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THE USE OF INDICATORS IN ACID-BASE TITRATIONS IN LIQUID AMMONIA

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Abstract - The pK values in liquid ammonia for acid-base indicators have been bracketted using buffer solutions prepared from acids with known pK values in liquid ammonia. The application of these indicators to some practical acid-base titrations has been demonstrated.

INTRODUCTION

Because ammonia is much more basic than water, many weak acids that have no detectable acidity in aqueous solution exhibit acidic behavior in liquid ammonia and can be titrated with strong bases such as potassium amide. However, in spite of its many potential applications, acid-base titrimetry in liquid ammonia has been neglected - mainly because of the lack of a simple method of end-point detection. End points of acid-base titrations in liquid ammonia have been detected using the glass electrode[1-3], the hydrogen electrode[4,5], other potentiometric methods[6,7], conductivity measurements[8], and acid-base indicators[9-12]. We believe that, of these methods, the use of acid-base indicators is the simplest. However, the intelligent use of indicators requires a knowledge of their pK values (i.e., the pH values corresponding to their color changes), and pK values are known for only a few indicators in liquid ammonia[13,14]. Thus our main objective in this study was to evaluate approximate pK values for a group of indicators spanning, as far as possible, the pH scale available in ammonia.

Other problems to be solved were those of devising simple methods for obtaining pure liquid ammonia and for gradually mixing the acidic and basic reagents. Many published methods for carrying out titrations in liquid ammonia require special equipment such as high-pressure apparatus[12], a vacuum line, or a buret for use with cold liquid ammonia solutions[8,15]. In the present study, we purposely avoided the use of anything more complicated than an unsilvered dewar flask fitted with a Dry Ice-cooled condenser. With this simple equipment we have carried

out a variety of practical acid-base titrations that illustrate the usefulness of a set of indicators of known pK values. In a future publication we shall describe the application of indicators to coulometric acid-base titrations in liquid ammonia.

EXPERIMENTAL

The reactions were performed in a straight-walled unsilvered dewar flask using ammonia at its normal boiling point. Stirring was achieved with a glass-enclosed magnetic stirring bar. The top of the reaction vessel was sealed with a wax-coated stopper having several holes for the introduction of ammonia, the introduction of reactants, and the escape of ammonia vapors. Occasionally we found cylinders containing ammonia of sufficient purity that the liquid could be drawn directly from the cylinder into the reaction vessel and then used without purification. More commonly it was necessary to draw gaseous ammonia from the cylinder and to condense it in the reaction vessel. In such cases the stopper of the vessel was fitted with a large cold-finger condenser. The ammonia gas was led into the reaction vessel from which it passed up into the condenser and out through a KOH drying tube. After flushing the air from the apparatus, Dry Ice and alcohol were placed in the condenser, thus causing the entering ammonia to condense and to collect in the dewar vessel. A more elegant all-glass version of the latter apparatus, which we recommend for accurate work, is shown in Figure 1. When about 180 ml of liquid ammonia collected in the reaction vessel, the Dry Ice cooling was stopped and the flow of ammonia from the cylinder was reduced. The evaporation of ammonia and the flow of ammonia from the cylinder caused an adequate flow of gas

from the vessel to prevent ingress of air. Liquid ammonia obtained in this way was sufficiently pure except on certain occasions when the last fraction of ammonia in a cylinder was withdrawn. The liquid ammonia was judged pure when addition of a tiny piece of freshly-cut sodium (about 1 mg) caused the formation of a blue solution, stable for at least 30 seconds.

Solutions of potassium amide or suspensions of sodium amide were prepared in the reaction vessel by the following procedure. In a nitrogen-filled dry bag, a piece of the appropriate alkali metal (0.2 - 0.8 g) was cut free of impurities and placed in a tared weighing bottle, and the bottle was reweighed. A tiny crystal of $Fe(NO_3)_3 \cdot 9H_2O$ (about 3 mg) was added to the liquid ammonia, and the mixture was stirred for several minutes. Then the alkali metal was added, and stirring was continued until the disappearance of the blue color (usually after 15-45 min.).

