THEORETICAL BASES OF THE AMMONIUM ION DETERMINATION BY FORMOL TITRATION

Yakov I. Tur'yan*

The National Physical Laboratory of Israel, Jerusalem 91904, Israel

Dedicated to the memory of Professor I.M. Kolthoff

ABSTRACT

This review covers the theoretical bases of the analytical reaction between ammonium ion and formaldehyde for ammonium ion determination by formol titration. The nature of the product reaction, the product formation equilibrium constants, the product acid dissociation constants, the product yield, the reaction kinetics, and the optimum conditions for the reaction have been considered.

Key words: ammonium ion formol titration, nature of analytical reaction, equilibrium formation and acid dissociation constants, kinetics, yield.

INTRODUCTION

NH_4^+ formol titration has been used for many years /1-6/. The optimum conditions for the titration have been established by Kolhoff /1-6/, and application of this analytical reaction for the polarographic determination of NH_4^+ has been further developed by Tur'yan *et al.* /7, 8/ and McLean *et al.* /9/. However, the substantiation of NH_4^+ formol titration has not been sufficiently considered. The goal of this review is to provide the

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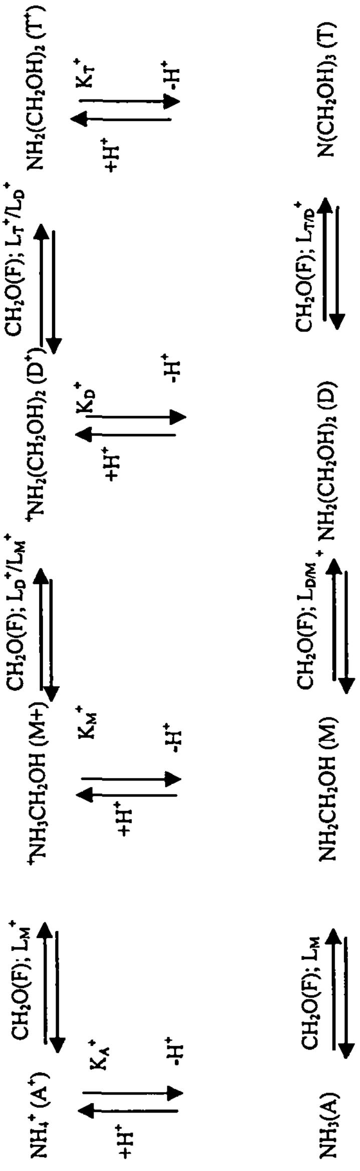
* Present address: 76 D Thurston Rd., Newton, MA 02464, USA.
E- mail: ituryan@yahoo.com

substantiation for the NH_4^+ formol titration in the following directions: the nature of the analytical reaction, the equilibrium constants of the products formation, the acid dissociation constants for the products, the yield of the analytical reaction, kinetics of the analytical reaction, the optimum conditions for the NH_4^+ formol titration developed by Kolthoff /1-6/.

1 THE NATURE OF THE ANALYTICAL REACTION

The almost complete consideration of this and similar reactions, including multistage equilibrium with participation of free and protonated compounds in acidic, neutral and weekly alkaline aqueous solutions, has been given by Tur'yan and Cheremukhina /8/ [NH_4^+ (NH_3)+ CH_2O] and Kallen and Jencks /10/ [amine(amine - H^+)+ CH_2O]. Since these reactions are nucleophylic, formaldehyde participates in these reactions in unhydrated form (CH_2O), but not in the dominating hydrated form [$CH_2(OH)_2$], as it was indicated /10/. At the same time, it should be noticed that in both cases the corresponding adducts are the same, i.e., the methylol derivatives of ammonia /8/ or amines /10/. The complete analytical reaction for NH_4^+(NH_3) can be written as reaction (1) /8/: where M^+(M), D^+(D), T^+(T) are mono-, di-, and trimethylol ammonia derivatives in protonated and unprotonated forms(adducts). In the case of polarographic analysis of NH_4^+ /7-9, 11/, additional reactions take place at an electrode, which are not considered here. Note, that in some publications /1, 2, 12, 13/, the hexamethylentetramine (HMTA) formation is proposed instead of reaction (1). However the proven tri-stage equilibrium 1 /8/ and the polarographic inactivity of HMTA /8, 9/ show that the HMTA formation can't have an essential influence on the NH_4^+ formol titration. In addition, it is necessary to note that the NH_4^+ formol titration /1, 6/ and also the NH_4^+ polarografic analysis /7-9/ were carried out at the large excess of formaldehyde. Therefore, the elimination of the methylol derivatives cyclization to HMTA could be expected /13/.


