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Chelate-exchange titrimetry in mixed solvents

CHELATE-EXCHANGE TITRIMETRY IN MIXED SOLVENTS: DETERMINATION OF BIS[4,4,4-TRIFLUORO-1-(2-THIENYL)-1,3-BUTANEDIONATO] COPPER(II)

by

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Abstract

The system 2-thenoyltrifluoroacetone (HTTA), 1-(2-Pyridylazo)-2-Naphthol (HPAN), Copper (II) was studied by spectrophotometry, in methanol-benzene mixtures at 15°C., 25°C. and 35°C. Algebraic equations were derived in order to calculate the apparent molar equilibrium constants K_1' and K_2' of the chelate exchange reactions $Cu(TTA)_2 + HPAN \rightleftharpoons Cu(TTAPAN) + HTTA$ and $Cu(TTAPAN) + HPAN \rightleftharpoons Cu(PAN)_2 + HTTA$ in these solvents. The temperature dependence of these constants was also determined. In benzene K_1' was 900 and this value decreased to 250 in pure methanol. In benzene K_2' was 0.007 and it increased to 0.600 in pure methanol. These changes in the values of K_1' and K_2' with change in methanol content of the methanol-benzene mixtures are discussed in terms of the activity coefficients, and the fact that the HTTA exists as enol, keto, enolate ion and solvates in the solutions at equilibrium.

Acknowledgements

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I am most grateful to Mr. d'Amboise for his cooperation and advice, and for making his data and the curve fitting computer programmes available before their publication.

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1 — Introduction

The spectrophotometric titration of a metal chelate in an organic solvent by a standard solution of a chelating agent also in an organic solvent was first proposed and developed by Gray and Cave[28]. They applied the method to the determination of microgram amounts of the dithizonates of Ag, Pb, Cu(II), Cd, Zn, and In in chloroform, by titration with a standard solution of sodium diethyldithiocarbamate in ethanol. They also demonstrated[29] its use in the determination of some metal 8-quinolinates in benzene, by titration with a standard solution of dithizone in benzene.

As part of his investigation, Gray[1] showed that the titration reaction occurred in simultaneous steps. For example, the titration in a low-dielectric solvent of the chelate of a bivalent metal, MX_2, by a chelating agent HY occurred as follows:

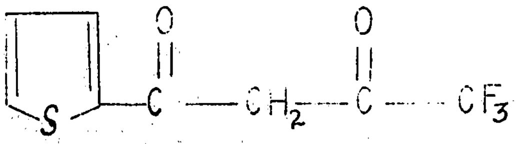
$$MX_2 + HY \overset{K_1}{=} MXY + HX$$

$$MXY + HY \overset{K_2}{=} MY_2 + HX$$

In some cases, adducts were also formed. They measured the values of K_1 and K_2 by using a spectrophotometric method.

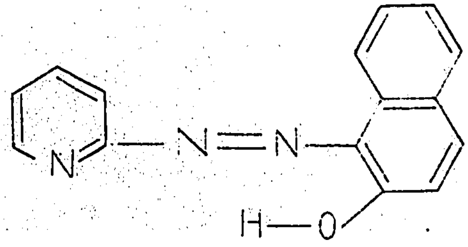
Gray and Cave[28,29] called this new area of volumetric analysis chelate-exchange titrimetry. It has some special advantages. Thus, a very large number of chelating agents are at the disposal of the analytical chemist. Until now, their use has been limited to gravimetric and colorimetric analyses. The concept of using them as titrants increases their usefulness. Further, chelate-exchange titrimetry can be accurate and precise, for very small amounts of metal.