The relative pK values of the indicators were usually determined by the following procedure. About 1 mg of indicator was added to the amide solution, and then an acid of known pK was added in an amount sufficient to make the concentration of the acid and its anion equal. When a color change was observed, we concluded that $pK_{ind} > pK_{acid}$. When no color change was observed, we concluded that $pK_{ind} < pK_{acid}$. [16] Some of the indicators (e.g., rosaniline hydrochloride, 2-4 dinitroaniline, and 2-methoxy-5-nitroaniline) appeared to undergo irreversible decomposition in the presence of excess amide. In such cases, the buffer solutions were prepared before adding the indicators.

Titrations were carried out by the gradual addition of acids to solutions or suspensions of amide containing indicators. In the case of polybasic acids, separate end points could sometimes be observed by the addition of different indicators at appropriate times during the titrations. For example, the first end point in the titration of potassium amide with sulfamide can be detected with rosaniline hydrochloride (green to golden yellow); the addition of tropeoline OO then permits detection of the second end point (violet to yellow). In most cases the acid (or the acid-generating substance) was added as a powdered or crystalline solid from a weighing bottle which was weighed immediately after the appearance of each end point. In one case the acid ($B_{10}H_{14}$) was added as a solution in diglyme from a buret.

DETERMINATION OF INDICATOR pK VALUES

The acids that were used to make buffer solutions for the estimation of the pK values of indicators are listed in Table I. Although the listed pK values[4, 5, 13, 17] for most of these acids correspond to -60° (a temperature about 27° below that at which we made our studies), we have used these values without correction. Thus our estimated indicator pK values probably appertain more closely to -60° than to the boiling point of ammonia (-33.4°)[18]. Nevertheless, any resultant errors in the indicator pK values probably have no effect on the application of the indicators to titrimetry.

Table I.

pK Values* of Acids Used to Make Buffers

Acids	pK	Ref.
Phenylthiourea	3.8	[5]
Thiosemicarbazide (pK_1)	4.7	[5]
o-nitroacetanilide	5.3	[13]
Thiosinamine	6.6	[5]
Diphenylsemicarbazide	7.7	[5]
Thiourea	8.5	[4]
Thiosemicarbazide (pK_2)	8.5	[5]
Ethylene glycol	9.5	[4]
Diphenylguanidine	10.7	[5]
Urea	12.9	[4]
Water (pK')†	15.6	[5]
Acetone (pK')†	17.9	[5]
2,5-dichloroaniline	24.5	[5, 17]
p-chloroaniline	27.4	[5]
Aniline	28.8	[5]

* Values obtained at -60° except in the case of o-nitroacetanilide (-55.6°).

† $K' = \frac{(NH_4^+)}{(HA)(K^+)}$, for saturated solutions of the potassium salts. Herlem and Thiebault [5] reported pK' values which ignored $(K^+) = 0.1$ and hence were high by 1 unit.

Many compounds have been proposed as acid-base indicators in liquid ammonia, but pK values are known for only four of these: p-nitroacetanilide (pK = 5.1)[13], o-nitroacetanilide (pK = 5.3)[13], di(p-tolyl) methane (pK = 27.1)[14], and di(p-methoxyphenyl) methane (pK = 28.6)[14]. The indicators that we studied are listed in Table II. Bacause each experiment gave only a qualitative measure of the pK relative to that of a standard acid, it was only possible to set upper and lower limits on the pK values. Using such data we have sorted the indicators into twelve pK ranges between 1 and about 32. Thus in Table II the indicators are grouped according to these pK ranges. The tabulated "acidic" and "basic" colors refer to the pH values equal to the lower and higher range-defining pK values, respectively. Several of the indicators show more than one color change on going from pH = 1 to pH = 32. In the case of rosaniline hydrochloride, all the color changes (at 0 - 3.8, 10.7 - 12.9, and 24.5 - 27.4) are sharp enough to warrant their inclusion in the table.