NH_4^+ (A$^+$)
CH_2O(F); L_M^+
$^+NH_3CH_2OH$ (M+)
CH_2O(F); L_D^+/L_M^+
$^+NH_2(CH_2OH)_2$ (D$^+$)
CH_2O(F); L_T^+/L_D^+
$NH_2(CH_2OH)_2$ (T$^+$)
K_A^+
K_M^+
K_D^+
K_T^+
+H$^+$
-H$^+$
+H$^+$
-H$^+$
+H$^+$
-H$^+$
+H$^+$
-H$^+$
NH_3(A)
CH_2O(F); L_M
NH_2CH_2OH (M)
CH_2O(F); $L_{D/M}$
$NH_2(CH_2OH)_2$ (D)
CH_2O(F); $L_{T/D}$
$N(CH_2OH)_3$ (T)

(1)

2 THE EQUILIBRIUM CONSTANTS FOR THE ADDUCTS FORMATION (REACTION (1))

The equilibrium constants and acid dissociation constants (see below) will be given in terms of concentration at the constant ionic strength. Also as in the NH_4^+ formol titration, the total formaldehyde concentration (C_F) is considerably larger than C_{NH4+}. Since the NH_4^+ formol titration is carried out at pH ≤ 9 /1, 6/, the acid dissociation of the formaldehyde hydrated form ($CH_2(OH)_2$) can be neglected (pKa of $CH_2(OH)_2$ equals 13.27 at 25°C /14/).

The equilibrium constants for reaction (1) can be described by the following equations:

$$L_{M+} = \frac{[M^+]}{[A^+][F]} \qquad (2)$$

$$L_{D+} = \frac{[D^+]}{[A^+][F]^2} \qquad (3)$$

$$L_{T+} = \frac{[T^+]}{[A^+][F]^3} \qquad (4)$$

$$L_M = \frac{[M]}{[A][F]} \qquad (5)$$

$$L_D = \frac{[D]}{[A][F]^2} \qquad (6)$$

$$L_T = \frac{[T]}{[A][F]^3} \qquad (7)$$

Acid dissociation constants could be expressed as:

$$K_{A+} = \frac{[A]\cdot[H^+]}{[A^+]} \qquad (8)$$

$$K_{M+} = \frac{[M]\cdot[H^+]}{[M^+]} \qquad (9)$$

$$K_{D+} = \frac{[D]\cdot[H^{+}]}{[D^{+}]} \tag{10}$$

$$K_{T+} = \frac{[T]\cdot[H^{+}]}{[T^{+}]} \tag{11}$$

Taking into account the formaldehyde hydration:

$$CH_2O(F) + H_2O \rightleftarrows CH_2(OH)_2\,(G) \tag{12}$$

and the hydration equilibrium constant:

$$K_G = \frac{[G]}{[F]} \tag{13}$$

$K_G = 2.0 \cdot 10^3$ at 25 °C, /15/ i.e. $K_G >> 1$, hence:

$$C_F = [F] + [G] = [F] \cdot (1 + K_G) \cong [F] \cdot K_G \tag{14}$$

On the basis of Eqs. (2-4, 13, 14) the following equations could be derived ($C_F >> C_{NH4+}$):

$$\bar{L}_{M+} = \frac{[M^{+}]}{[A^{+}]C_F} \tag{15}$$

$$\bar{L}_{D+} = \frac{[D^{+}]}{[A^{+}]C_F^{2}} \tag{16}$$

$$\bar{L}_{T+} = \frac{[T^{+}]}{[A^{+}]C_F^{3}} \tag{17}$$

where:

$$\bar{L}_{M+} = L_{M+} / K_G \tag{18}$$

$$\bar{L}_{D+} = L_{D+} / K_G^{2} \tag{19}$$

$$\bar{L}_{T+} = L_{T+} / K_G^{3} \tag{20}$$

The constants $\bar{L}_{M+}$, $\bar{L}_{D+}$, $\bar{L}_{T+}$, K_{M+}, K_{D+}, K_{T+}, (reaction (1)) have been determined by polarographic method /8/ at ionic strength equals 1 (activity coefficients for ions with charge ±1 equals 1 (activity coefficients for ions with charge ± 1 equals co. 1) /16/ and temperature 25°C (Tables 1, 2). The constants L_{M+}, L_{D+}, L_{T+} (Table 1) were calculated from Eqs. (18-20). The constants L_{M}, L_{D}, L_{T} (Table 1) have been calculated from equations :

