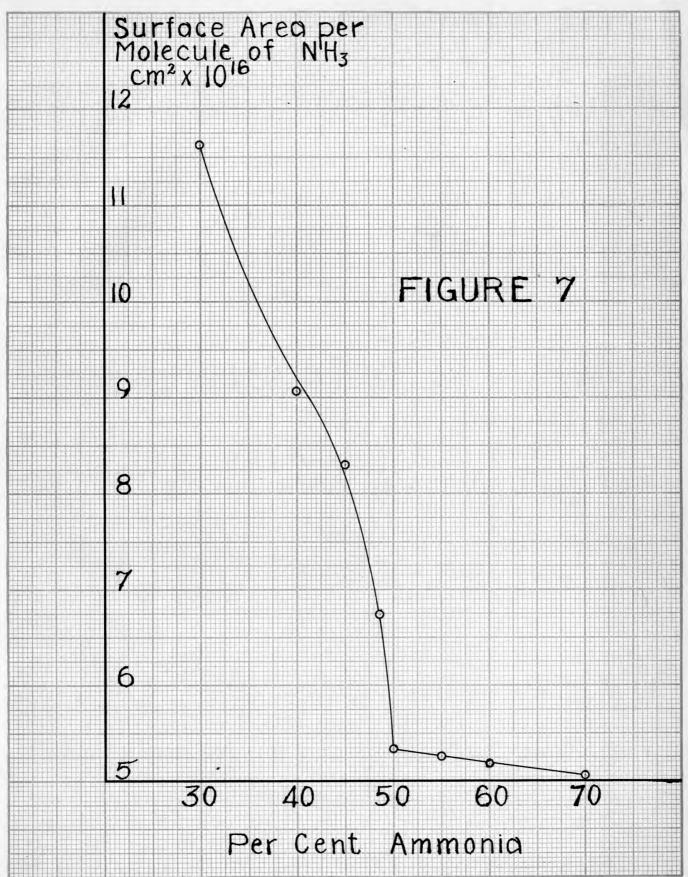


Table V. Experimental Data

Item	:Per cent : NH3	: :Cap. rad.:	cor.	:Solution : demsity		:Surface : tension	:Mols per :1. water	: Mols per l
1	:100.0	:0.033348 :	2.2400	:0.6088	:0.007474	: 22.014		: 35.745
2	:100.0	:0.033348 :	2.2400	:0.6088	:0.007474	: 22.014	:	: 35.745
3	:100.0	:0.03455 :	2.1475	:0.6088	:0.007474	: 21.865	:	: 35.745
4	:100.0	:0.03334 :	2.2362	:0.6088	:0.007474	: 21.976	:	: 35.745
5	:100.0	:0.03335 :	2.2383	:0.6088	:0.007474	: 21.999	:	: 35.745
6	: 97.355	:0.03344 :	2.2600	:0.6213	:0.00722	: 22.742	: 0.91218	: 35.514
. 7	: 97.174	:0.03477 :	2.1685	:0.6220	:0.00722	: 22.714	: 0.97568	: 35.488
8	: 96.665	:0.03477 :	2.1895	:0.6245	:0.0071	: 23.032	: 1.1578	: 35.444
9	: 96.636	:0.033343 :	2.2764	:0.6246	:0.00716	: 22.965	: 1.1663	: 35.482
10	: 90.906	:0.0345 :	2.2589	:0.6510	:0.00676	: 24.604	: 3.2861	: 34.747
11	: 89.754	:0.033348 :	2.3604	:0.6563	:0.00671	: 25.056	: 3.7325	: 34.585
12	: 89.670	:0.033348 :	2.3681	:0.6568	:0.00668	: 25.158	: 3.7660	: 34.588
13	: 91.376	:0.03344 :	2.3426	:0.6490	:0.00680	: 24.651	: 3.1067	: 34.818
14	: 80.858	:0.03472 :	2.3876	:0.7003	:0.00618	: 28.052	: 7.4448	: 33.246
15	: 78.208	:0.033348 :	2.5530	:0.7090	:0.00607	: 29.323	: 8.5763	: 32.557
16	: 72.443	:0.03466 :	2.5381	:0.7347	:0.00580	: 31.420	:11.238	: 31.209
17	: 70.350	:0.033348 :	2.7325	:0.7437	:0.00555	: 32.963	:12.240	: 30.719
18	: 64.35	:0.03472 :	2.7539	:0.7696	:0.00475	: 35.837	:15.229	: 29.071
19	: 63.519	:0.033397 :	2.8938	:0.7730	:0.00466	: 36.393	:15.653	: 28.822
20	: 60.99	:0.03468 :	2.8574	:0.7838	:0.00433	: 37.850	:16.972	: 28.068
21	: 54.200	:0.03468 :	3.0335	:0.8103	:0.00342	: 41.590	:20.600	: 25.786
22	: 53.304	:0.033397 :	3.2114	:0.8138	:0.00330	: 42.595	:21.093	: 25.479
23	: 47.237	:0.03346 :	3.4265	:0.8357	:0.00242	: 46.437	:24.475	: 23.178
24	: 44.347	:0.033385 :	3.4831	:0.8457	:0.00205	: 48.073	:26.125	: 22.020
25	: 35.732	:0.03347 :	3.6559	:0.8740	:0.00115	: 52.339	:31.179	: 18.336
26	: 29.529	:0.03349 :	3.8136	:0.8896	:0.00068	: 55.600	:34.798	: 15.423
27	: 23.976	:0.03347 :	3.8921	:0.9101	:0.00042	: 58.017	:38.405	: 12.810
28	: 14.485	:0.033492 :	4.0304	:0.9423	:0.00018	: 62.250	:44.729	: 8.0216
29	: 7.608	:0.033496 :	4.1507	:0.9668	:0.00008	: 65.783	:49.581	: 4.3187
30	: 0.343	:0.033494 :	4.4444	:0.9967		: 72.613	:55.134	: 0.20072