Some of the color changes do not correspond to the simple loss of protons from the indicator molecules. A case in point is m-nitroaniline. Although one would expect this molecule to have a pK (corresponding to simple deprotonation) very close to that for o-nitroaniline, [19] the pK corresponding to the prominent color change of m-nitroaniline (24.5 - 27.4) is much higher than that of o-nitroaniline (4.7 - 6.6). We propose that the o-nitroaniline color change does correspond to deprotonation of the NH_2 group, whereas the m-nitroaniline color change corresponds to the addition of an NH_2^- ion to the ring of the $O_2NC_6H_4NH^-$ ion (i.e., to the formation of a Meisenheimer complex).[17]

Table II.

Acid-Base Indicators in Liquid Ammonia

Indicator	pK lower limit	pK upper limit	Color acidic	Color basic
Rosaniline hydrochloride	0	3.8	colorless	golden yellow
Phenolphthalein	0	3.8	colorless	violet
Metanil Yellow*	4.7	5.3	yellow	violet
Tropeoline OO* (Orange IV or Tropaeolin OO)	4.7	5.3	yellow	violet
o-nitroaniline*	4.7	6.6	yellow-green	red
α-phenyl-azodiphenylamine*	4.7	6.6	yellow	purple
o-nitro-p-toluidine* (4-methyl-2-nitroaniline)	6.6	7.6	yellow-green	red-orange
Carmine (Carminic acid)	8.5	9.5	violet	grey-green
2-amino-5-azotoluene	8.5	10.7	yellow	magenta
o-toluazo-o-toluidine* (4-o-tolylazo-o-toluidine)	9.5	10.7	yellow	red
Hydrazobenzene	9.5	10.7	light yellow	dark brown
Azoxybenzene*	10.7	12.9	light yellow	dark brown
Neutral red	10.7	12.9	yellow	green-blue
Rosaniline hydrochloride	10.7	12.9	golden yellow	green
Safranine A* (Safranin O)	10.7	12.9	red	blue
Fluorene	10.7	12.9	colorless	yellow-green
2,4 dinitroaniline*†	12.9	21‡	purple-red	yellow

Table II. (continued)

Indicator	pK lower limit	pK upper limit	Color acidic	Color basic
Rosaniline hydrochloride*	24.5	27.4	green	blue (unstable)
m-nitroaniline*	24.5	27.4	yellow	blue-green
2-methoxy-5-nitroaniline	24.5	27.4	yellow	blue-green
Triphenylmethane*	27.4	28.8	colorless	red
p-naphtholbenzein	27.4	28.8	green-blue	brown
2-methoxy-4-nitroaniline	28.8	~32	yellow	blue
Diphenylmethane	28.8	~32	colorless	dark yellow
p-nitroaniline	28.8	~32	yellow	orange
Benzalacetophenone (Chalcone)	28.8	~32	colorless	violet
Crystal violet	28.8	~32	grey yellow	dark red
Malachite green	28.8	~32	yellow	red
Dibenzalacetone (1,5-diphenyl-3-pentadienone)	28.8	~32	yellow	violet

*These indicators give sharp, easily distinguished color changes.

†This indicator showed an intermediate color (orange) in an H_2O/KOH buffer for which we calculated pH = 18.2. This value may be taken as the approximate pK of the indicator.

‡Calculated pH of an acetone buffer.

ACID-BASE TITRATIONS

The only previous applications of indicators to acid-base titrations in ammonia of which we are aware were titrations of strong acids with potassium amide, viz., the titrations of ammonium nitrate with potassium amide (using o-nitroaniline) [12] and of boron trifluoride ammine with potassium amide (using triphenylmethane). [10, 11] In order to demonstrate the usefulness of the pK data in Table II, we studied the reaction of various weak mono-, di-, tri-, and tetrabasic acids with amide. When an acid H_nA, having n removable protons, is gradually added to an amide solution, the initial reaction is