Chelate-exchange titrimetry has been extended by d'Amboise[3], to include a study of the titration of the 2-thenoyltrifluoroacetonates of some metals by pyridylazonaphthol as titrant. The respective chelating agents are:



(HTTA')

and



(HPAN)

However, HTTA exists as enol, keto, and solvates. D'Amboise[3] studied the chelate-exchange reactions

$$\text{(A)} \quad Cu(TTA)_2 + HPAN \overset{K_1}{=} Cu(TTAPAN) + HTTA$$

$$\text{(B)} \quad Cu(TTAPAN) + HPAN \overset{K_2}{=} Cu(PAN)_2 + HTTA$$

for microgram amounts of copper. He determined the apparent equilibrium constants for reactions (A) and (B) in benzene and in methanol by a spectrophotometric method, and used a novel method of treating the data. He found that the value of K_1' was 900 in benzene, and 250 in methanol; and the value of K_2' was 0.007 in benzene and 0.600 in methanol. It was in fact an apparent equilibrium constant (K_1' and K_2') rather than a true equilibrium constant

(K_1 and K_2) that was measured. This matter is clarified in the Discussion section of the present thesis.

D'Amboise also noticed that these reactions were faster in methanol than in benzene. From a kinetic point of view then, methanol would be the better solvent for the determination of Cu(II) at trace levels. However, from an equilibrium point of view, benzene is the better solvent. In methanol, K_2' is sufficiently large to cause reaction (B) to occur to a significant degree during the titration; and K_1' is smaller than it is in benzene. As a result, the end-point in methanol was less sharp than it was in benzene.

The present investigation arose from these findings of d'Amboise, on the effects of solvents benzene and methanol on the chelate-exchange reactions (A) and (B). It was decided to measure K_1' and K_2' of these two reactions in the mixed solvent benzene-methanol, for various mole fractions of methanol. The purposes were: to study precisely how the values of K_1' and K_2' changed with the mole fraction of methanol, and to explain as far as possible the trends in K_1' and K_2' with change in solvent composition. From this study, it was hoped that a practical choice of the best solvent could be made.

A study of mixed solvents in chelate-exchange titrimetry has not previously been made on any systems. The present investigation is an exploratory one, intended to clarify at least some of the factors that affect K_1' and K_2', and to specify what factors need study, in order to be able to calculate K_1 and K_2 themselves.

2 — Plan of Research

A purpose of the present investigation was the evaluation and interpretation of the apparent molar equilibrium constants K_1' and K_2' of reactions (A) and (B)

$$\text{(A)}\quad Cu(TTA)_2 + HPAN \overset{K_1}{\rightleftharpoons} Cu(TTAPAN) + HTTA$$

$$\text{(B)}\quad Cu(TTAPAN) + HPAN \overset{K_2}{\rightleftharpoons} Cu(PAN)_2 + HTTA$$

in methanol-benzene solutions, by a spectrophotometric method. Here, $K_1' = K_1\varphi/r$, and $K_2' = K_2\varphi/p$, where φ is a function which takes into account the various species of HTTA in equilibrium; and p and r are activity-coefficient quotients.

The identification of the participating species, and the calculation of K_1' and K_2' of reactions (A) and (B) in pure benzene and pure methanol, had previously been done by d'Amboise[3].

As a first exploratory step, a study was made of the chelate exchange between $Cu(TTA)_2$ and HPAN according to reaction (A). This was needed in order to determine whether or not reaction (B) occurred to a significant degree during this step (reaction (A)), and particularly to determine the extent to which the methanol content of the methanol-benzene mixtures affected the degree to which reaction (B) occurred.

Accordingly, spectrophotometric titrations of $Cu(TTA)_2$ in these solvents were carried out with a standard solution of HPAN, at room temperature, and the degree of curvature of the titration graphs was recorded.

The first spectrophotometric method tried for the evaluation of K_1' and K_2' of reactions (A) and (B) respectively, consisted in recording absorbance values of solutions, in which the concentration of $Cu(TTA)_2$ was kept constant and the concentration of HPAN added was varied.

Absorbances were recorded at 5 nm. intervals, over the spectral range 400 nm. to 570 nm. From these spectral data, 37 absorbance equations were formulated. These equations, together with the relevant mass-balance equations, were normalized by least-squares, and solved for the unknown concentrations. This method proved to be unsatisfactory for the reliable calculation of K_1', because its value was too high for the method.

However, a reasonably good value of K_2' was obtained, and it was used as a guide for the rest of the work.

The second method used for the calculation of K_1' and K_2' consisted in spectrophotometrically following the equilibrium concentrations of Cu(TTAPAN) and/or $Cu(PAN)_2$ in reactions (A) and (B), at room temperature.

