

Stoichiometry of Quinol/Ammonium-Nitrogen Complex Using Spectrophotometry

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Summary: Quinol (1,4-dihydroxybenzene) forms instantaneous pink complex with aqueous ammonium-nitrogen ($\text{NH}_4^+\text{-N}$). Hydrogen peroxide accentuates the colour. This complex, which we now refer to as Q/ $\text{NH}_4^+\text{-N}$ complex, can be the basis for the spectrometric determination of $\text{NH}_4^+\text{-N}$ in aqueous solution. Aqueous $\text{NH}_4^+\text{-N}$ is a very important pollution index in water pollution studies. Therefore, it is imperative that the stoichiometry of this complex be thoroughly understood. In this work, Job's method of continuous variations [1,2,3,4] and the molar-ratio method [5,6,7] were used in a corroborative manner to study and establish the Q/ $\text{NH}_4^+\text{-N}$ complex as $\text{Q}(\text{NH}_4)_4$, where Q stands for quinol.

Introduction

Earlier work by the author [1] has shown that quinol/ammonium-nitrogen (i.e. Q/ $\text{NH}_4^+\text{-N}$) complex can form the basis for the spectrophotometric determination of $\text{NH}_4^+\text{-N}$ in aqueous solution. It is therefore important that the stoichiometry of the reaction between quinol (1,4-dihydroxybenzene) and ammonium-nitrogen ($\text{NH}_4^+\text{-N}$) is known for the purpose of quantitative calculations and so that analytical procedures can be properly defined. Since the complex is coloured (pink), its stoichiometry can be established using visible spectrometry to measure the absorbance of solutions of known composition.

One method that is widely applicable is Job's method of continuous variation [2-5]. Separate standard solutions of the electropositive ion and the complexing agent are mixed in different molar proportions such that the total molarity is constant, i.e. the mole fraction of both the electropositive ion and reagent are varied within a fixed total molarity. Absorbance readings for the series of solutions are plotted against the mole fractions of the electropositive ion and reagent to give two intersecting straight lines, the point of intersection corresponding to the stoichiometry of the complex in terms of the mole ratio. The system must obey Beer-Lambert Law.

Another popular method for the determination of stoichiometry of a complex is the mole-ratio (or the molar-ratio) method [6-8]. If the molar ratio method is used, a series of solutions are prepared in which the concentration of the other component is varied. The absorbances of the solutions are

measured and plotted as a function of the ratio of ligand concentration to electropositive-ion concentration or the inverse. Alternatively, the absorbances can be plotted as a function of the concentration of the varied component in each solution or a function of some other variable (such as volume) that is proportional to the concentration of the varied component. If relative stable complexes are formed and if only the complex absorbs radiation at the chosen wavelength, the absorbance of each solution increases with increased concentration of the varied component until the concentration is sufficient to cause all of the constant-concentration component to react. Further increase in concentration do not cause increased absorbance. The ratio of the ligand to the electropositive ion at the extrapolated intersection of the two linear portions of the plot corresponds to the ratio in the complex.

Other methods include: equilibrium shifting method [9] and logarithmic method [10,11,12].

Theoretical Background

In phenols, the -OH group can reinforce the nucleophilic properties of the benzene ring, and thus is a powerful influence in aiding electrophilic attack on the ring at the ortho- and para-positions.¹³ The orienting and activation effects of the -OH group and the other electron donating groups have been discussed extensively [13]. The polyphenols (e.g. quinol) are much more reactive to nucleophilic substitution than phenol. For example, substitution into the rings of resorcinol (1,3-dihydroxybenzene)

and pyrogallol (1,2,3,-trihydroxybenzene) is extremely facile. Resorcinol, with two meta-disposed hydroxy groups, is subject to electrophilic attack at the 4-position by reagents that are too weakly electrophilic to attack benzene or monophenols. It is apparent that the electron-donating powers of the two hydroxy groups are both directed to the 4-position, since it is ortho to one and para to the other as shown below:

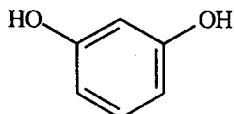


Fig. 1: Orienting and Activating effects of electron-donating groups in resorcinol.