$$1/n\ H_nA + NH_2^- \rightarrow 1/n\ A^{n-} + NH_3$$

and an end point occurs when the acid/NH_2^- ratio equals 1/n. When n is 2 or more, further addition of acid causes a second reaction,

$$1/[n(n-1)]\ H_nA + 1/n\ A^{n-} \rightarrow 1/(n-1)\ HA^{(n-1)-}$$

with an end point at acid/NH_2^- = 1/(n - 1). When n is 3 or more, further addition of acid causes a third reaction,

$$1/[(n-1)(n-2)]\ H_nA + 1/(n-1)\ HA^{(n-1)-} \rightarrow 1/(n-2)\ H_2A^{(n-2)-}$$

with an end point at acid/NH_2^- = 1/(n - 2). In Table III are listed the acids and indicators used in the titrations, the indicator pK ranges, and the experimental acid/NH_2^- ratios.

Table III.

Titration Data

Acid	Indicator and pK Range	Acid/NH_2^- Ratio
Urea	2-methoxy-4-nitroaniline(28.8-32)	.52*
$(NH_2)_2CO$	2-methoxy-5-nitroaniline(24.5-27.4)	1.00†
Sulfamide	Rosaniline hydrochloride(24.5-27.4)	.49
$(NH_2)_2SO_2$	Tropeoline 00(4.7-5.3)	1.00
Guanidinium	2-methoxy-4-nitroaniline(28.8-32)	.34*
thiocyanate	Rosaniline hydrochloride(24.5-27.4)	.69†
$C(NH_2)_3SCN$	Tropeoline 00(4.7-5.3)	1.00
Malonamide	Malachite green(28.8-32)	.34*
$CH_2(CONH_2)_2$	2-methoxy-5-nitroaniline(24.5-27.4)	.47‡
	Safranine A(10.7-12.9)	1.02
Phthalhydrazide	Triphenylmethane(27.4-28.8)	.41*
$C_6H_4CONHNHCO$	Rosaniline hydrochloride(24.5-27.4)	.50
	Metanil Yellow(4.7-5.3)	.99
p-toluenesulfonhydrazide	Malachite green(28.8-32)	.73†
$p\text{-}CH_3C_6H_4SO_2NHNH_2$	m-nitroaniline(24.5-27.4)	.75†
	Triphenylmethane(27.4-28.8)	.85†
	Rosaniline hydrochloride(24.5-27.4)	.97
	o-nitro-p-toluidine(6.6-7.6)	.99
	o-nitroaniline(4.7-6.6)	1.02
	Metanil Yellow(4.7-5.3)	1.04†

Table III. (continued)

Acid	Indicator and pK Range	Acid/NH_2^- Ratio
3-amino-1,2,4-triazole	Triphenylmethane(27.4-28.8)	.89*†
NHN:C(NH_2)N:CH	Rosaniline hydrochloride(24.5-27.4)	.99
	o-toluazo-o-toluidine(9.5-10.7)	1.00
	o-nitro-p-toluidine(6.6-7.6)	1.01
	Metanil Yellow(4.7-5.3)	1.06†
		.50-.80‡
Tetrasulfurtetraimide	Triphenylmethane(27.4-28.8)	.25*
$S_4N_4H_4$	Rosaniline hydrochloride(24.5-27.4)	.52†‡
Decaborane	Triphenylmethane(27.4-28.8)	.48
$B_{10}H_{14}$		
Ammonium chloride	Triphenylmethane(27.4-28.8)	.97
NH_4Cl		

*formation of a precipitate from the beginning of the titration.

†an unsharp end-point.

‡dissolution of the precipitate complete here.

According to Franklin [20], urea and sulfamide are dibasic acids and the guanidinium ion and malonamide are tribasic acids. Our titration data for urea and sulfamide (end points at or near acid/NH_2^- ratios of 1/2 and 1), for guanidinium thiocyanate (end points at or near acid/NH_2^- ratios of 1/3 and 1) and for malonamide (end points near 1/3, 1/2, and 1) are consistent with these statements. In the case of the guanidinium ion, none of the listed indicators showed a color change at acid/NH_2^- = 1/2. Probably the first and second ionization constants are very close.

