HEATS OF SOLUTION IN LIQUID AMMONIA

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Introduction

Liquid ammonia is a polar solvent of remarkable properties, some of which are similar to those of water, and others of which are strikingly different. Much of the present-day work with it stems from the investigations of Franklin[1] and his co-workers, chief among whom is Kraus. Heats of solution were studied at Brown University by Kraus and Ridderhof[2], Kraus and Prescott[3], and Kraus and Schmidt[4]. More recently published results have come from Union College by Schmidt, Sottysiak and Kluge[5], and Schmidt, Studer and Sottysiak[6]. Also there are available various Departmental theses.

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The present work consists in measurements of the integral heat of solution of dimethylamine hydrochloride, and its isomer, ethyl ammonium chloride, and preliminary measurements on phenylamine hydrochloride.

Experimental

The apparatus used was the same as that used in previous work, in fact, the apparatus and technique were those described by Zuhr[7], except for the fact that in 1940 a new thermocouple was installed. This was calibrated according to the vapor pressure data supplied by the U. S. Bureau of Standards[8]. The constants used were: heat of vaporization of NH_3, 327.7 cal/gm; specific heat of NH_3 at boiling point, 1.067 cal/deg; amount of ammonia used in calorimeter, 48.27 gms (2.839 mols); radiation constant of the calorimeter, 0.10 cal/deg. min;(therefore, small enough to be neglected); calorimeter constant, 9.16 cal/deg.

A short description of the prodedure will be beneficial at this time.

A weighed amount of salt was sealed in a small glass bulb under reduced pressure, ca. 10 microns. The bulb was then fused to a "crusher" rod and placed in the reaction flask. The entire system was then sealed off and evacuated down to 10 microns. Addition of a new stopcock, previously, made it possible to evacuate portions of the apparatus at a time. First the pipette-side was evacuated, then while the calorimeter was being evacuated, pure ammonia from a storage tank was allowed to distill into the liquid ammonia jacketed pipette. When the pipette was filled to a marked off level (29.89 grams of liquid ammonia), the tank was shut off and this ammonia was allowed to distill over into the reaction flask, which was then jacketed by liquid NH_3 held by a silvered Dewar flask. The jacket was then removed from the pipette. When all the ammonia had boiled over, the pipette was closed off, the ammonia escape adjusted, and the magnetic stirrer started after equilibrium was reached. When the temperature had become constant over a period of one minute as indicated by a thermocouple, one end of which was in the reaction flask and the other in a freezing mixture of ice and water, the bulb was broken. (accomplished by pushing down on "crusher" rod). Temperature readings were taken every 15 seconds or as soon as convenient, until equilibrium was again reached. Volatillized ammonia was collected over the escape valve by distilled water. The solution was diluted up to 500 cc ina volumetric flask and titrated in aliquote portions by standard sulphuric acid. The value (cc x N of acid) multiplied by the heat of vaporization of ammonia gave the number of calories measured by the vaporized ammonia. The change in temperature in millivolts/degree temp. gave the rise in temperature in degrees centigrade. This rise multiplied by 60.66 gave the number of calories absorbed by the calorimeter. These two values gave the total heat for the given sample. By ratios we can find the molar heat of solution very easily.

Due to the high hydroscopic nature of the salts used, the reagent grade commercial salts were recrystallized twice from ethyl alcohol, just before using, then ground fine. The bulbs were pumped down to about 10 microns in a boiling water bath and were sealed off while evacuated. In the case of phenylamine hydrochloride due to splashing effects when in the fine powdered state, it was pressed into small pills, diameter 2 to 3 mm, by using 1/2 inch thick steel plate with holes drilled in it of the correct diameter.

Discussion

The dimethylamine hydrochloride data, Table I , was obtained with difficulty. Most of the results were obviously anomalous. At first the points did not follow any pattern to obtain a curve. At one time, we thought that the salt was ammonalysing, contrary to all expectations. However, our difficulty was finally narrowed down to the presence of water in the salt. There was no trouble in obtaining results which determined the curve in Figure 1 after the salts were recrystallezed from alcohol. This curve was obtained by plotting the molar heat effect against the concentration (mols/NH3/mol sample). The heat of solution approaches 4700 cal/mol salt at infinite dilution.

Lack of time prohibited us from obtaining sufficient data for a curve on phenylamine hydrochloride. However, the splashing effects which slowed down work with this salt appeared to be remedied by pressing the salt into small pills. Further work will be done with this salt using it in the form of pills in the future.

Two runs were done on the isomer, ethylamine hydrochloride. Work is being done on this salt in order to determine the relative heats of solution of this homologous series of salts. The heat effect of this salt was less and it looks as if this series may f follow the results of the alcohols. If sufficient work is done on this salt the rest of the data and the curve will be added as an agenda to this thesis.

Summary

The molar heats of solution of dimethylamine hydrochloride were determined over a wide range of concentrations. Measurements were made on phenlyamine hydrochloride and difficulties were ironed out for improving the chances of obtaining accurate future results.

