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Summary

1. A large number of organic bases have been titrated with perchloric acid in glacial acetic acid solution.

2. It is shown that the relative strengths of the bases in acetic acid and in water are nearly proportional and that it is possible to determine by titration in acetic acid the "water" strength of certain bases which cannot be studied in water.

3. A large part of the published data on the strength of bases in water has been critically resurveyed and the values "corrected" to 25° where necessary in accordance with new determinations of the temperature coefficient of pK_H for bases of different strengths.

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A STUDY OF THE DENSITY, SURFACE TENSION AND ADSORPTION IN THE WATER-AMMONIA SYSTEM AT 20°¹

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In view of the fact that liquid ammonia behaves as an ionizing medium for electrolytes it was thought that the determination of its behavior as a polar liquid toward adsorbed substances containing polar groups would be of interest. As a preliminary step this investigation is concerned with the surface tension of water-ammonia mixtures as compared with the theoretical values for ideal mixtures obtained by Whatmough's rule.² The resemblance of these two liquids as a solvent can be thus quite satisfactorily indicated. Incidentally some indication of the extent to which ammonia is associated in the liquid state may be observed.

Surface tension in liquid ammonia has been investigated by Berthoud³ but the range of his work was not extensive. Rice⁴ recently has made

¹ Contribution No. 155, Department of Chemistry.

² W. H. Whatmough, *Z. physik. Chem.*, **39**, 129 (1901).

³ A. Berthoud, *Helv. Chim. Acta*, **1**, 84 (1918).

⁴ O. K. Rice, *J. Phys. Chem.*, **32**, 584 (1928).

determinations upon solutions up to a concentration of 14 moles per liter. Apparently Rice's method lacked certain refinements, particularly precautions relating to distillation from the capillary surface, thorough mixing and density determinations.

It was necessary to develop a method for determining the density of solutions, for no data upon the density of ammonia-water mixtures at 20° could be found in the literature for concentrations above 50% ammonia.

Experimental Procedure

The capillary height method was used to determine the surface tension. The apparatus, a modification of the Richards and Coombs type, was constructed of a heavy grade pyrex tubing (Fig. 1-A). The cylindrical bowl, 35 mm. 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. 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 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.

Gaseous ammonia was condensed into the tube by carbon dioxide snow. Figure 1 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 tubes were dried, weighed and then filled with sulfuric acid-dichromate cleaning solution and allowed to stand until the next fill.

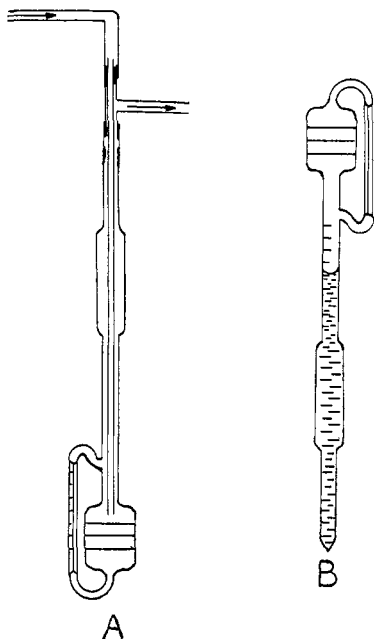


Fig. 1.—A, Showing method of introducing ammonia vapor into apparatus where it is condensed; B, showing method of measuring volume of vapor phase in density determination. The total volume is determined subsequently.

They were then thoroughly rinsed with surface tension water and dried only when to be filled with pure ammonia.

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. In this manner air was excluded while the tube was being sealed. In measurements where density determinations were to be made, 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 solutions above 50% ammonia at 20° were determined by weighing the tube before and after filling and measuring the volume of the pycnometer on the calibrated volume scale, the tube being in the inverted position shown in Fig. 1-B while volume readings were taken. The water sample was weighed in, ammonia was 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. The volume of the liquid was determined by difference after the total volume of the tube had been 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 the 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. I, p. 73. Corrections for air buoyancy were made on all weighings.

Obviously the vapor, especially at high pressures, would contain enough ammonia to affect the calculated value of the density. The tables of Wilson⁵ were used to give the total vapor pressure of ammonia-water mixtures and the composition of the vapor phase corresponding to each solution composition studied. The density of the vapor present was assumed to be directly proportional to the pressure and the mean molecular weight of the vapor.