The symmetry of quinol causes all four available positions to be equivalent.

From the foregoing and NH_4^+ as the electrophile, the reaction between quinol and ammonium in aqueous solution may therefore be written as in fig 2.

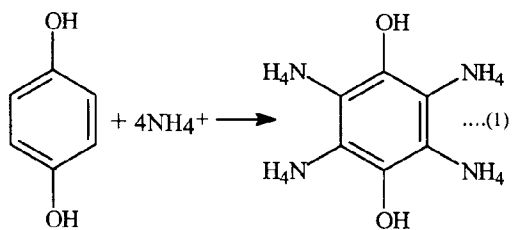


Fig. 2: Chemistry of quinol NH_4 reaction

Results and Discussion

(a) Job's method

From Table 1 and figure 3, the value of X (mole-ratio of quinol) at the point of inflection = 0.203.

But $X = n / (1+n) \dots\dots\dots(5)$

Where n = number of moles of quinol that react with one mole of NH_4^+-N

$\therefore 0.203 = n / (1+n)$

or $n = 0.2573$.

Substituting for n in the formula NH_4Q_n , we get

Table-1. Stoichiometry of NH_4^+-N /Quinol Complex (Job's Method of Continuous Variations)

S/N	Mol. Fraction of quinol (x)	Absorbance (A)	Corrected Absorbance (Ac)
1	0.1	0.103	0.085
2	0.2	0.16	0.144
3	0.3	0.185	0.171
4	0.4	0.2	0.188
5	0.5	0.195	0.185
6	0.6	0.2	0.192
7	0.7	0.2	0.194
8	0.8	0.2	0.196
9	0.9	0.2	0.198

absorbance of solution I = 0.02

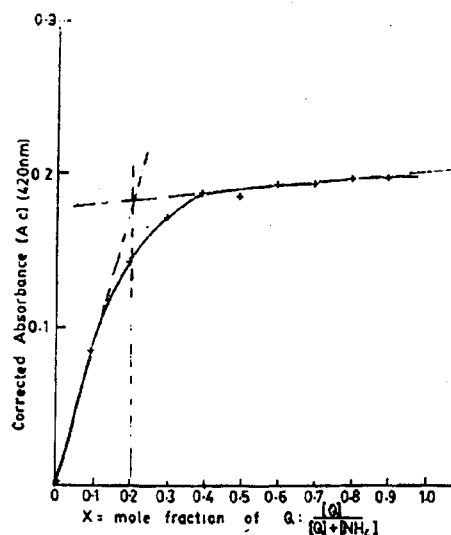
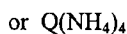
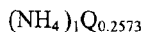


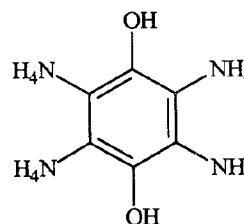
Fig. 3: Stoichiometry of Quinol- NH_4^+-N Complex (Job's method of continuous variation).



The stoichiometry of $\text{Q}/\text{NH}_4^+-\text{N}$ complex may therefore be established as:



The suggested structure is:



Alternatively,

$$X = \frac{[Q]}{[Q] + [NH_4]} = \text{mole - ratio of quinol.}$$

From graph, fig 3.

$$X = 0.203 \approx \frac{2}{10} \approx \frac{1}{5}$$

$$\therefore [Q] = 1$$

$$\text{and } [NH_4] = 5 - 1 = 4$$

$$\text{i.e. } Q[NH_4]_4$$

(b) Molar - ratio Method:

From Table 2 and fig 4, the value of mole ratio, $[NH_4]/[Q]$, at the point of inflection = 4.1

$$\text{That is } [NH_4]/[Q] \approx 4.1/1 \approx 4/1$$

Table-2. Stoichiometry of Quinol/ NH_4^+ -N (Molar-ratio method)

