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The Isotopic Discrimination of Some Solutes in Liquid Ammonia

By
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Abstract

The nitrogen isotopic discrimination of some salts and metals, studied in liquid ammonia solution at -50°C, decreases in magnitude in the order Pb^{++}, Ca^{++}, Li^{+}, Ag^{+}, Na^{+}, Li, K^{+}, Na, K. The isotopic discrimination appears to provide qualitative information about the strength of the cation-solvent interaction in liquid ammonia.

Introduction

Dissolving an anhydrous salt in water brings about a small change in the ratio of the activity of $H_2{}^{18}O$ to that of $H_2{}^{16}O$. This isotopic discrimination effect has been studied for a number of salts by H. M. Feder and H. Taube.[2-4]

Study of the isotopic discrimination of solutes in a non-aqueous solvent offers an opportunity to gain perspective on the isotopic

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(2) H. M. Feder, Ph.D. Thesis, University of Chicago, 1954.

(3) H. M. Feder and H. Taube, J. Chem. Phys., 20, 1335 (1952).

(4) H. Taube, J. Phys. Chem., 58, 523 (1954).

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fractionation method as well as on the results in aqueous solution. An important question about the method is whether the principal contribution to the observed fractionation comes from nearest-neighbor interactions of the ions with the solvent molecules, or whether on the other hand there is a major contribution from a long-range disruption of solvent structure.

The purpose of the present study was to extend isotopic fractionation studies to liquid ammonia (involving $^{15}NH_3$ and $^{14}NH_3$) to determine whether the fractionation results still show a reasonable correlation with other information about the strength of the cation-solvent interaction. Several points are of interest. One is that the vapor-liquid fractionation for bulk liquid ammonia even at -50°C is substantially smaller than for bulk water at room temperature.[5,6] However, the effects brought about by cation-solvent interactions are probably greater at lower temperatures as Feder has pointed out. Finally, it seems interesting to compare the behavior of metal-ammonia solutions with that of ordinary salts in liquid ammonia.

Experimental Section

Reagents. Anhydrous ammonia was condensed into a glass tube on a vacuum line, dried by condensing onto potassium metal, and distilled into a small stainless steel cylinder on the line for storage. The cylinder could be removed from the line and weighed. All the ammonia in storage was used in running a reference and in running the corresponding solution. Lithium metal was supplied by Lithium Corporation of America,

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(5) H. G. Thode, J. Am. Chem. Soc., 62, 581 (1940).

(6) M. H. Wahl and H. C. Urey, J. Chem. Phys., 3, 411 (1935).

potassium metal by Fisher, and silver iodide by Mallinckrodt, and Matheson, Coleman and Bell. It was also prepared from Goldsmith silver nitrate and Baker and Adamson potassium iodide. Mallinckrodt $Ca(NO_3)_2 \cdot 4H_2O$ was dehydrated on a vacuum line for several days, and finally heated in a tube furnace. $T \gtrsim 200°C$ in center of furnace. Chemicals not otherwise specified were reagent grade materials.

Apparatus. The parameter to be measured experimentally is the enrichment factor $\alpha = 10^3(R_o-R)/R_o$, where R_o denotes the number ratio of $^{15}NH_3$ to $^{14}NH_3$ in the NH_3 vapor in equilibrium with a sample of pure NH_3, and R is the same ratio for vapor in equilibrium with a liquid ammonia solution made from this same ammonia. The equilibrations were carried out at $-50 \pm 0.6°C$. Each vapor sample was oxidized completely to N_2 by circulation over CuO at about 625°C. Though the $^{14}N^{15}N/^{14}N^{14}N$ isotope ratio is twice the $^{15}NH_3/^{14}NH_3$ isotope ratio in the NH_3 sample from which the N_2 was formed, the respective $^{14}N^{15}N/^{14}N^{14}N$ isotope ratios can be taken as R_o and R, since the proportionality factors cancel in α. The isotope ratios of the nitrogen samples were measured mass spectrometrically by Professor John P. Hunt (Department of Chemistry, Washington State University, Pullman, Washington).

