GLOBAL JOURNAL OF PURE AND APPLIED SCIENCES VOL. 17, NO.3, 2011: 307-310
COPYRIGHT© BACHODU SCIENSE CO. LTD PRINTED IN NIGERIA ISSN 1118-0579
www.globaljournalseries.com, Email: info@globaljournalseries.com

STOICHIOMETRY OF PYROGALLOL/AMMONIUM-NITROGEN COMPLEX USING SPECTROPHOTOMETRY

P.O. OKOLO AND E.N. DIBIE

(Received 22 April 2010; Revision Accepted 30 August 2010)

ABSTRACT

Pyrogallol (1,2,3-Trihydroxybenzene) forms instantaneous pale-yellow complex with aqueous ammonium-nitrogen (NH_4^+-N). This complex, which we now refer to as P/NH_4^+-N complex, can be the basis for the spectrophotometric determination of NH_4^+-N in aqueous solution. Aqueous NH_4^+-N is a very important pollution index. Therefore it is imperative that the stoichiometry of this complex be thoroughly understood. In this work, Job's method of continuous variations and the molar-ratio method were used in a corroborative manner to study and establish the P/NH_4^+-N complex as $P(NH_4)_2$, where P stands for pyrogllol.

KEYWORDS: Stiochiometry, pyrogallol/ammonium-nitrogen complex, spectrophotometry

INTRODUCTION

Pyrogallol/ammonium-nitrogen (P/NH_4^+-N) complex may form the basis for the spectrophotometric determination of NH_4^+-N in aqueous solution (Okolo, P.O., and Jideonwo, A., 2003). It is therefore important that the stoichiometry of the reaction between pyrogallol (1,2,3-trihydroxybenzene) and ammonium-nitrogen (NH_4^+-N) is known for the purpose of quantitative calculations and so that analytical procedures can be properly defined. Since the complex is coloured (pale-yellow), its stoichiometry can be established using visible spectrometry to measure the absorbance of solutions of known composition.

One method widely applicable is Job's method of continuous variations (Kealy, D., 1986; Mukoyama, T., 1971; Ameanu, V., and Costinescu, P., 1960; and Demetrius, G.T., et al., 1995). Separate standard solutions of the electropositive ions 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 (Bruan, R.D., 1987, Elsirafy, A.A., 1980; Gowda, H.S. et al., 1981). 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 function of the ratio of ligand concentration to electropositive-ion concentration or the inverse. Alternatively, absorbances can be plotted as a function of the concentration of the varied component in each solution or as a function of some other variable (such as volume) that is proportional to the concentration of varied component.

If relatively stable complexes are formed and if only the complex absorbs radiation at the chosen wavelengths, the absorbance of each solution increases with increasing concentration of the varied component until the concentration is sufficient to cause all of the constant-concentration component to react. Further increases 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 (Yu-rui, Z. et al., 1995) and logarithmic method (Briski, F. et al., 1993; Marczenke, Z., and Jarozi, M., 1981; and Neena, N., and Mishra, P.K., 1995).

THEORETICAL BACKGROUND

In phenols, the –OH group can reinforce the nucleophillic properties of the benzene ring, and thus is a powerful influence in aiding electrophilic attack on the ring at the ortho-and para-positions (Geissman, T.A., 1962). The orienting and activation effects of the –OH group and the other electron-donating groups have been discussed extensively (Geissman, T.A., 1962). The polyphenols (e.g. pyrogallol) are much more reactive to nucleophillic substitution than phenol. For example, substitution into the ring of resorcinol (1,3-dihydroxybenzene) and pyrogallol is extremely facile. In pyrogallol, the electron-donating –OH groups (+1 inductive effect) direct electrons predominantly to positions 3 and 5, since these two positions are jointly ortho and para with respect to (w.r.t) two OH groups (b) and (c) see fig. 1:

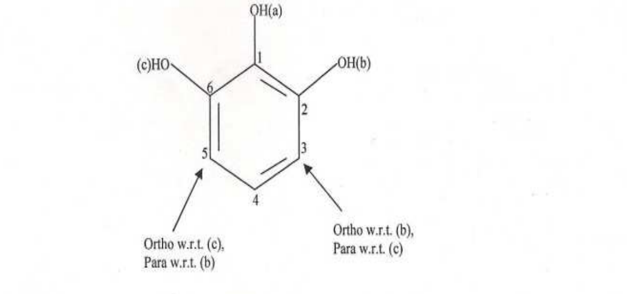

Fig 1: Orienting and activation effects of electron-donating groups in pyrogallol

P. O. Okolo, Department of Chemistry, University of Benin, Benin City, Nigeria.
E. N. Dibie, Department of Chemistry, University of Benin, Benin City, Nigeria.