S/N	ml of solu. A	ml of solu. B	Mole ratio $[NH_4]/[Q]$	Absorbance (420nm)
Blank	0.00	0.28	0	0.000
1	0.42	"	1	0.020
2	0.83	"	2	0.075
3	1.25	"	3	0.090
4	1.67	"	4	0.100
5	2.08	"	5	0.130
6	2.50	"	6	0.130
7	2.92	"	7	0.130
8	3.33	"	8	0.130

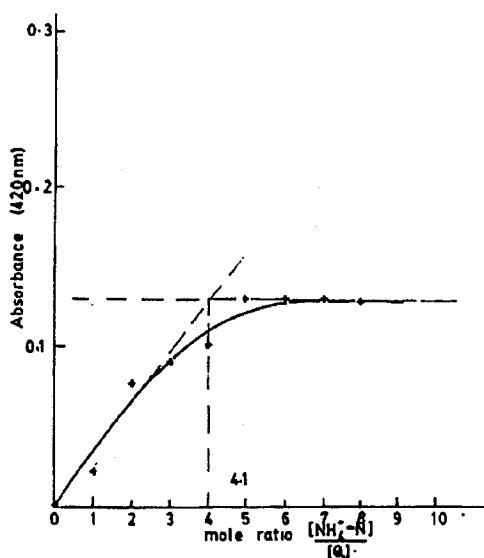
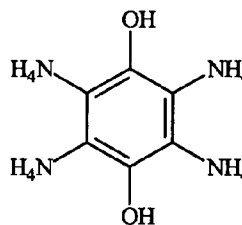


Fig. 4: Stoichiometry of Quinol- NH_4^+ -N Complex (Molar-ratio method).

The stoichiometry of the Quinol/ NH_4^+ -N complex may therefore be established as $Q(NH_4)_4$

The suggested structure is:



Experimental

Apparatus

A Unicam sp500 series ultraviolet and visible spectrophotometer with matched 1-cm silica cells was used for absorbance measurements. A model 3020 pH meter (Jenway) was employed for pH measurement.

For Job's Method of Continuous Variations.

Reagents

(AnalaR from BDH only): 1M HCL and 1M NaOH, Solution A: 0.06M or 848.505 $\mu\text{g/ml}$ in NH_4^+ -N: Dissolve 1.0g $(NH_4)HPO_4$ in distilled or deionised water and dilute to 250ml.

Hydrogen Peroxide: 58% m/v hydrogen peroxide

Solution i: $2.0 \times 10^{-3}M$ NH_4^+ -N: Pipette 8.33ml of solution A into a 250 - ml calibrated flask and make up to mark with water. This is $2.0 \times 10^{-3}M$ in NH_4^+ -N. Call this solution i. Solution ii: $2.0 \times 10^{-3}M$ in quinol: Weigh 0.055g quinol (previously dried at 105°C to constant weight and cooled to room temperature) into a calibrated flask, dissolve and make up to mark with distilled or deionised water. This is $2.0 \times 10^{-3}M$ in quinol. Call this solution ii.

For molar - ratio method:

Reagents

(AnalaR from BDH only) 1M HCL and 1M NaOH

Solution A: as in Job's Method

Solution B: 0.09M or 1.0% m/v in quinol: Dissolve 1.0g quinol (dried at 105°C to constant weight and cooled to room temperature) in distilled or deionised water and dilute to 100ml.

Hydrogen Peroxide: as in Job's method.

Procedure for Jobs method

Pipette 0.02ml of the H₂O₂ into each of the nine 100-ml conical flasks.

Prepare 9 solutions of NH₄⁺-N/quinol complex by mixing solutions i and ii dispensed from separate burettes into the conical flasks and according to the following scheme (Table 3).

Table-3: Job's Method for Determining the Stoichiometry of Quinol / NH₄⁺-N Complex.