In carrying out the equilibration and sampling, the glass vessel containing the solution and vapor was immersed in a thermostatting bath. About 20-50 g. of ammonia was used in the vessel of volume 350-400 cc. Solution and vapor were stirred (sealed magnetic stirrer) for an hour or more. A sample of ammonia vapor was then slowly withdrawn into the vacuum line through two sintered glass frits in series, usually over a period of 4-25 minutes. The volume of ammonia vapor removed was generally in the range of one to five times the volume of vapor in the thermostatted vessel. After oxidation of the ammonia vapor sample over cupric oxide at about 625°C, the resulting N_2 sample was freed of water by prolonged circulation through a trap cooled with liquid nitrogen. (In a few instances, the nitrogen samples were further circulated through magnesium perchlorate.) Oxidation of the ammonia sample to N_2 appeared to be quantitative to within one or two per cent. Part of the nitrogen sample was then admitted to an evacuated gas sample bulb fitted with a high vacuum stopcock and ⅀ 14/35 male joint.

Isotope ratios were read in respective pairs: each solution sample with its reference sample from vapor in equilibrium with pure liquid ammonia. Precision (machine reproducibility) in each isotope ratio is estimated to be 0.03 to 0.04%. Since α involves the difference between the two isotope ratios, the precision in it is presumably somewhat lower, perhaps ±0.5 parts per thousand. In three instances, the presence of air or other impurities was noted by Professor Hunt in the course of the isotopic analyses; these three results have accordingly been discarded.

The sampling of vapor from a liquid ammonia solution was always carried out *after* obtaining the corresponding reference sample from vapor in equilibrium with pure liquid ammonia, so that the same ammonia was used in both cases. The ammonia was transferred into the small stainless steel cylinder by distillation, for storage between the two equilibrations.

Results. Table I reports $\alpha = 10^3(R_o - R)/R_o$ and $(\alpha - am)$, for solutions of specified molal concentration. The parameter a is defined by the relation $\alpha = am$, and was calculated for each solute by a least squares analysis of the data. m denotes the molal concentration. Table II reports a and the average deviation $\langle|\alpha - am|\rangle$ for each solute.

TABLE I

α AND (α-am) FOR THE LIQUID AMMONIA SOLUTIONS STUDIED

Solute	Molal Concentration	α	(α-am)[a]
$LiNO_3$	1.9_9	2.2	0.7
	3.0_8	3.6	1.2
	4.9_4	3.4	-0.4
	4.9_9	3.4	-0.5
	5.0_1	3.7	-0.2
$NaNO_3$	1.9_6	1.1	0.3
	3.0_0	1.5	0.2
	3.0_2	1.8	0.5
	5.0_2	2.0	-0.1
	5.0_4	1.7	-0.4
NaI	2.9_8	1.1	0.0
	3.0_2	1.1	0.0
NaSCN	4.5_8	1.5	0.2
	4.7_8	2.0	0.6
	8.7_9	2.2	-0.4
	8.8_7	2.6	0.0
KI	4.9_9	1.1	0.4
	4.9_9	1.0	0.3
	5.0_2	0.0	-0.7
AgI	5.7_4	2.5	0.0
	5.7_6	2.6	0.0
$Ca(NO_3)_2$	3.9_9	4.8	0.2
	4.0_3	4.5	-0.2
$Pb(NO_3)_2$	0.90	1.8	0.1
	0.90_4	1.7	-0.1

TABLE I--Continued

Solute	Molal Concentration	α	$(\alpha - am)$[a]
Li	4.5_9	1.0	-0.2
	4.8_6	0.0	-1.3
	12.0_4	2.9	-0.3
	12.0_4	3.3	0.1
	12.2_8	4.8	1.5
	12.6_9	3.0	-0.4
	13.9_0	3.3	-0.4
Na	5.1_7	-0.3	-0.4
	5.3_9	-0.3	-0.4
	10.9[b]	0.7	0.5
	10.9[b]	0.0	-0.2
K	4.6_3	-1.0	-0.5
	5.6_8	-1.0	-0.4
	10.2_2	-0.7	0.4
	10.3_5	-1.1	0.0

[a] Values of a shown in Table II. [b] Saturated solution.