This makes the positions 3 and 5 most susceptible to attacks by incoming electrophiles. Only one-OH group, (a), is directing electrons to position 4 [position 4 is para to (a)], and so this position is comparatively less susceptible to attacks by incoming electorphiles.

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

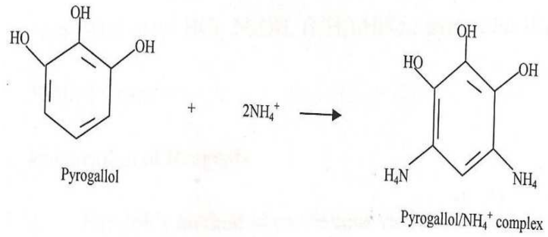

Fig 2: chemistry of pyrogallol/NH_4^+ reaction

MATERIALS AND METHODS

a. Materials and Reagents

Unicam sp 500 series ultraviolet and visible spectrophotometer with matched 1-cm silica cells, model 3020 pH meter (Jenway), analytical balance, volumetric (calibrated) flasks, beakers and conical flasks. All reagents were of Analar quality and from BDH only: HCl, NaOH, $(NH_4)_2HPO_4$, pyrogallol $[C_6H_3\ (OH)_3]$, distilled water.

b. Preparation of Reagents

i. For Job's method of continuous variations:

Solution A: 848.505gmL^{-1} or 0.06M in NH_4^+-N

1.00g $(NH_4)_2HPO_4$ (previously dried at 105^0C to a constant weight) was weighed out using analytical balance. This was dissolved in distilled water and finally diluted to 250mL in a calibrated (volumetric) flask.

Solution 1: 2.0 x 10^{-3}M NH_4^+-N

8.33mL of solution A was pipette into a 250-mL calibrated flask and made up to mark with distilled water. This was 2.0 x 10^{-3} moll^{-1} in NH_4^+-N and labelled solution 1.

Solution 2: 2.0 x 10^{-3}M pyrogallol:

0.063g pyrogallol (earlier dried at 105^0C to a constant weight) was weighed out, dissolved in distilled water and finally diluted to 250mL in a calibrated flask. This was 2.0 x 10^{-3}moll^{-1} in pyrogallol and labelled solution 2.

ii. For Molar-ratio Method:

Solution A: 848.505 gmL^{-1} or 0.06M in NH_4^+-N

This was the same "solution A" as prepared under job's method of continuous variations.

Solution B: 1.0% (m/v) or 0.079M pyrogallol

1.00g pyrogallol was weight out, dissolved in distilled water and finally diluted to 100mL in a calibrated flask. This was 1.0% (m/v) or 0.079M in pyrogallol and labeled solution B.

c. Stoichiometry Determinations

i. Job's Method:

Nine (9) solutions of NH_4^+-N/pyrogallol complex were prepared by mixing solutions 1 and 2 dispensed from separate burettes into 100-mL conical flasks and according to the following scheme (Table 1).

Table 1: Job's method for determining the stoichiometry of NH_4^+-N/pyrogallol complex

S/N	mL of solution 1	mL of solution 2	Mole fraction of pyrogallol, X
1	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

35 minutes were allowed for maximum colour development, and their pH was adjusted to 7.0, using 1.00M HCl or 1.00M NaOH solutions. Absorbance readings were taken at 400nm in matched 1-cm silica cells. Distilled water was used as blank. Also, the absorbance reading of solution 1 was taken at 400nm in matched 1-cm silica cells.

Ii Molar-ratio Method

Nine (9) solutions of NH_4^+-N/pyrogallol complex were prepared by keeping the concentration of pyrogallol constant at 1.0 x 10^{-3}M and varying that of NH_4^+-N (Table 2) according to the scheme: 0.00, 0.42, 0.83, 1.25, 1.67, 2.08, 2.50, 2.92, 3.33 and 3.75mL of solution A were respectively pipette into ten 25-mL calibrated flasks.