$$L_M = L_{M+} \frac{K_{M+}}{K_{A+}} \tag{21}$$

$$L_D = L_{D+} \frac{K_{D+}}{K_{A+}} \tag{22}$$

$$L_T = L_{T+} \frac{K_{T+}}{K_{A+}} \tag{23}$$

where K_{M+}, K_{D+}, and K_{T+} are given in Table 2.

Table 1

Equilibrium constants for protonated and unprotonated adducts of formaldehyde and NH_4^+ (NH_3)

L_{M+}, M^{-1} $1.3 \cdot 10^{-2}$	L_{D+}, M^{-2} $1.8 \cdot 10^{-2}$	L_{T+}, M^{-3} $2.0 \cdot 10^{-2}$
$\bar{L}_{M+}$, M^{-1} 26	$\bar{L}_{D+}$, M^{-2} $7.2 \cdot 10^{4}$	$\bar{L}_{T+}$, M^{-3} $1.6 \cdot 10^{8}$
$\bar{L}_{M}$, M^{-1} $7.5 \cdot 10^{2}$	$\bar{L}_{D}$, M^{-2} $1.3 \cdot 10^{3}$	$\bar{L}_{T}$, M^{-3} $1.8 \cdot 10^{3}$
L_{M}, M^{-1} $1.5 \cdot 10^{6}$	L_{D}, M^{-2} $5.1 \cdot 10^{9}$	L_{T}, M^{-3} $1.4 \cdot 10^{13}$

Table 2

Acid dissociation constants of NH_4^+ and protonated adducts of formaldehyde and ammonia

pK_{A+} /16/	pK_{M+}	$pK_{D\pm}$	$pK_{T\pm}$
9.25	4.50	4.40	4.30

The constants $\bar{L}_M$, $\bar{L}_D$, $\bar{L}_T$

$$\bar{L}_M = \frac{[M]}{[A]C_F} \tag{24}$$

$$L_D = \frac{[D]}{[A]C_F^2} \tag{25}$$

$$L_T = \frac{[T]}{[A]C_F^3} \tag{26}$$

have been found from the following equations:

$$L_M = \bar{L}_M / K_G \tag{27}$$

$$L_D = \bar{L}_D / K_G^2 \tag{28}$$

$$L_T = \bar{L}_T / K_G^3 \tag{29}$$

Using data from Table 1, the equilibrium constants have been calculated:

$$L_{D+/M+} = \frac{[D^+]}{[M^+][F]} = \frac{L_{D+}}{L_{M+}} \tag{30}$$

$$L_{T+/D+} = \frac{[T^+]}{[D^+][F]} = \frac{L_{T+}}{L_{D+}} \tag{31}$$

$$L_{D/M} = \frac{[D]}{[M][F]} = \frac{L_D}{L_M} \tag{32}$$

$$L_{T/D} = \frac{[T]}{[D][F]} = \frac{L_T}{L_D} \tag{33}$$

These constants together with L_{M+} and L_M correspond to the stepwise equilibrium constants of reaction (1) (Table 3).

The following correlations for equilibrium constants (Tables 2 and 3) have been found as:

$$pK_{A+} >> pK_{M+} \cong pK_{D+} \cong pK_{M+} \qquad (34)$$

$$\{K_{M+}(K_{D+}, K_{T+})/ K_{A+}\} \cong 10^5 \qquad (35)$$

$$L_M >> L_{D/M} \cong L_{T/D} \cong L_{D+/M+} \cong L_{T+/D+} >> L_{M+} \qquad (36)$$

Table 3

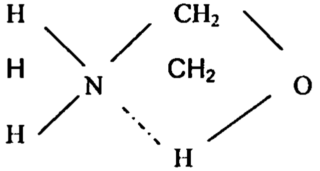
Stepped equilibrium constants for protonated and unprotonated adducts of formaldehyde and NH_4^+ (NH_3)