TABLE II

a AND $\langle|\alpha - am|\rangle$ FOR SOLUTES IN LIQUID AMMONIA

Solute	a	$\langle|\alpha - am|\rangle$
$LiNO_3$	0.77	0.6
$NaNO_3$	0.42	0.3
NaI	0.37	0.0
NaSCN	0.29	0.3
KI	0.14	0.5
AgI	0.44	0.0
$Ca(NO_3)_2$	1.16	0.2
$Pb(NO_3)_2$	1.94	0.1
Li	0.26	0.6
Na	0.02	0.3
K	-0.11	0.3

Discussion

Feder[7] has shown that for the general case in aqueous solution,

$$\alpha = 10^3 \sum_s \frac{n_s m_s (K_s - 1)}{55.51},$$

where the sum is over all species s in solution, of molality m_s and containing n_s equivalent water molecules. K_s refers to the equilibrium

$$H_2{}^{18}O(l) + H_2{}^{16}O(s) \overset{K_s}{\rightleftharpoons} H_2{}^{16}O(l) + H_2{}^{18}O(s),$$

with l referring to bulk solvent and s to species s. The obvious extension to liquid ammonia solutions gives

$$\alpha = 10^3 \sum_s \frac{n_s m_s (K_s - 1)}{58.72} = \sum_s n_s m_s (K_s - 1)M,$$

where M is the molecular weight of the solvent. The equilibrium in this case is

$${}^{15}NH_3(l) + {}^{14}NH_3(s) \overset{K_s}{\rightleftharpoons} {}^{14}NH_3(l) + {}^{15}NH_3(s)$$

If the fractionation originates entirely in the first solvation shell of the cation, this reduces to

$$\alpha = n_c m_c (K_c - 1)M$$

In this case, α should be linear in the molality of the salt. The linearity of α vs. m_c in most of Feder's data, and the reasonable trends of $n(K_c - 1)$ in his work are at least encouraging, even though not conclusive. Taube[4] has also pointed out a reasonable correlation between

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(7) Reference 2, page 9.

the effect of a cation in promoting acidity and in producing isotopic discrimination.

In discussing the data on isotopic fractionation in solutions of electrolytes and metals in liquid ammonia, trends in a, from the equation $\alpha = am$, will be considered. If the data are analyzed from the point of view that the isotopic fractionation originates in the first solvation shell of a single predominant cationic species, then

$$a = \frac{10^3}{58.72} n_s(K_s-1).$$

In such a case, one can obtain K', the equilibrium constant for the exchange reaction

$$^{15}NH_3(g) + {}^{14}NH_3(s) = {}^{14}NH_3(g) + {}^{15}NH_3(s)$$

(where $NH_3(s)$ refers to a molecule of NH_3 coordinated in the cationic species), from a and the known vapor-liquid isotopic equilibrium constant, if n_s (the number of NH_3 molecules coordinated in the cationic species) is known. In general, n_s is not known with confidence. However, in Table III are listed the values of $10^3 n_s(K_s-1)$ and $10^3(K'-1)$ obtained for what we believe are reasonable values of n_s.

For these values of n_s, $(K'-1)$ appears to decrease in the order

$$Pb^{++} > Ca^{++} \gtrsim Li^{+} \gtrsim Ag^{+} \sim Na^{+} \gtrsim Li > K^{+} > Na > K.$$

$n_s(K_s-1)$ also decreases in approximately the same order.