0.32mL of solution B was added to each flask and made up to mark with distilled water. 35 minutes were allowed for maximum colour development. Their pH was adjusted to 7.0 with 1.00M HCl or 1.00M NaOH solutions. The absorbance reading of each reaction mixture was taken against the reagent blank (first flask) at 400nm in matched 1-cm silica cells.

Table 2: Molar-ratio method for determining the stoichiometry of NH_4^+-N/pyrogallol complex

S/N	Pyrogallol conc. (moll^{-1})	NH_4^+-N conc (moll^{-1}) x 10^{-3}
1	1 x 10^{-3}	1.0
2	1 x 10^{-3}	2.0
3	1 x 10^{-3}	3.0
4	1 x 10^{-3}	4.0
5	1 x 10^{-3}	5.0
6	1 x 10^{-3}	6.0
7	1 x 10^{-3}	7.0
8	1 x 10^{-3}	8.0
9	1 x 10^{-3}	9.0
Blank	1 x 10^{-3}	0.00

RESULTS AND DISCUSSION

1. Job's method

The molar absorptivity (ε) of solution 1 was calculated using the Beer-Lambert Law:

$$A_{(NH_4^+-N)} = \varepsilon_{(NH_4^+-N)}.b.c \quad - \quad - \quad (1)$$

Where $A_{\left(NH_4{}^+-N\right)}$ is the measured absorbance of solution 1, $\varepsilon_{\left(NH_4^+-N\right)}$ is the molar absorptivity of solution 1, b is the path-length of the cell in cm and c is the concentration of NH_4^+-N in solution 1 ($\text{mol}l^{-1}$). The corrected absorbance, A_c, for each of the 9 reaction mixtures were calculated, (Table 3), using the relation.

$$Ac = A - \left\lfloor \varepsilon_{\left(NH_4{}^+-N\right)} (1-x).b.c. \right\rfloor \quad - \quad - \qquad (2)$$

Where A is the uncorrected absorbance for each of the 9 reaction mixtures, and x is the mole fraction of pyrogallol. A graph of A_c against x was plotted and the value of x, where the extrapolated straight-line portions of the graph intersected, was located (Fig. 3)

The stoichiometry of NH_4^+-N/pyrogallol complex was established by evaluating "n" in the expression

$$x = \frac{n}{1+n} \quad - \quad - \quad - \qquad (3)$$

From Table 3 and figure 3, the value of x (the mole fraction of pyrogallol) at the point of inflection was 0.4.

But $x = \dfrac{n}{1+n}$

Where n is the number of moles of pyrogallol that reacts with one mole of NH_4^+-N.

Therefore,

$$0.4 = \frac{n}{1+n}$$

or

$$n = 0.6667$$

Substituting for n in the formular, $NH_4(P)_n$, gives

$NH_4(P)_{0.6667}$

or

$(NH_4)_2\ (P)_{1.3}$

or

$(NH4)_2\ (P)_1$

The stoichiometry of the NH_4^+-N/pyrogallol complex may therefore be established as $P(NH_4)_2$.

Alternatively,

$$x = \frac{[P]}{[P]+[NH_4]}$$

From graph (fig 3)

$$x = 0.4 = \frac{4}{10} = \frac{1}{2.5} \approx \frac{1}{3}$$

$$\therefore [P] = 1 \qquad and \qquad [NH_4] = 3 - 1 = 2$$

The stoichiometry may therefore be established as $P(NH_4)_2$

ii. Molar-ratio Method

A plot of absorbance against mole ratio, $[NH_4]/[P]$, was made (Table 4 and fig. 4) and the value of mole ratio, where the extrapolated straight-line portions of the graph intersected, was located. From Table 4 and figure 4, the value of mole ratio at the point of inflection was 2.