The high heat effect accompanying the solution of aniline hydrochloride is no doubt due to more or less complete ammonolysis of this salt into aniline and ammonium chloride, according to the equation:

$$C_6H_5NH_3Cl + NH_3 \rightleftharpoons C_6H_5NH_2 + NH_4Cl$$

The heat of solution of solid aniline in liquid NH_3 is 3220 cals/mol. Solid aniline dissolves in a solution of NH_4Cl (equivalent) in liquid NH_3 yielding 3170 cals[9]. The difference between these two heat effects is within the experimental error of the calorimeter. This is an indication of complete ammonolysis of $C_6H_5NH_3Cl$.

Heats of Solution in Liquid Ammonia

Table I - Dimethylamine Hydrochloride

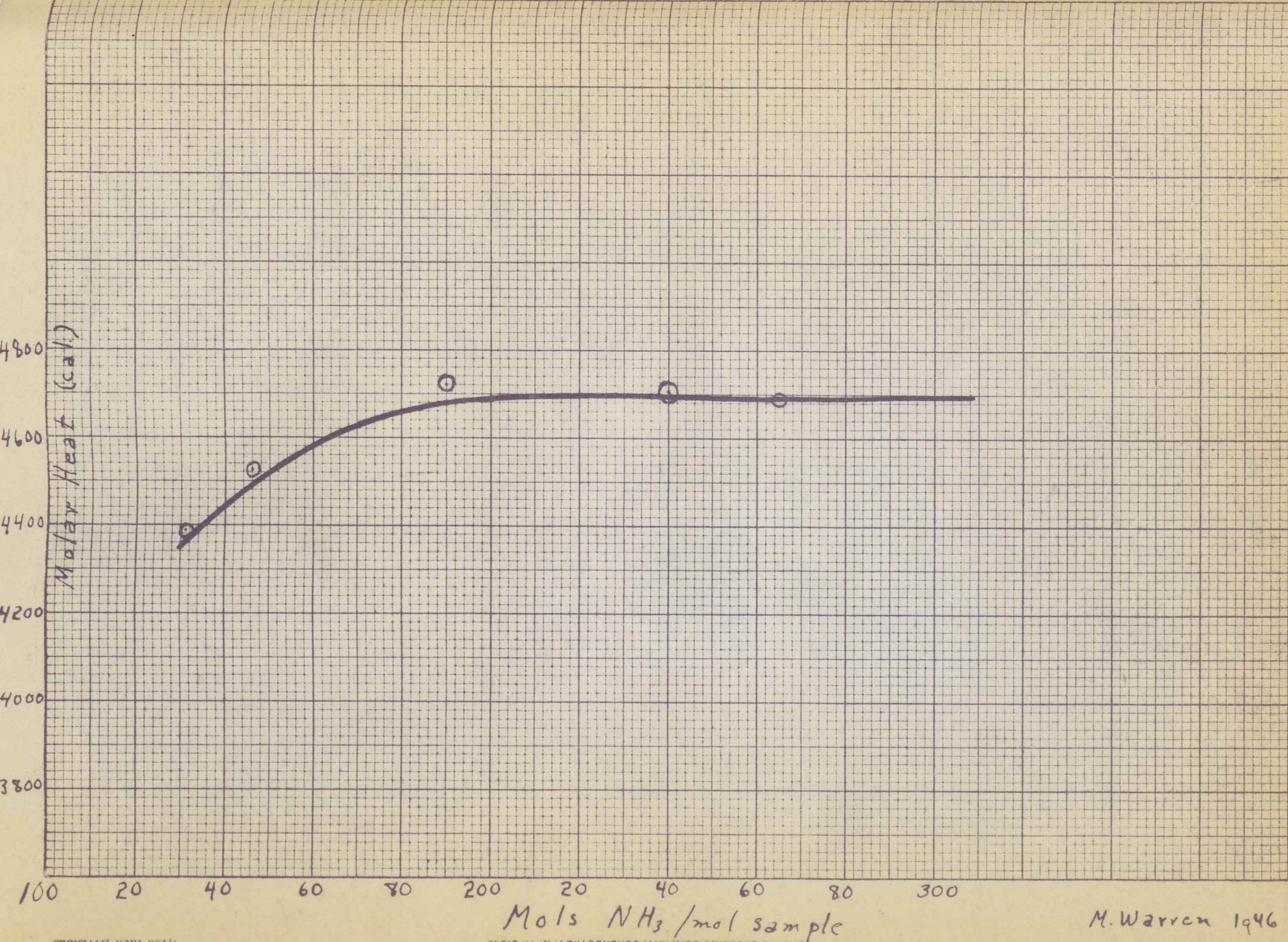
Sample (gms)	t Deg.	Total heat effect (cals.)	Mols NH_3 per mol. salt	Molar heat effect
0.8731	.26	50.1	265	4679
0.9625	.26	55.5	240	4702
1.2256	.43	70.8	190	4720
1.5759	.26	87.5	146	4525
1.7623	.61	94.9	131	4391

Table II - Ethylamine Hydrochloride

1.5316	.31	60.7	152	3232
2.0490	.31	61.2	113	2435

Table III - Phenylamine Hydrochloride

1.0936	.16	104.1	337	12336
1.1780	.36	113.0	312	12431



M. Warren 1946

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