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

in which D_a , P_a and M_a 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% of water vapor, no objectionable error was introduced by omitting the second proportionality factor from density calculations. The density of saturated ammonia vapor at 20° was taken as 0.007474 from the Landolt-Börnstein Tables. However, in the data for pure liquid ammonia the vapor and liquid densities were taken from the Bureau of Standards Circular No. 142, Tables of Thermodynamic Properties of Ammonia.

Sufficient density determinations were made to determine the curve

⁵ T. A. Wilson, *Univ. Illinois, Eng. Exptl. Sta. Bull.* No. 146 (1925).

plotted in Fig. 2. These were plotted on sufficiently large scale to be read to the fourth significant figure.

Apparatus.—All pieces of apparatus were carefully calibrated. The diameters of the capillaries were carefully determined by measuring the length of a weighed pellet of mercury at successive positions in the capillary. An additional check was made with the purest obtainable thiophene-free benzene.

The formula used for calculating surface tension was

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

in which r is the radius of the capillary, h the capillary height, d the density of the liquid, and D the density of the vapor.

Discussion of Results

The surface tension of liquid ammonia as determined in this work agrees closely with Berthoud's⁵ value at 11.1° if his data are calculated by the corrected capillary height formula as given above. Measurements at 0° were made in a transparent Dewar tube.

In the range of 0–20° the molecular weight of liquid ammonia was calculated by the differential method of Ramsay and Shields.⁶ The value of K was found to be 1.662, indicating an apparent molecular weight of 24.5, or approximately $3/2 \text{ NH}_3$. Such a condition must indicate an equilibrium mixture of two or more molecular components, as possibly $(\text{NH}_3)_2$ (60%) \rightleftharpoons 2NH_3 (40%). The surface tension–temperature data in Table II when plotted appear to lie in a nearly straight line, indicating a temperature coefficient of 0.220 dyne per degree centigrade.

The determined densities of solutions above 50% NH_3 are tabulated in Table I and plotted in Fig. 2 along with data from Mittasch, Kuss and Schlueter,⁷ and with data from the "International Critical Tables."

⁵ Ramsay and Shields, *Z. physik. Chem.*, 12, 431 (1893).

⁷ Von A. Mittasch, E. Kuss, and H. Schlueter, *Z. anorg. allgem. Chem.*, 159, 1 (1926).

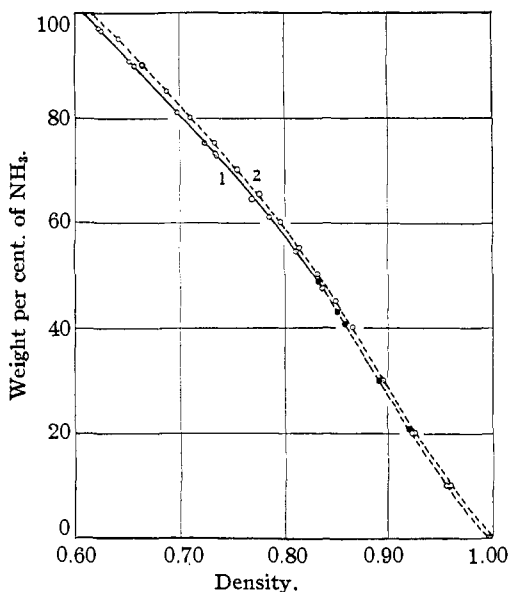


Fig. 2.—1, Densities of water–ammonia mixtures at 20°. Solid line covers range of experimental determinations. Solid circles are determinations by Mittasch, Kuss and Schlueter. Lower points from "International Critical Tables." 2, Densities at 15° for comparison taken from "International Critical Tables."

