UCRL-16617

University of California

Ernest O. Lawrence Radiation Laboratory

PROTON EXCHANGE IN SOLUTIONS
OF WATER IN LIQUID AMMONIA

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

~~Submitted to the Journal of the American Chemical Society~~ ND

UCRL-16617

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract W-7405-eng-48

PROTON EXCHANGE IN SOLUTIONS OF WATER IN LIQUID AMMONIA

Thomas Birchall and William L. Jolly

January, 1966

Proton Exchange in Solutions of Water in Liquid Ammonia

Thomas Birchall and William L. Jolly

Contribution from the Department of Chemistry
of the University of California
and the Inorganic Materials Research Division
of the Lawrence Radiation Laboratory
Berkeley, California 94720

Proton magnetic resonance spectra have been observed for liquid ammonia solutions 0.76 M in sodium bromide, 0.82 – 3.96 M in water, and saturated in sodium hydroxide. The line widths of the NH_3 signal have been interpreted in terms of the proton exchange processes $NH_3 + NH_4^+ \rightarrow NH_4^+ + NH_3$ and $NH_4^+ + H_2O + NH_3 \rightarrow NH_3 + H_2O + NH_4^+$. The rate constants determined near room temperature are 5×10^{10} M^{-1} sec^{-1} and 2×10^{10} M^{-2} sec^{-1}, respectively.

Introduction

The proton magnetic resonance spectrum of pure liquid ammonia is a triplet because of spin-spin coupling with the nitrogen-14 nucleus ($I = 1$). Ogg[1] found that the addition of a small amount of water to liquid ammonia caused this triplet to collapse to a single line; furthermore, no separate signal attributable to water appeared. These results indicate that rapid proton exchange was occurring, and Ogg proposed that the reaction responsible for the exchange was the ionization of water:

$$H_2O + NH_3 \rightarrow NH_4^+ + OH^-$$

He suggested a bimolecular rate constant 4.6×10^8 l. mole^{-1} sec^{-1} for the reaction. We have recently shown[2] that this reaction is not a rapid process and that it does not contribute appreciably to the proton exchange process. (Indeed, using an argument that we shall present in the Discussion, it may be shown that the bimolecular rate constant for the ionization of water in ammonia is probably about 10^{-7} l. mole^{-1} sec^{-1} or lower.) Because at equilibrium the forward rate equals the reverse rate, it is clear that the reaction of ammonium ions with hydroxide ions does not contribute to the proton exchange process.

In this paper we shall present n.m.r. evidence that at least two different processes are responsible for the exchange of protons between ammonia molecules in liquid ammonia solutions of water. Our choice of experiments was guided by the results of Meiboom, Loewenstein and Alexander,[3] who found that, in aqueous solutions, the reactions principally

responsible for the exchange of protons between ammonium ions were the following:

$$NH_4^+ + NH_3 \xrightarrow{k_1} NH_3 + NH_4^+ \qquad (1)$$

$$NH_4^+ + H_2O + NH_3 \xrightarrow{k_2} NH_3 + H_2O + NH_4^+ \qquad (2)$$

We therefore designed our experiments to determine the effect of varying the concentrations of ammonium ion and water on the rate of the proton exchange.

Experimental and Results

Buffered solutions were prepared by distilling previously purified ammonia (dried over sodium) onto known quantities of aqueous 1 M sodium hydroxide solution contained in n.m.r. tubes. Each n.m.r. tube also contained a quantity of sodium bromide such that the concentration of sodium bromide in the final solution was 0.76 M. The tubes were sealed off under vacuum, and brought to room temperature. In all cases, a precipitate of sodium hydroxide was present in the tube after the tube had reached equilibrium. The n.m.r. spectra were recorded on a Varian A-60 spectrometer at 31°.