If $(K'-1)$, or perhaps $n_s(K_s-1)$, is regarded as a parameter related to the strength of the cation-solvent interaction, this order of decreasing $(K'-1)$ appears qualitatively reasonable. For the four d° ions in the series, $(K'-1)$ is observed to decrease with decreasing

TABLE III

$10^3 n_s(K_s-1)$ AND $10^3(K'-1)$ FOR SOLUTES IN LIQUID AMMONIA

	$10^3 n_s(K_s-1)$	$10^3(K'-1)$[a]		
Solute		$n_s=2$	$n_s=4$	$n_s=6$
$LiNO_3$	$45._2$		$14._7$	
$NaNO_3$	$24._7$		$9._6$	$7._5$
NaI	$21._7$		$8._8$	$7._0$
NaSCN	$17._0$		$7._6$	$6._2$
KI	$8._2$		$5._4$	$4._8$
AgI	$25._8$	$16._3$	$9._8$	$7._7$
$Ca(NO_3)_2$	$68._1$		$20._4$	$14._8$
$Pb(NO_3)_2$	$113._9$		$31._9$	22.4
Li	$15._3$		$7._2$	
Na	$1._2$		$3._7$	$3._6$
K	$-6._5$		$1._8$	$2._3$

[a] K' refers to the equilibrium

$$^{15}NH_3(g) + {}^{14}NH_3(s) = {}^{14}NH_3(g) + {}^{15}NH_3(s)$$

where $NH_3(s)$ refers to NH_3 coordinated to the cation. K_s refers to the equilibrium

$$^{15}NH_3(l) + {}^{14}NH_3(s) = {}^{14}NH_3(l) + {}^{15}NH_3(s).$$

If K refers to the vapor liquid equilibrium

$$^{15}NH_3(g) + {}^{14}NH_3(l) = {}^{14}NH_3(g) + {}^{15}NH_3(l),$$

then $K' = K_sK$. $K \approx 1.003_4$ at -50°C.[5]

charge and increasing cationic radius. d^{10} ions may be considered to form bonds of greater covalent character than comparable d° ions.

The three sodium salts show much the same value of a. In aqueous solution too,[2] changing the identity of the anions affects the values of α very little. However, for each alkali element studied the solution of the metal shows a value of a much lower than that of the corresponding salt (the order Li > Na > K is, however, preserved for the metals). The fractionation measurements for the metals were made in the metallic range of metal-ammonia solutions. The effective charge on the cation is expected to be higher in salt solutions than in the metallic range of metal-ammonia solutions, where some shielding of the cation by the conduction band electrons can probably take place, reducing the effective charge on the metal species somewhat. It is of course not surprising that the electrons in concentrated metal solution do not act simply like anions.

In aqueous solution, Ishimori[8] has measured the equilibrium constant for the exchange reaction

$$M(^{14}NH_3)_n + {}^{15}NH_3(aq) \overset{K_1}{\rightleftharpoons} M(^{14}NH_3)_{n-1}(^{15}NH_3) + {}^{14}NH_3(aq)$$

at 30°C for M = Cu^{++}, Zn^{++}, Cd^{++}, Ag^{+}, and Ni^{++} by an ion-exchange technique. Of these five ions only Ag^{+} has been studied in liquid ammonia. If it is assumed that in aqueous solution K' may be obtained from K_1/n via the equilibrium

$${}^{15}NH_3(g) + {}^{14}NH_3(aq) = {}^{14}NH_3(g) + {}^{15}NH_3(aq),$$

with equilibrium constant 1.005 at 25°C[9] and if in addition $n_s = 2$ for

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(8) T. Ishimori, *Bull. Chem. Soc. Japan*, **33**, 520 (1960).

(9) I. Kirshenbaum, J. S. Smith, T. Crowell, J. Graff, and R. McKee, *J. Chem. Phys*., **15**, 440 (1947).

Ag^+ in liquid ammonia solution at -50°C, then (K'-1) = 0.014 in aqueous solution at 25-30°C, and (K'-1) = 0.016 in liquid ammonia at -50°C. Although (K'-1) might have been expected to be somewhat larger than this at the lower temperature, in view of the rather substantial changes of conditions of solvent and temperature probably only order of magnitude agreement can be expected.