L_{M+}, M^{-1}	$L_{D+/M+}$, M^{-1}	$L_{T+/D+}$, M^{-1}
26	$2.8\cdot10^3$	$2.2\cdot10^3$
L_M, M^{-1}	$L_{D/M}$, M^{-1}	$L_{T/D}$, M^{-1}
$1.5\ 10^6$	$3.4\cdot10^3$	$2.7\cdot10^3$

These correlations can be explained by the effect of the following factors:

1. Taking into account the closeness of Taft's constants /17/ for -H ($\sigma^* = 0.490$) and CH_2OH ($\sigma^* = 0.555$) groups, the inductive effects change on L_M, $L_{D/M}$ and $L_{T/D}$ (Table 3) at the substitution of -H on -CH_2OH groups can be neglected. This is in agreement with conclusions by Kallan nad Jencks /10] for amines.

The formation of inner molecular hydrogen bond (typical for α - aminocarbinols) takes a main role:



(37)

The effect of inner molecular hydrogen bond on acid dissociation constants has been also noted for other compounds /18/. This bond corresponds to the nitrogen's fourth valence in M, D, T, and the hydrogen bond is formed with one -CH_2OH group. As compare with the first -CH_2OH group, the second -CH_2OH addition is inhibited due to hydrogen bond (37) including possible increase of the inductive effects. These effects remain for the third -CH_2OH group's addition. The analysis carried out explains the obtained correlation (36).

2. The formation of M^+,D^+, T^+ (reaction (1)) from A^+, M^+ D^+, respectively, includes the deprotonation of A^+, M^+, D^+ followed by M, D, T formation (reaction with CH_2O) and their protonation.. This gives an additional explanation to correlations (36) using correlations (34).

3 THE ACID DISSOCIATION CONSTANTS OF M^+, D^+, T^+

These constants (Table 2) are about 5 orders larger than the acid dissociation constants of NH_4^+ (K_{A+}), correlation (35). The fact that NH_4^+ behaves as a middle strength acid in the aqueous solution is very important for carrying out the NH_4^+ formol titration. The main reason for the K_{M+}, K_{D+}, K_{T+} increase, as compared to K_{A+}, is the inner molecular hydrogen bond formation in M, D, and T, as discussed above. This bond, in addition to possible increase of the inductive effects ($\sum$ s*), inhibits the protonation of M, D, T, and hence, considerable increase of K_{M+}, K_{D+} , K_{T+}, as compared to K_{A+} (Table 2), takes place. The above-indicated description of the hydrogen bond (37) also explains the closeness values of K_{M+}, K_{D+}, K_{T+}, (correlation (34)). Note, that by analogy with alkyl substituted amines /10/, the decrease of ionic hydration ($^+NH\cdots OH_2$) in the direction of $A^+ > M^+ > D^+ > T^+$ can be expected. This corresponds to the increase of the acid dissociation constants. However, in our case, the increase of the acid dissociation constants was observed in a very small degree (Table 2) probably due to ionic hydration of participating hydroxyl groups ($-CH_2OH \cdots OH_2$).

4 THE YIELD OF THE ANALYTICAL REACTION.

Two parameters will be considered: pH and the formaldehyde concentration, which correspond to the large excess of formaldehyde as compare with initial NH_4^+ concentration.

The yield of analytical reaction (1) (η) could be expressed using equilibrium concentrations from Eqs. (8-11) and (15-17):

$$\eta = \frac{[M^+]+[M]+[D^+]+[D]+[T^+]+[T]}{[A^+]+[A]+[M^+]+[M]+[D^+]+[D]+[T^+]+[T]} \cdot 100\% \qquad (38)$$

$$\eta=\frac{\left(1+\frac{K_{M+}}{[H^+]}\right)\bar{L}_{M+}C_F+\left(1+\frac{K_{D+}}{[H^+]}\right)\bar{L}_{D+}C_F^2+\left(1+\frac{K_{T+}}{[H^+]}\right)\bar{L}_{T+}C_F^3}{1+\frac{K_{A+}}{[H^+]}+\left(1+\frac{K_{M+}}{[H^+]}\right)\bar{L}_{M+}C_F+\left(1+\frac{K_{D+}}{[H^+]}\right)\bar{L}_{D+}C_F^2+\left(1+\frac{K_{T+}}{[H^+]}\right)\bar{L}_{T+}C_F^3}\cdot 100\% \qquad (39)$$