The rates of exchange were calculated from the broadening of the individual components of the ammonia triplet, assuming conditions for slow exchange and using the relation

$$1/T_2' = 1/T_2 + 1/\tau$$

where T_2' and T_2 have their usual meaning[4] and τ is the average lifetime of a proton bonded to nitrogen of a given spin state. The experimental data are presented in Table 1. A value for $1/T_2 = 32.2\ sec^{-1}$ was determined by reducing the water concentration until a constant line width was obtained.

The reaction

$$H_2O + Na^+ + NH_3 = NH_4^+ + NaOH_{(s)}$$

reached equilibrium in all our n.m.r. tubes. Using available free energy data,[5,6,7] we evaluate the equilibrium constant for this reaction at 25°:

$$K = \frac{a_{NH_4^+}}{a_{H_2O} \cdot a_{Na^+}} = 5.8 \times 10^{-10}$$

Although our n.m.r. spectra were determined at 31°, we assume that this constant can be used for our data. We also assume that the activity coefficients for NH_4^+ and Na^+ are equal and, for simplicity, we take the activity of water equal to its molarity. Thus we can write $(NH_4^+) = K(Na^+)(H_2O)$, and, because the sodium ion concentration was always 0.76 M in our experiments,[8] we obtain $(NH_4^+) = 4.4 \times 10^{-10}(H_2O)$.

There is reason to suspect that $NaOH \cdot H_2O$, rather than NaOH, might have been the stable solid phase in the n.m.r. tubes. Thus, if one assumes that the partial pressure of water vapor over our solutions containing sodium bromide were the same as those over corresponding $H_2O - NH_3$ solutions not containing sodium bromide,[10] one calculates that the partial pressures of water vapor ranged from 0.44 to 2.2 mm in our

Table 1

Nuclear Magnetic Resonance Data

Water Concentration, M	$1/\tau$, sec^{-1}
0.82	5.47
1.14	9.40
1.54	13.3
1.94	23.1
1.94	19.9
2.21	24.2
2.58	30.3
2.69	31.4
2.96	36.4
3.25	44.7
3.46	50.8
3.80	64.4
3.96	70.3

solutions. This pressure range exceeds the equilibrium pressure (0.14 mm. at 25°) over the system NaOH + NaOH · H_2O,[11] and so one might expect the following equilibrium to be attained.

$$Na^+ + 2H_2O + NH_3 = NH_4^+ + NaOH \cdot H_2O_{(s)}$$

However, we believe that NaOH was the solid phase because when the data were treated as described in the following section, under the assumption of NaOH · H_2O as the solid phase, the plot analogous to that in Figure 1 had a much worse scatter of points than that shown in Figure 1. We believe that the dissolved sodium bromide preferentially ties up water molecules and thus reduces the activity of water below that required by the NaOH · H_2O phase. Such a preferential coordination of water molecules is reasonable in view of the fact that hydration energies are slightly greater than ammoniation energies for ionic compounds.[6]

The spectra of the dilute water solutions showed a broad line due to the water protons. In the more concentrated solutions, this line was shifted to higher fields and became even broader. Thus it is clear that the protons of the water molecules were undergoing some sort of exchange reaction.

Discussion

If reactions 1 and 2 are the only processes which contribute to the collapse of the ammonia triplet, then the rate of proton exchange should be given by the following expression,

$$\text{Rate} = k_1(NH_4^+)(NH_3) + k_2(NH_4^+)(H_2O)(NH_3).$$

The mean lifetime of an ammonia proton between exchanges is $\frac{\text{Rate}}{3(NH_3)}$. Hence we may write

$$1/\tau = \frac{2}{3} \cdot \frac{1}{3} k_1(NH_4^+) + \frac{1}{3} k_2(NH_4^+)(H_2O) \qquad (3)$$

The additional factor of 2/3 is introduced in the first term to account for the fact that, in reaction 1, only proton transfers between nitrogen atoms with different spin states are effective in broadening the signal. By rearranging equation 3, and substituting $4.4 \times 10^{-10}(H_2O)$ for (NH_4^+), we obtain

$$1 = 0.98 \times 10^{-10} k_1(H_2O)\tau + 1.47 \times 10^{-10} k_2(H_2O)^2 \tau$$