#### SUMMARY

- 1. The surface tension of liquid ammonia at  $0^{\circ}$ ,  $10^{\circ}$ , and  $20^{\circ}$  was determined.
- 2. Insufficient data was obtained to determine the coefficient of association of liquid ammonia but such as was obtained indicated little if any association.
- 3. Tubes smaller than 34 mm. in diameter gave low results for surface tension of pure ammonia.
- 4. A method is shown whereby the surface tension and density of a solution may be determined in the same sealed tube without removing the contents.
- 5. A correction for menisci volumes and one for weight of the vapor above solutions is given to permit accurate density and per cent composition calculations.
- 6. Curves showing (a) surface tension of pure ammonia plotted against temperature, (b) surface tension of ammoniawater solutions plotted against per cent composition, (c) density of ammonia-water solutions against per cent composition as determined in this work, compared with work

of others, (d) surface tension against the logarithm of the concentration, and (e) adsorption against concentration.

7. Tables are included to show (a) a comparison of density determinations of pure ammonia with the values of other workers, (b) experimental data for density obtained with solutions of various per cent compositions above 50 per cent ammonia, (c) all surface tension data obtained and the data from which it was calculated, (d) adsorption at various compositions, (e) density and surface tension of ammonia-water system at 20° in 5 per cent steps, (f) the the surface concentration and area occupied by the molecules in the surface of solutions, and (g) change of surface tension of pure ammonia with change of temperature.

#### LITERATURE CITED

Andreef

1905. Density of Liquid Ammonia.

Landolt Bornstein Tabellen Verlag

von Julius Springer, Berlin, p. 253.

Berthoud, A.

Determination of the Surface Tension and Critical Density of Ammonia.
Helvetia Chimica Acta, 1:84.

Drewes.

1905. Density of Liquid Ammonia.

Landolt Bornstein Tabellen Verlag

von Julius Springer, Berlin, p. 253.

Gould, F. A.
1926. Volumes of Liquid Menisci.
International Critical Tables, 1:73.

Harkins, William D., Brown, F. E., and Davies, E. C. H.

1917. The Structure of the Surfaces of Liquids, and Solubility as Related to the Work Done by the Attraction of Two Liquid Surfaces as they Approach Each Other.

Jour. Amer. Chem. Soc., 39:354.

Harkins, William D., Davies, E. C. H., and Clark, George L.
1917. The Orientation of Molecules in the
Surfaces of Liquids, the Energy Relations
at Surfaces, Solubility, Adsorption,
Emulsification, Molecular Association, and
the Effect of Acids and Bases on Interfacial Tension.
Jour. Amer. Chem. Soc., 39:541.

King, H. H. and Wampler, R. W.
1922. The Adsorption and Orientation of the
Molecules of Dibasic Organic Acids and
their Ethereal Salts in Liquid-Vapor
Interfaces.

Jour. Amer. Chem. Soc., 44:1894.

Lange
1905. Density of Liquid Ammonia.
Landolt Bornstein Tabellen Verlag von
Julius Springer, Berlin, p. 253.

Langmuir, Irving
1917. The Constitution and Fundamental Properties of Solids and Liquids.
Jour. Amer. Chem. Soc., 39:1848.

Mittasch, Von A., Kuss, E., and Schlueter, H.
1926. Zeitschrift Fur Anorganischer und
Allgemeine Chemie, 159:1.

Quinn, Elton L.

The Surface Tension of Liquid Carbon
Dioxide. Jour. Amer. Chem. Soc., 49:2704.

Rice, Oscar Knepler
1928. The Surface Tension and the Structure of
the Surface of Aqueous Ammonia Solution.
Jour. Phys. Chem., 32:584.

Wilson, Thomas A.

1925. Total and Partial Vapor Pressures of
Aqueous Ammonia Solutions.
University of Illinois, Bulletin No. 23,
Vol. 22.