That is $$\frac{[NH_4]}{[P]} = \frac{2}{1}$$

The stoichiometry of the NH_4^+-N/pyrogallol complex may therefore be established as $P(NH_4)_2$

Table 3: Stoichiometry of pyrogallol/ NH_4^+-N complex (Job's method of continuous variations)

S/N	Mole fraction of Pyrogallol (x)	Absorbance (A)	Corrected Absorbance (Ac)
1	0.1	0.360	0.356
2	0.2	0.490	0.486
3	0.3	0.540	0.537
4	0.4	0.560	0.557
5	0.5	0.550	0.548
6	0.6	0.540	0.538
7	0.7	0.500	0.499
8	0.8	0.430	0.429
9	0.9	0.360	0.360

Absorbance of solution 1= 0.005

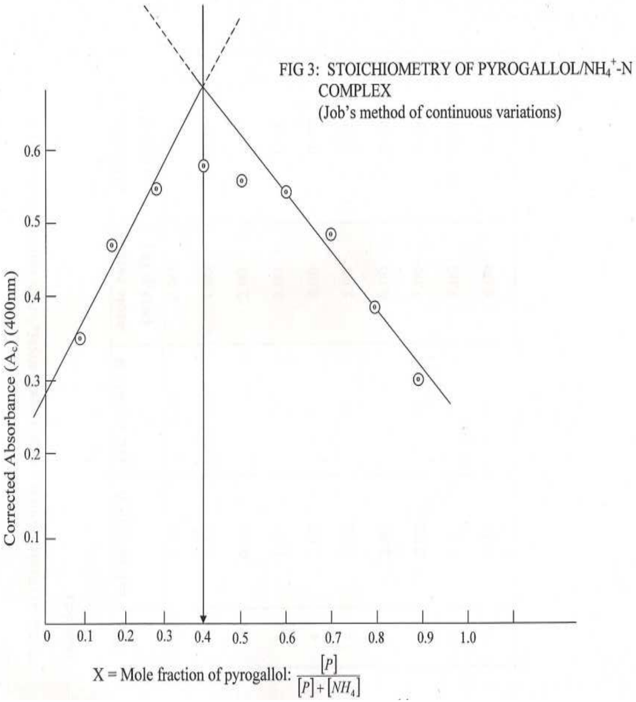

FIG 3: STOICHIOMETRY OF PYROGALLOL/NH_4^+-N COMPLEX
(Job's method of continuous variations)

Table 4: Stiochiometry of pyrogallol/NH_4^+-N complex (Molar-ratio method)

S/N	mL of Soln A	mL of Soln B	Mole ratio: $[NH_4]/[P]$	Absorbance (400nm)
Blank	0.00	0.32	0.00	0.00
1	0.42	"	1.00	0.41
2	0.83	"	2.00	0.43
3	1.25	"	3.00	0.43
4	1.67	"	4.00	0.42
5	2.08	"	5.00	0.41
6	2.50	"	6.00	0.40
7	2.92	"	7.00	0.39
8	3.33	"	8.00	0.38
9	3.75	"	9.00	0.38

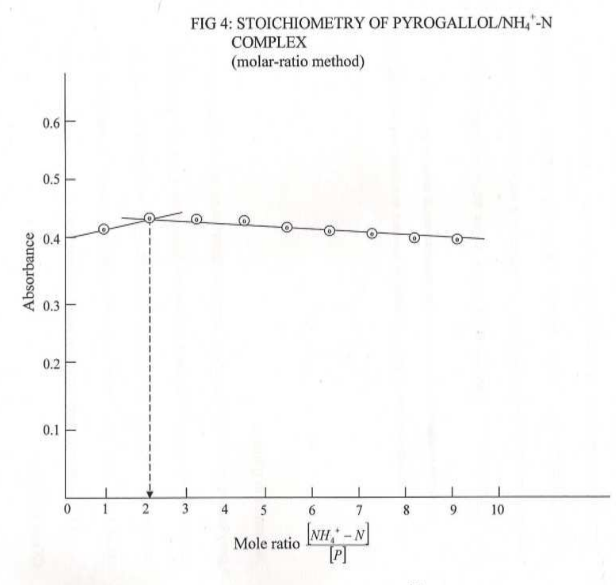
FIG 4: STOICHIOMETRY OF PYROGALLOL/NH_4^+-N COMPLEX (molar-ratio method)

CONCLUSION

The two methods (Job's method of continuous variations and molar-ratio) have thus been used in a corroborative manner to establish the stoichiometry of NH_4^+-N/pyrogallol complex. This stoichiometry may be represented as $P(NH_4)_2$, where P stands for pyrogallol. From the theoretical background discussed earlier, the proposed structure of this complex may be written as in figure 5.