It can be seen that a straight line with intercepts of $1/(0.98 \times 10^{-10}k_1)$ and $1/(1.47 \times 10^{-10}k_2)$ should be obtained by plotting $(H_2O)\tau$ against $(H_2O)^2\tau$. Such a plot, using our experimental data, is given in Figure 1. From the intercepts of the line drawn through the points, we calculate

$$k_1 = 5 \times 10^{10}\ \underline{M}^{-1}\ sec^{-1} \quad \text{and} \quad k_2 = 2 \times 10^{10}\ \underline{M}^{-2}\ sec^{-1}.$$

The values for these rate constants in aqueous solution[3] are

$$k_1 = 1.06 \times 10^9\ \underline{M}^{-1}\ sec^{-1} \text{ and } k_2 = 1.6 \times 10^6\ \underline{M}^{-2}\ sec^{-1}.$$

The increase in rate constants on going from aqueous solution to liquid ammonia solution is probably due to the corresponding decrease in viscosity of the solvent. It will be noted that the ratio k_2/k_1 is much greater in liquid ammonia than in water.

It is interesting to consider data which may be used to estimate the rate constant for the reaction

$$H_2O + NH_3 \rightarrow NH_4^+ + OH^-$$

The equilibrium constant at 25° for this reaction[6] is 10^{-18}. The reverse reaction, even if it were diffusion-controlled, could not have a rate constant greater than about 10^{11} $\underline{M}^{-1}$ sec^{-1}, and probably the rate constant is somewhat lower. Thus we conclude that the forward rate constant for the ionization of water in liquid ammonia is about 10^{-7} $\underline{M}^{-1}$ sec^{-1} or lower. Now the magnitude of this estimated rate constant is in poor agreement with the value ~ 0.02 sec^{-1} (or $\sim 10^{-3}$ $\underline{M}^{-1}$ sec^{-1}) which has been reported for the analogous ionization of ethanol in liquid ammonia, based on the kinetics of the ethanol-sodium reaction in ammonia.[12] It seems incredible that the rate constant for the ionization of ethanol would be 10^4 times faster than that for water. We believe that the rate constant determined for ethanol does not refer to the reaction

$$EtOH + NH_3 \rightarrow NH_4^+ + EtO^-$$

but rather to a reaction in which the ethoxide ion is complexed by ethanol, e.g.

$$(1 + x)EtOH + NH_3 \rightarrow NH_4^+ + EtO \cdot xEtOH^-$$

That ethanol forms a strong complex with ethoxide is suggested by the fact that the solubility in ammonia of alkali metal ethoxides is increased markedly by the addition of ethanol.[13] Similar effects have been observed for sodium hydroxide and water in ammonia.[9,14]

Acknowledgement

This work was performed under the auspices of the United States Atomic Energy Commission.

References

1. R. A. Ogg, Jr., Disc. Faraday Soc., 17, 215 (1954).
2. T. Birchall and W. L. Jolly, J. Am. Chem. Soc., 87, 3007 (1965).
3. S. Meiboom, A. Loewenstein and S. Alexander, J. Chem. Phys., 29, 969 (1958).
4. J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, p. 221.
5. W. M. Latimer and W. L. Jolly, J. Am. Chem. Soc., 75, 4147 (1953).
6. W. L. Jolly, J. Phys. Chem., 58, 250 (1954).
7. W. M. Latimer, "Oxidation Potentials," 2nd ed., Prentice-Hall, Englewood Cliffs, N.J., 1952.
8. The data of Ayres,[9] although not accurate enough to make a firm decision in our case, suggest that the solubility of sodium hydroxide in our solutions is negligibly small. Perhaps our best evidence for this is the fact that an appreciable precipitate of sodium hydroxide formed in all our tubes, even though relatively small amounts of sodium hydroxide were added. And even in the run in which we added the most sodium hydroxide, if all of it had dissolved, its concentration would have amounted to only 0.072 M.
9. F. D. Ayres, J. Phys. Chem., 49, 366 (1945).
10. J. H. Perry, editor, "Chemical Engineer's Handbook," McGraw-Hill, New York, 1950, p. 171.