Thus, sets of solutions in methanol-benzene mixtures were prepared, in which the initial concentration of Cu(TTAPAN) was kept constant, and the initial concentration of HTTA or HPAN was changed. The absorbances of these solutions in the spectral range 540 nm. to 580 nm. were recorded. Rigorous equations to calculate K_1' and K_2' were derived, in order to treat these absorbance data. Additional information required was: (i) the initial absorbance before the addition of HTTA or HPAN to the Cu(TTAPAN) solutions; (ii) the molar absorptivities of Cu(TTAPAN) and of $Cu(PAN)_2$ in methanol-benzene mixtures, in the spectral range 540 nm. to 580 nm.; (iii) the relevant mass-balance equations. Then for each solution composition in Cu(TTAPAN) and HTTA or HPAN in one particular methanol-benzene mixture, and for each wavelength used, a value of K_1' or K_2' was obtained, at room temperature.

Measurements similar to those described above for 25°C. were also performed at 15°C. and 35°C., in pure methanol, pure benzene and in 40.9 mol% methanol in benzene. The purpose was to observe the variation of the equilibrium constants with temperature.

3 — Experimental

3.1 Apparatus

3.1.1 Spectrophotometers

a) Beckman Model D.U., and titration assembly

The titration assembly used in the present work was designed and described by Gray[1]. A synopsis of his description follows.

The conventional cell compartment of the Beckman Model D.U. spectrophotometer was replaced by a special non-magnetic compartment, which could accomodate a rectangular 65-ml. glass cell flanked by two rectangular copper tanks through which constant-temperature water was circulated. Into the center of the removable lid of the compartment, a 1-in.x1/8-in. disc of silicone elastomer was countersunk.

A calibrated 1-ml. Koch microburet with a 60-ml. reservoir, two-way Teflon stopcock, detachable tip and a Luer joint at this tip was used for the delivery of titrant to the analyte in the cell. However, it was modified as follows:

A platinum-rhodium hypodermic needle fitted with a Kel-F Luer joint (2 in. long and 28 standard gauge bore) replaced the glass capillary tip normally supplied with the buret. In use, the hypodermic needle was inserted through the silicone disc in the lid of the phototube compartment, and the tip was always immersed in the solution to be titrated in the cell.

The Beckman phototube compartment was isolated from organic solvent vapours by a thin fused-silica plate placed over the shutter opening.

A conventional magnetic stirrer was placed directly under the cell compartment, in order to allow stirring of the solution during titrations. A small Teflon-coated magnetic stirring bar was used in the cell itself, to stir the solution therein.

The cell compartment and the Koch microburet are illustrated in plate 1.

b) Beckman Model D.B. spectrophotometer, coupled to a Sargent Model SRLG Recorder, with a 10-mv. span.

c) Unicam SP 500 manual spectrophotometer, with thermostat for temperature control of the solutions.

Matched 1-cm. silica cells, labelled S (sample) and B (blank), were used in all investigations with the Beckman D.B. and Unicam S.P. 500 spectrophotometers.

3.1.2 Thermostats

a) Sargent-Welch Thermostatic Water Bath (cat. No. S-84810), control to $\pm 0.01^\circ$ C; thermistor controlled (cat. No. S-82052).

b) Sargent-Welch Thermostatic Water Bath (cat. No. S84880) for external circulation, control to $\pm 0.1^\circ$ C.