TABLE I
EXPERIMENTAL DATA FOR SURFACE TENSION OF WATER-AMMONIA MIXTURES (TEMP.,
20 ± 0.01°)

Wt. % NH ₃	Rad. of cap., cm.	Density of soln.	Cap. ht. (corr.), cm.	Surf. tens., dynes/cm.	Moles/liter NH ₃	Ammonia adsorption moles/sq. cm. × 10 ¹¹
100.00	0.61029	22.03	35.836	0.000
97.36	0.03344	.6232	2.2600	22.81	35.628	0.000
97.18	.03477	.6240 ^a	2.1681	22.78	35.608
96.68	.03477	.6262 ^a	2.1895	23.09	35.550
96.66	.03334	.6263 ^a	2.2764	23.02	35.548
91.41	.03344	.6505	2.3426	24.70	34.917
90.94	.03450	.6530	2.2359	24.42	34.870
90.81	.03470	.6531 ^a	2.3261	24.57	34.826
89.81	.03335	.6577 ^a	2.3604	25.11	34.682	0.000
89.72	.03335	.6585	2.3681	25.22	34.693
80.95	.03472	.6984 ^a	2.3876	28.11	33.198	0.000
78.38	.03335	.7094	2.5530	29.34	32.651
75.07	.03464	.7240 ^a	2.5061	30.57	31.915
72.49	.03335	.7356 ^a	2.6700	31.84	31.312
72.56	.03466	.7354 ^a	2.5381	31.44	31.334	+32.013
70.47	.03336	.7443	2.7325	32.99	30.799	+29.271
64.51	.03472	.7705 ^a	2.7539	35.87	29.187	+18.879
63.64	.03340	.7744	2.8938	36.40	28.940	+18.879
61.16	.03468	.7850 ^a	2.8574	37.90	28.192	+18.879
54.40	.03468	.8111 ^a	3.0335	41.63	25.909
53.48	.03340	.8149	3.2114	42.65	25.591	+11.491
47.45	.03346	.8363 ^a	3.3965	46.42	23.302
44.56	.03339	.8458	3.4831	48.08	22.132	- 3.283
35.98	.03347	.8730	3.6559	52.29	18.444	- 3.283
29.70	.03349	.8890	3.8136	55.58	15.504	- 5.746
24.14	.03347	.9094	3.8948	58.02	12.891	- 5.746
14.61	.03349	.9409	4.0304	62.15	8.072	- 7.387
7.72	.03350	.9661	4.1507	65.74	4.378	- 3.283
0.45	.03349	.9960	4.4444	72.55	0.264	+ 9.850

^a Densities determined. Other densities taken from curve.

TABLE II
TEMPERATURE COEFFICIENT OF SURFACE TENSION OF PURE AMMONIA

Temp., °C.	Radius of cap., cm.	Cap. ht., cm.	$d - D$	Surface tension
0.0	0.03609	23.554	0.63511	26.44
0.0	.03625	23.423	.63511	26.42
0.5	.03458	24.501	.63433	26.33
10.0	.03609	22.181	.61985	24.31
10.0	.03625	22.029	.61985	24.25
20.0 ^a60360	22.03

^a Average of twelve determinations ranging from 21.94 to 22.09.

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 lower curve in Fig. 2 represents the values de-

terminated experimentally. The accuracy is indicated from the fact that the density curve joins closely with the points obtained by Mittasch, Kuss and Schlueter⁷ and that the curve follows closely the character of the 15° density curve. The eight density determinations on pure ammonia, averaging 0.61026 (range 0.6100–0.6107) compared with the Bureau of Standards value of 0.61029, is additional evidence to show the accuracy and dependability of the method used in this work.

The surface tension values found in Table I were calculated from experimental data, the densities being taken from the curve. All surface tension determinations were made under conditions such that the percentage composition of the solution could be determined even though the volume were not such as to make a density determination possible.

Rice⁴ 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. Rice ascribed fluctuations in capillary height to the action of ammonia on glass; they could equally as well be ascribed to a state of unequilibrium because of difficulty in obtaining thorough mixing in the system, also to the fact that the apparatus was not enclosed in a thermostat.

The pyrex glass apparatus used in this work 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 observed surface tension values were compared with theoretical values obtained by Whatmough's² modification of the Volkmann rule

$$\gamma = (V_1\gamma_1 + V_2\gamma_2)R$$

in which V_1 and V_2 are the volume fractions of the components, γ_1 and γ_2 are the surface tensions of the pure components, and R is the ratio of the calculated to the observed density. The values are shown graphically in Fig. 3. It is to be observed that the theoretical and observed surface tensions are in good agreement except in the middle region, where a divergence of less than six dynes occurs. It is of interest to note that the vapor pressure of the system goes through a marked depression from the normal in this region, thereby conforming to Worley's rule⁵ of perfectly miscible liquids. Worley shows for a number of mixtures that abnormalities of surface tension tend to move contrariwise to abnormalities in vapor pressure.