J. P. Hunt and co-workers[10] have studied the isotopic discrimination of Cr^{3+} by a direct exchange determination. For the exchange reaction

$$Cr(^{14}NH_3)_6^{3+} + {}^{15}NH_3 \;=\; Cr(^{14}NH_3)_5(^{15}NH_3)^{3+} + {}^{14}NH_3$$

they find $K_{eq} = 6.100$ at 20°C. This gives $10^3 n_s(K_s-1) = 100$ at 20°C for Cr^{3+}, with $n_s = 6$. This value of $10^3 n_s(K_s-1)$ at 20°C is nearly as large as the value 114 which we have found for Pb^{++} at -50°C; one would of course expect that Cr^{3+} would have a larger value at the lower temperature, but even making allowance for this, the effect of Pb^{2+} relative to Cr^{3+} is, in view of the lower charge and larger radius of Pb^{2+}, surprisingly large. The explanation may be that Pb^{2+} has an unsymmetrical coordination sphere and that it interacts very strongly with a small number of molecules at short distances. Just as acidity is increased by a reduction in coordination number, it is reasonable that the isotopic fractionation effect would be increased, the benefit to the intensity factor more than offsetting the loss because of reduction in the number of molecules interacting. A similar explanation may also apply to Ca^{2+} compared to Pb^{2+}, where the larger ion has a larger effect.

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(10) T. W. Swaddle, L. F. Coleman, and J. P. Hunt, Inorg. Chem., **2**, 950 (1963).

If the magnitude of the isotopic discrimination effect, as represented by $a = \alpha/m$, is regarded as an indication of the strength of the cation-solvent interaction (this could only be expected to hold at constant n_s), then the concentration dependence of a should, in principle, provide some clue as to the range of the interaction. If the fractionation is due to interactions primarily within the nearest-neighbor shell of solvent molecules around the cation, then α vs. m should remain linear until an appreciable number of solvent molecules are affected by more than one cation, i.e. until sharing of solvent molecules between two cations begins to take place. Ordinarily, this is not expected to occur much before the mole ratio of solvent to salt approaches the coordination number of the cation. On the other hand, if the isotopic discrimination effect receives substantial contributions from long-range alteration of solvent structure, solvent molecules will begin to be affected by more than one cation (or perhaps anion) at a lower concentration, and deviations from linearity should ensue.[2]

The pertinent data on linearity or non-linearity of α vs. m in liquid ammonia solutions are shown in Table I. The imprecision in α due to instrumental precision in the isotope ratios is thought to be about $\pm$ 0.5.

Variation of α with molal concentration is not, strictly speaking, distinguishable from a linear dependence of α on m, since the average deviations from linearity, $\langle|\alpha - am|\rangle$, are of about the same magnitude as the imprecision expected from the mass spectrometric analyses. There are, however, some indications that α/m may decrease slightly with concentration for salts and either remain constant or increase slightly with concentration for metal-ammonia solutions. If real, these trends may suggest some distortion of solvent structure beyond the nearest-neighbor shell of ammonia molecules in salt solutions. A greater increase of α/m with concentration in the case of the metals might be explained either by less distortion of the solvent structure by the metal, due to a lower effective charge on M^+ in $M\text{-}NH_3$ solutions than in MX-ammonia solutions, or by an increasingly strong interaction between the metal and the surrounding NH_3 molecules with increasing concentration in the metallic region, in line with the discussion by LePoutre and Patterson.[11]

Improvement in the instrumental precision by an order of magnitude would be needed in order to settle the question of linearity with any degree of confidence. If the observed isotopic discrimination is contributed to appreciably by alterations of solvent structure beyond the first coordination sphere of the cation, however, it appears that the variability introduced by such contributions is not so large as to bring about gross changes from a reasonable order of increase of α/m among cations.

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(11) G. LePoutre and A. Patterson, Jr., Bull. Soc. Chim. France, 1961, 989.