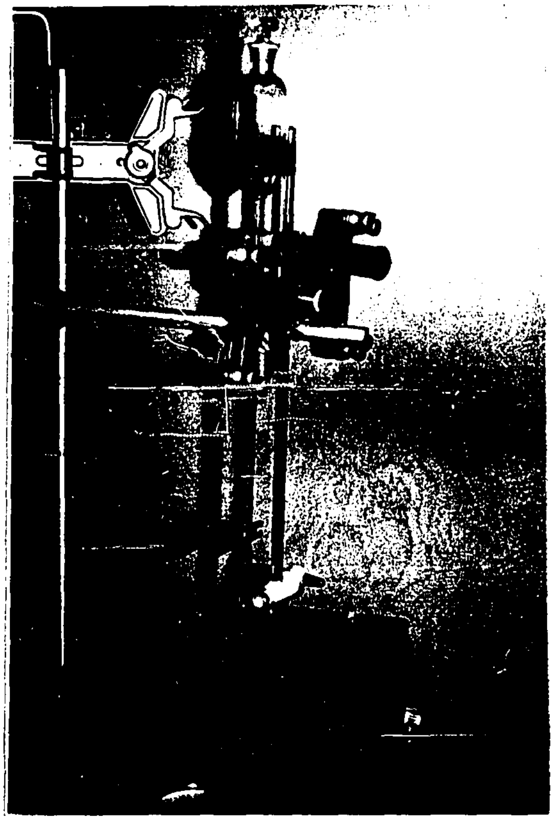
PLATE I

SPECTROPHOTOMETRIC TITRATION
APPARATUS

A- Cell compartment used for spectrophotometric titrations, with the Koch microburet positioned

B- Rectangular titration cell in cell compartment

C- Delivery needle attached to buret tip



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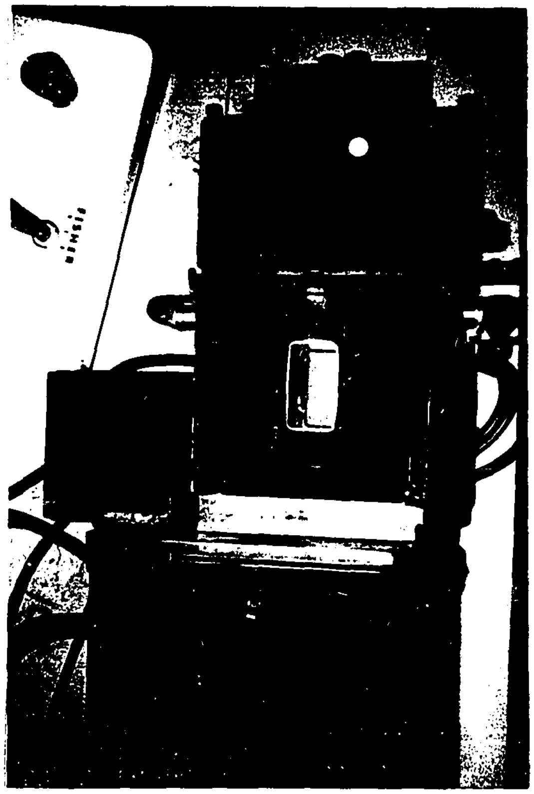

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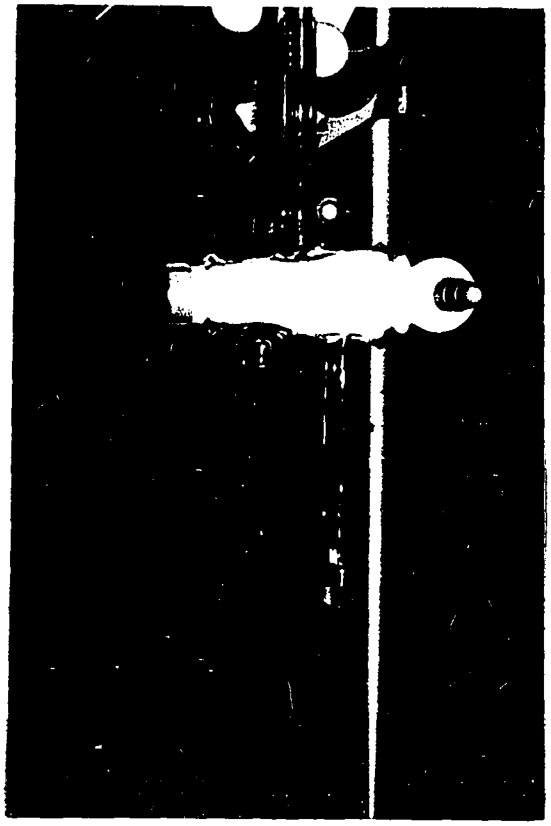