As far as we know, phthalhydrazide and p-toluenesulfonhydrazide have never been studied in liquid NH_3. Phthalhydrazide reacts slowly with potassium amide to form first a dipotassium salt and then a monopotassium salt, as shown by the titration data. Both these salts are yellow, air-sensitive solids, insoluble in liquid ammonia. The data for p-toluenesulfonhydrazide indicate that this acid is only monobasic in liquid ammonia.

Strain [21] prepared the monosodium salt of 1,2,4-triazole and the corresponding silver, magnesium, calcium, and copper(I) salts. The compound 3-amino-1,2,4-triazole might be expected to be polybasic, however the indicator expected to be data give no evidence of more than one replaceable proton. On the other hand we observed, from the beginning of the titration, the formation of a precipitate which then redissolved and disappeared around acid/NH_2^- = 0.50 to 0.80. This result suggests that in the very basic solutions there was formed an insoluble tripotassium salt and then a slightly soluble dipotassium salt.

The data for tetrasulfurtetraimide are consistent with the formation of $K_4S_4N_4$ (end point at acid/NH_2^- = 1/4) and $K_4H_2S_4N_4$ (end point near acid/NH_2^- = 1/2). The corresponding sodium compounds have been prepared by the reaction of $S_4N_4H_4$ with the sodium salt of triphenylmethane. [22] Meuwsen [23] has reported that $S_4N_4H_4$ reacts with potassium amide in ammonia to give an insoluble yellow solid of empirical composition $KNS \cdot KNH_2$. The latter compound was probably the initial precipitate in our titration, and it was probably converted to $K_4S_4N_4$ at acid/NH_2^- = 1/4.

The result of the decaborane titration suggests the formation of the $B_{10}H_{12}^{2-}$ ion, previously reported by Wilks and Carter. [24] However this reaction will require much more study before the nature of the product can be inferred.

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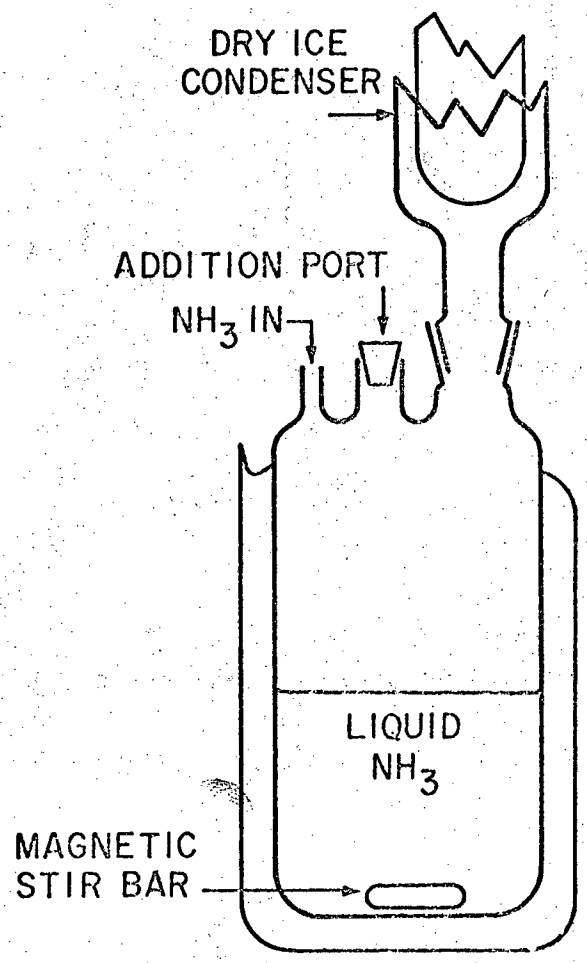

Figure 1. Apparatus for Studying Reactions in Liquid Ammonia.

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