11. L. E. Murch and W. F. Giauque, J. Phys. Chem., 66, 2052 (1962).

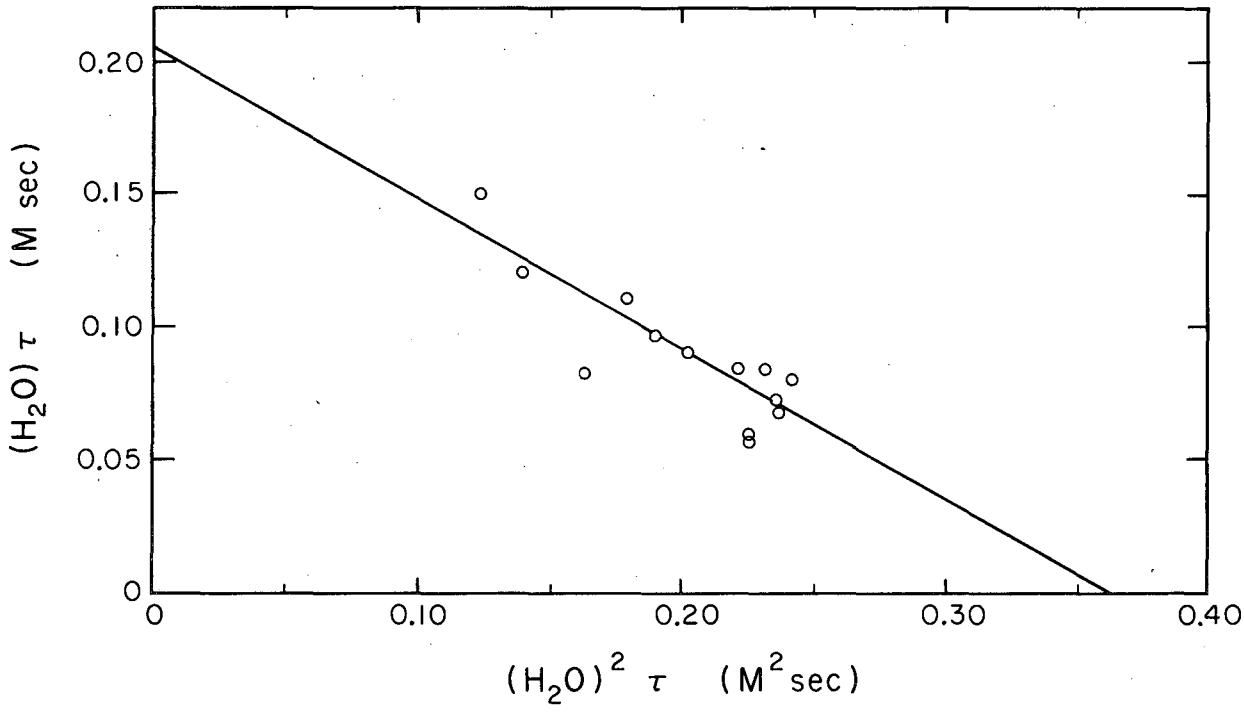
12. E. J. Kelly, H. V. Secor, C. W. Keenan, and J. F. Eastman, J. Am. Chem. Soc., 84, 3611 (1962); W. L. Jolly, Chapter 3 in "Solvated Electron," No. 50 in Advances in Chemistry Series, American Chemical Society, Washington, D. C., 1965, p. 27.

13. G. F. White, A. B. Morrison and E. G. E. Anderson, J. Am. Chem. Soc., 46, 961 (1924).

14. M. Skossarewsky and N. Tchitchinadzé, J. chim. phys., 14, 153 (1916).

Figure Captions

1. Plot of $(H_2O)\tau$ <u>vs.</u> $(H_2O)^2\tau$ for the determination of proton exchange rate constants.



MUB-9006

Fig. 1

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.