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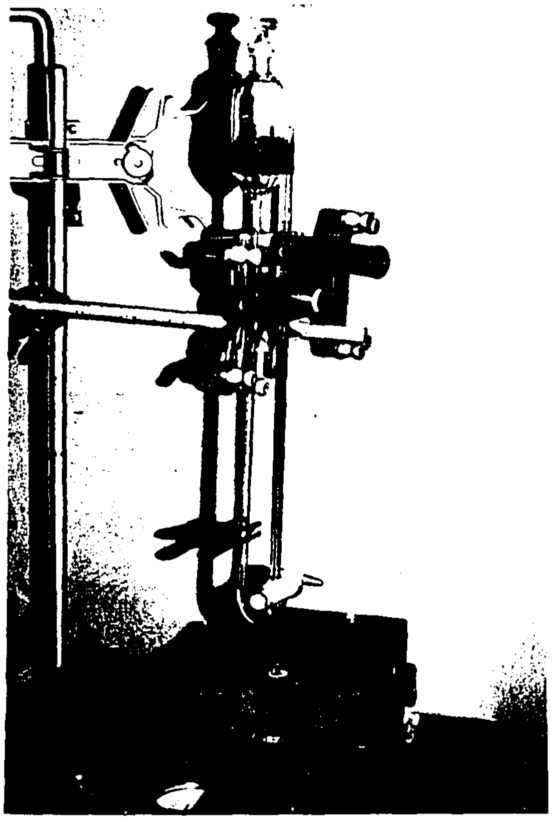

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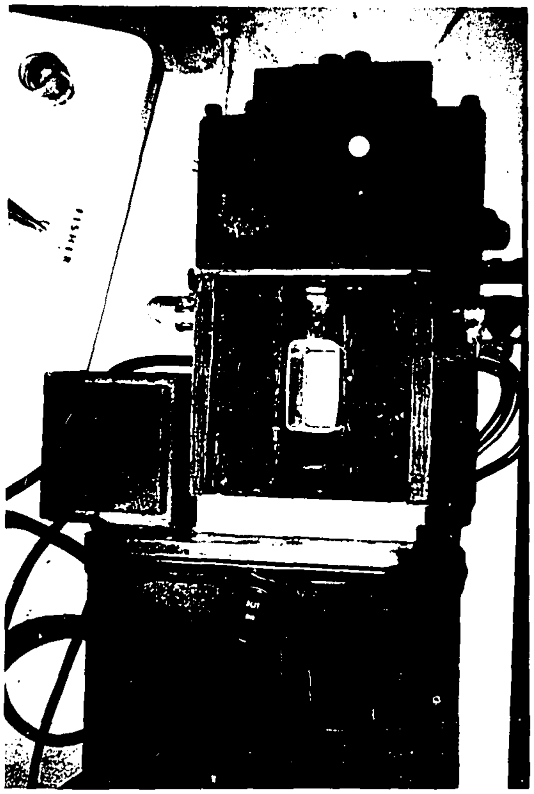

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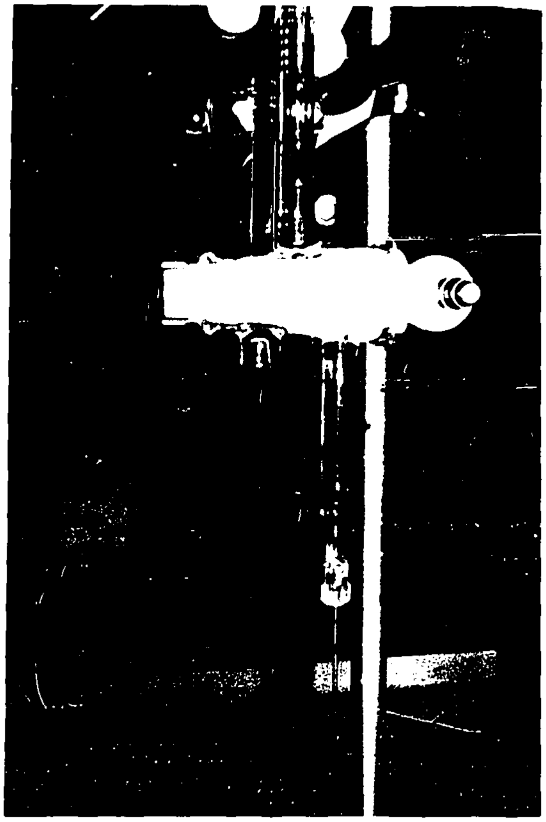