⁵ Worley, *J. Chem. Soc.*, **105**, 273 (1914).

It is evident from the surface tension and thermodynamic standpoint that the system does not deviate radically from what is to be expected of a perfect mixture. No doubt the formation of ammonium hydroxide contributes to such deviation, but no attempt is made to take it into account. Consequently it is to be expected that liquid ammonia would behave as a polar liquid similar to water, and that orientation of substances on the surface of liquid ammonia would be quite similar to their orientation on water surfaces. The surface tensions of solutions of ammonium salts of aliphatic acids in liquid ammonia are being investigated at present in this Laboratory with the intention of determining the surface adsorption.

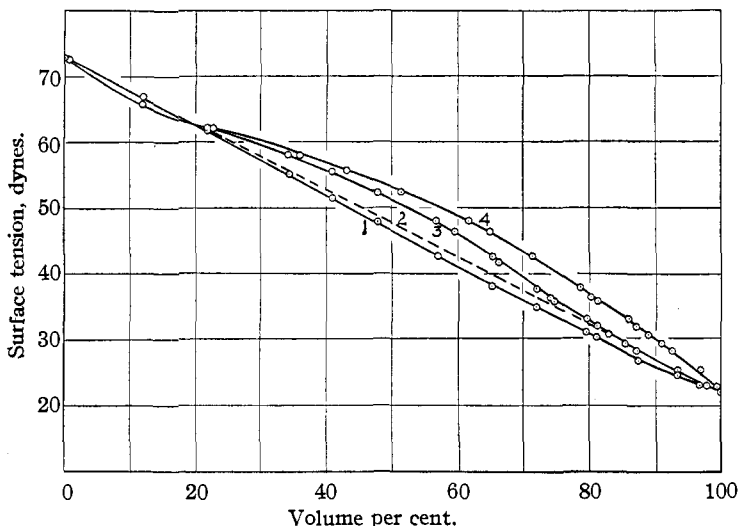


Fig. 3.—Theory of admixtures applied to surface tension of ammonia-water mixtures. 1, Surface tensions calculated by Whatmough's rule; 2, theoretical values for a perfect mixture; 3, observed values for volume per cent., $V_a/V_a + V_w$; 4, observed values for volume per cent., $V_a/V_{sol.}$.

Deviation of the ammonia-water system from the rule of admixtures might be due to adsorption of one or the other component in the surface. Assuming such to be the case, and assuming that deviation of the slope of the surface tension-log activity curve from the normal curve derived from the rule of admixtures would indicate the adsorption when used in the Gibbs equation

$$\mu = -\frac{1}{RT} \left(\frac{d\gamma(\text{obs.})}{d \ln a} - \frac{d\gamma(\text{theor.})}{d \ln a} \right)$$

such values have been assembled in Table I. They consist of from 1 to 5% of the normal surface concentration. It is of interest to note that it changes sign in the region of 50% ammonia, being negatively adsorbed in dilute solutions and positively adsorbed in the upper range of concentration,

The activities of ammonia in the mixtures were calculated by the approximate method of Lewis and Randall,⁹ taking the activity equal to the concentration in pure liquid ammonia.

Summary

1. The surface tension of liquid ammonia at 0, 10 and 20°, and its temperature coefficient were determined.
2. By the differential method of Ramsay and Shields the molecular weight of liquid ammonia is found to be 24.5.
3. Surface tension and density of water-ammonia mixtures from 50-100% NH₃ at 20° are given for the first time.
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. 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.
6. 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.

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THE QUANTITATIVE PRECIPITATION OF SULFIDES IN BUFFERED SOLUTIONS.¹ I. COBALT SULFIDE

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Introduction

The separation of metals by means of sulfide precipitation in acid or basic solution has long been practiced. However, the regulation of the degree of acidity and the conditions under which a thoroughly satisfactory precipitate may be obtained have not been the subject of much careful study. Fales and Ware² carefully investigated the conditions under which zinc sulfide might be precipitated quantitatively, but practically nothing else is available. Such a study on cobalt sulfide seemed desirable because the methods for the determination of this element are neither so numerous nor

⁹ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923.

¹ Part of a thesis submitted by Martin Leatherman in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Maryland.

² Fales and Ware, *THIS JOURNAL*, **41**, 487 (1919).