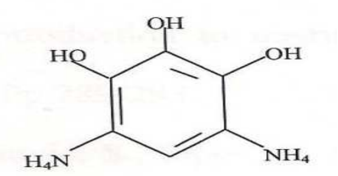

Fig 5: Proposed structure of NH_4^+-N/pyrogallol complex as established using Job's method of continuous variations and corroborated using molar-ratio method.

This study is a veritable contribution to the environmental chemistry involving ammonium-nitrogen (NH_4^+-N), which is a very important pollution index (Manahan, S.E., 1994; Jackson, A.R.W and Jackson, J.M., 1997). Accurate knowledge of its concentration in aqueous system is essential in pollution studies (APHA et al., 1989; Tebbutt, T.H.Y., 1977, and Rudolph, 1931).

REFERENCES

Ameanu, V., and Costineseu, P., 1960. Colorimetric micro-methods for the determination of calcium based on the formation of coloured azo-derivatives of 8-hydroxyquinoline. Rev. Chim., Bucharest, 11(6): 343-345.

APHA, AWWA, and WPCF, 1989. Standard methods for the examination of Water and Wastewater. 17th Ed., pp 4 -100 to 4 – 111.

Braun, R.D., 1987. Introduction to instrumental analysis. McGraw-Hill, New York. Pp. 289-293

Briski, F., Cerjan-Stetanovic, S., Sipos, L., 1993. Monitoring of nitrifying processes in groundwater by ion-chromatography. Int. J. Environ Anal. Chem., 52(1-4): 137-148

Demetrius, G.T., George, A.Z., and Stratis, J.A., 1995. Selective spectrophotometric determination of cobalt (II) using 2,2-Dipyridyl-2-pyridyhydrazone and a flow injection manifold. Analyst, 120, 1597.

Elsirafy, A.A., 1980. Spectrophotometric determination of palladium using solochrome red B, Analyst, 105, 914.

Geissman, T.A., 1962. Principles of organic chemistry, 2nd ed., W.H., Freeman and Company, London. Chap, 19, 20, 21, 26 & 27.

Gowda, H.S., Podmaji, K.A., and Thimaiah, K.N., 1981. Simultaneous spectrophotometric determination of palladium (II) and gold (III) with methiomeprazine hydrochloride: Analysis of alloys and minerals. Analyst*,* 106, 202.

Jackson, A.R.W. and Jackson, J.M., 1997. Environmental Science, Longman Group Limited, Singapore P. 110

Kealey, D., 1986. Experiments in modern analytical chemistry. Chapman and Hall, New York, P. 53

Manahan, S.E., 1994. Environmental Chemistry. 6th Ed., Lewis Publishers, London. P. 190

Marezenke, Z., and Jarozi, M., 1981. Flotation-Spectrophotometric determination of palladium with thiocyanate and methylene blue. Analyst*,* 106, 753.

Mukoyama, T., and Hasebe, T., 1971. Spectrophotometry of copper (II) with dithiocarbamate derivatives. Analyst. 20, 961-966.

Neena, N., Mishra, P.K., 1995. Spectrophotometric determination of uranium (IV) with thorin and N-hydroxy-N,N'-diphenylbenzamidine, Analyst, 120. 199.

Okolo, P.O., and Jideonwo, A., 2003. Pyrogallol as a reagent for spectrophotometric determination of NH_4^+-N in aqueous solution. Pak. J. Sci. Ind. Res. 46(2): 141-144

Rudulph, Z., 1931. Principles of the Determination of the Physical and Chemical Standards of Water for Drinking, Industrial and Domestic Purposes. Wat. Pollut. Sbs.4.

Tebbutt, T. H.Y., 1977. Principle of Water Quality Control, 2nd Ed., Pergamon Press Ltd., England. Pp. 12, 23, & 17.

Yu-rui, Z., Wang, C., Chen, J., Wan-quanainag, and Gu, J., 1995. Spectrophotometric determination of cadmium by the chromogenic reagent 2-pyridinediazoaminoazobenzene in the presence of triton X-100, *Analyst,* 120, 2855.