S/N	ml of H ₂ O ₂	ml of solution i	ml of solution ii	mole fraction of quinol (x)
1	0.02	45	5	0.1
2	"	40	10	0.2
3	"	35	15	0.3
4	"	30	20	0.4
5	"	25	25	0.5
6	"	20	30	0.6
7	"	15	35	0.7
8	"	10	40	0.8
9	"	5	45	0.9

Allow 35 minutes for maximum colour development. Adjust the pH of each reaction mixture to 5.0 with 1M HCL or 1M NaOH. Take the absorbance readings at 420nm in matched 1-cm silica cells, using water as blank. Also take the absorbance reading of the NH₄⁺-N solution (solution i) under the same conditions.

Treatment of Data

1. Calculate the molar absorptivity (ϵ) of solution i, using the Beer-Lambert Law:

$$A_{(NH_4^+-N)} = \epsilon_{(NH_4^+-N)} \cdot b \cdot c \text{ ----- (2)}$$

where $A_{(NH_4^+-N)}$ is the measured absorbance of the NH₄⁺-N solution (solution i), $\epsilon_{(NH_4^+-N)}$ is the molar absorptivity of the NH₄⁺-N solution (solution i), b is the path length of the cell in cm and c is the concentration of the NH₄⁺-N in solution i (mol⁻¹)

2. Calculate a corrected absorbance, A_c , for each of the 9 reaction mixture, using the relation:

$$A_c = A - [\epsilon_{(NH_4^+-N)} \cdot (1 - X) \cdot b \cdot c] \text{ (3)}$$

where A is the uncorrected absorbance for each of the 9 reaction mixtures

3. Plot a graph of A_c against X and locate the value of X where the extrapolated straight – line portions of the graph intersect.

4. Establish the stoichiometry of the NH₄⁺-N/quinol complex by evaluating n in the expression:

$$X = n / (1+n) \text{ (4)}$$

Procedure for Molar – ratio Method

Keep the concentration of quinol constant at $1.0 \times 10^{-3}M$ and vary that of NH₄⁺-N, following the scheme below (Table 4):

Table 4: Molar – ratio Method for Determining the Stoichiometry of Quinol/ NH₄⁺-N Complex.

S/N	Quinol conc (mol ⁻¹)	NH ₄ ⁺ -N – conc (mol ⁻¹) x 10 ⁻³
1	1.0×10^{-3}	1.0
2	"	2.0
3	"	3.0
4	"	4.0
5	"	5.0
6	"	6.0
7	"	7.0
8	"	8.0
Blank	"	0.0

Pipette out 0.02ml of the H₂O₂ into each of nine 25-ml calibrated flasks. Add 0.00, 0.42, 0.83, 1.25, 1.67, 2.08, 2.50, 2.92, and 3.33ml of solution A, respectively. Finally add 0.28ml of solution B to each flask and make up to mark with water. Allow them to stand for 35minutes before adjusting their pH to 5.0 with 1M HCl or 1M NaOH solution. Take the absorbance readings of the reaction mixtures against the reagent blank (first flask) at 420nm in matched 1-cm silica cells.

Data Treatment

Plot a graph of absorbance against mole-ratio, $[NH_4] / [Q]$, and locate the value of mole ratio where the extrapolated straight – line portions of the graph intersect. From this value work out the mole – ratio $[NH_4] / [Q]$.

Conclusions

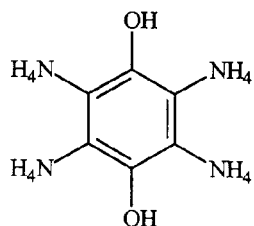
The two methods, Job's and Molar – ratio methods, are therefore in agreement over the stoichiometry of the quinol/NH₄⁺-N complex.

This stoichiometry may be represented as:



where Q stands for quinol.

From the theoretical background discussed earlier, the structure of this complex may be written as:



Quinol / $\text{NH}_4^+\text{-N}$ complex

This study provides some insight into the environmental chemistry involving ammonium-nitrogen ($\text{NH}_4^+\text{-N}$). Ammonium-nitrogen is a very important pollution index and knowledge of its concentration in aqueous systems is essential in pollution studies.

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