C

3.1.3 Filtration Apparatus

It was required to prepare saturated solutions of the copper chelates in benzene and methanol. In order to separate the solid metal chelates from the saturated solutions a special filtration apparatus was used. It consisted of a separatory funnel specially adapted to a filter tube with a B 14/23 ground glass joint. The filter tube assembly, which was first described and used by Khin[2], was adapted to a filtrate-collector reservoir, with a B 19/26 ground glass joint.

This apparatus is illustrated in Plate 2.

3.1.4 Glassware

The special procedure used by Gray for cleaning glassware was also used in this work. Thus, all volumetric flasks, separatory funnels and beakers were first rinsed with acetone followed by tap water. Then they were filled with a warm 4:1 (V/V) mixture of concentrated sulfuric acid and concentrated nitric acid[!], and then allowed to stand for one hour. After that they were rinsed five times with tap water, five times with distilled water, and finally with deionized water.

The volumetric flasks were dried in an oven at 130° C. before use. The other glassware was rinsed with absolute alcohol and stored in a dust-free cabinet.

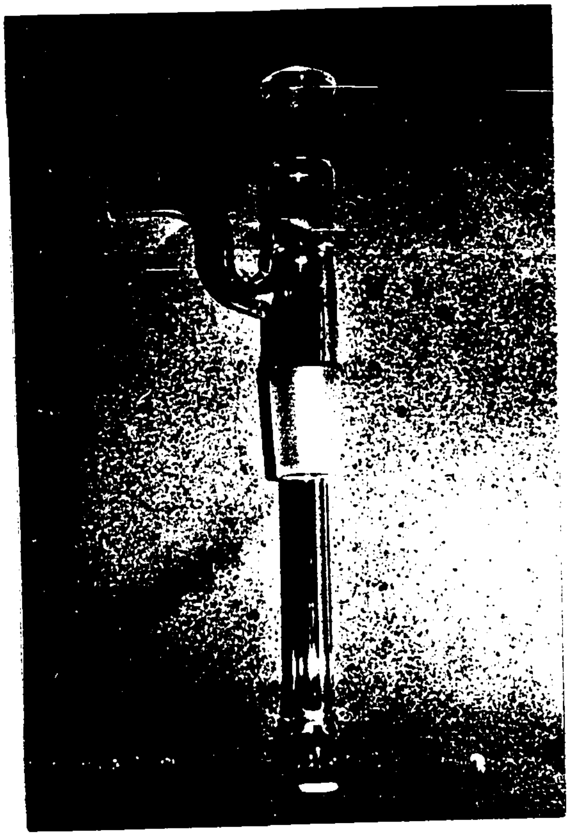
All glassware previously cleaned and dried as described above, was rinsed with methanol and/or benzene just before use.

[!] Substitution of a warm saturated solution of disodium ethylenediaminetetraacetate (henceforth abbreviated to EDTA) for this acid mixture proved to be satisfactory.