On the basis of the equilibrium constants (Tables 1 and 2) and Eq. (39), the yield of analytical reaction depending on pH and C_F has been calculated (Table 4). The value of η increases with extension of pH and C_F (Table 4). The effect of pH is caused by higher L_M, L_D, L_T as compared to L_{M+}, L_{D+}, L_{T+} (Table 1), respectively. The effect of C_F can be explained by shift of reaction (1) equilibrium to the right with the C_F increase. In acid solutions, the η value is < 100% and in neutral and weakly alkaline solutions (pH = 7-9) the η value is 100% at C_F = (2.0- 4.0) M (Table 4). These data are important for the NH_4^+ formol titration, since this titration is finished at pH ≅ 9 (see below). Unlike the NH_4^+ formol titration, for the polarographic determination of NH_4^+ which is also based on reaction (1) /8/, the condition η =100% is not required. Only the achievement of the equilibrium in reaction (1) is essential /8/.

Table 4

Yield of analytical reaction (1) (%) ; C_{NH4+} = 0.01 -0.1 M, $C_F >> C_{NH4+}$

pH		C_F, M	
	1.0	2.0	4.0
3.0	5.0	21	63
4.0	6.8	28	71
5.0	21	59	91
6.0	69	92	99
7.0	95	99	100
8.0	100	100	100

5 KINETICS

The rate of reaction (1) increases with the increase of pH especially at pH > 4 /8/. This can be explained mainly by participation of unprotonated forms in reaction (1). McLean *et al.* /9/ have shown that at pH=4 the equilibrium in the analytical reaction between NH_4^+ and CH_2O is achieved within 15 minutes. This is consistent with data /8/. While at pH = 5.0 - 5.3 and $C_F = 1.9$ M the equilibrium is reached in 5 min /7/ it is achieved in 1-2 min at pH = 7 and $C_F = 2.0$ M /8/.

6 OPTIMUM CONDITIONS FOR THE NH_4^+ FORMOL TITRATION

Kolthoff /1, 6/ has developed the optimum conditions for the NH_4^+ formol titration: 1) large excess of formaldehyde (20 – 200 fold), 2) preliminary neutralization of formaldehyde solution up to pH ≅ 9.0 (controlled by phenolphthalein), 3) preliminary neutralization of the NH_4^+ sample up to pH ~ 5.2 (controlled by methyl red (anions of strong acids)) or up to pH ~7.6 (controlled by neutral red (anions of weak acids), 4) it is necessary to wait for 1 minute after mixing of NH_4^+ (up to 0.01 - 0.1 M) and CH_2O (up to $C_F = 2.0$ M) solutions to reach the reaction equilibrium, 5) the formol titration proceeds with alkali (controlled by phenolphthalein, pH ≅ 9.0). Taking into account reaction (1), the titration reaction can be written as:

$$(M + D + T)\,H^+ + OH^- \longrightarrow (M + D + T) + H_2O \qquad (40)$$

The waiting for 1 minute after mixing the solutions of NH_4^+ and CH_2O causes considerable decrease of pH from 9.0 to 3-4 due to reaction (1), based on values of K_{M+}, K_{D+} , K_{T+} (Table 2). For example, it was found that pH = 3.7 for 1% NH_4^+ conversion at the initial $C_{NH4+} = 0.1M$ (anions of strong acids) and $C_F = 2.0M$, using Table 2 and Eqs. (34, 41-44):

$$\frac{[M^+]+[M]+[D^+]+[D]+[T^+]+[T]}{C_{NH4}+} = 0.01 \qquad (41)$$

$$\frac{[H^+]([M]+[D]+[D]+[T])}{[M^+]+[D^+]+[T]} = 4\cdot 10^{-5} = \frac{K_{M+} + D_{D+} + K_{T+}}{3} \qquad (42)$$

$$[H^+]=[M]+[D]+[T] \tag{43}$$

$$\frac{[H+]^2}{0.01C_{NH4+}-[H^+]}=4\cdot 10^{-5} \tag{44}$$

This decrease of pH does not allow 100% yield (η) of the analytical reaction to be obtained. It was found (Table 4), that at pH 3-4, η equals only 21-28% independently on waiting time (1min /1, 6/ or 5min /2/). Hence, it follows that 100% yield for the reaction (1) under conditions proposed by Kolthoff /1, 6/ is achieved automatically during titration (reaction (40) at pH = 7-9 (Table 4).

Thus, the given analysis proves Koltholf's optimum conditions for ammonium ion determination using formal titration.

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