PLATE II

A) Filtration Apparatus
    A.1 Filter tube
    A.2 Filter assembly

B) Column containing a mixed-bed ion-exchange resin



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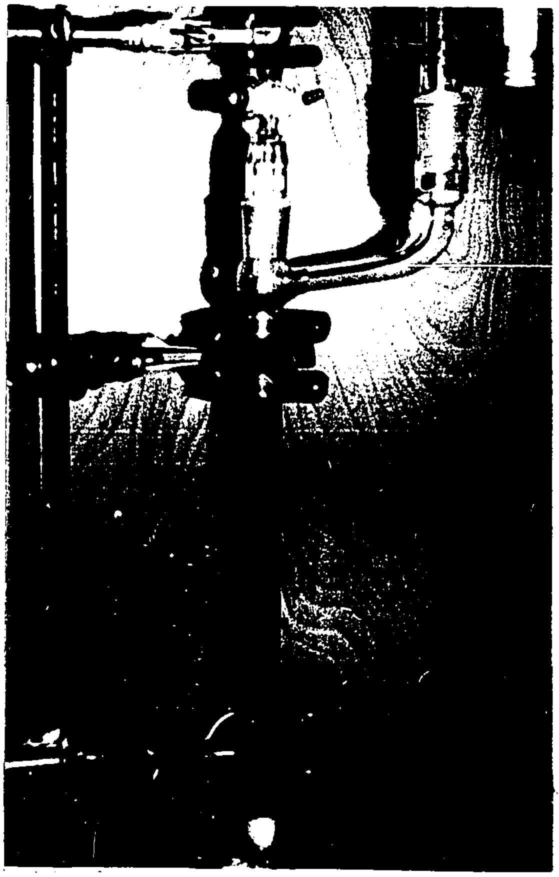

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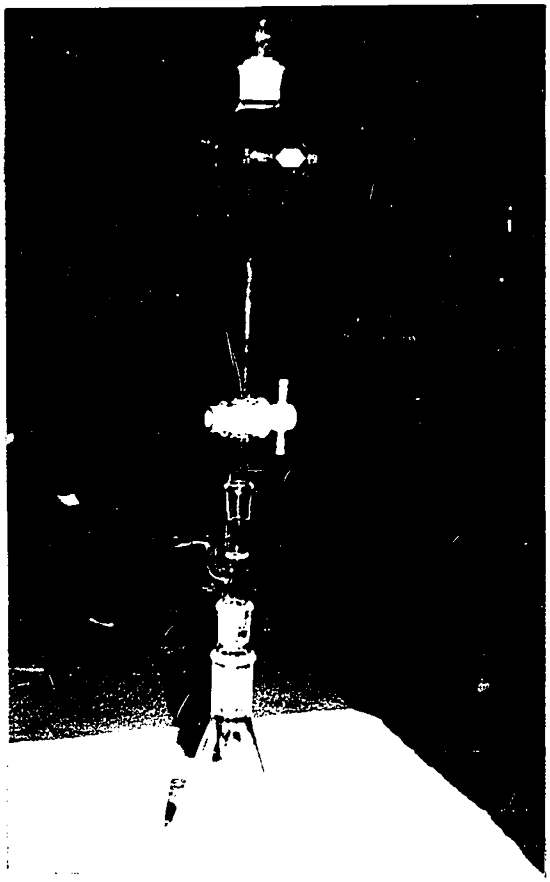

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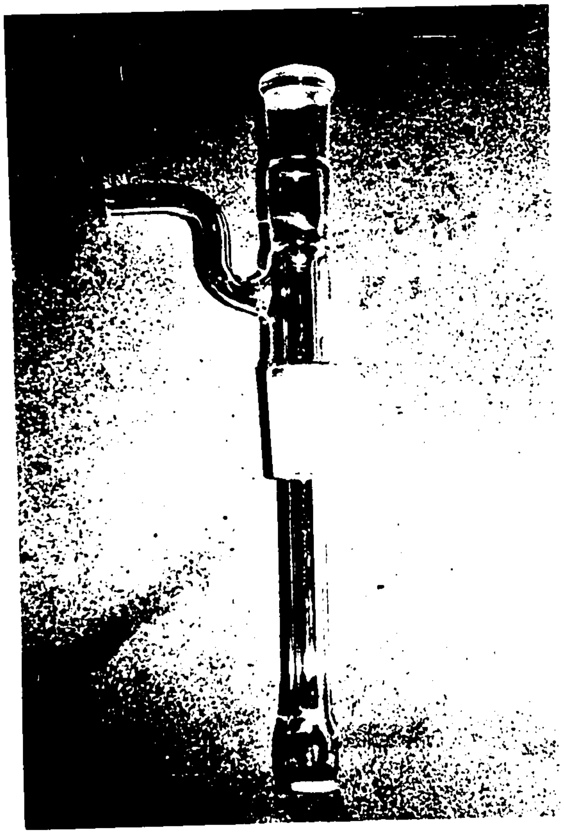

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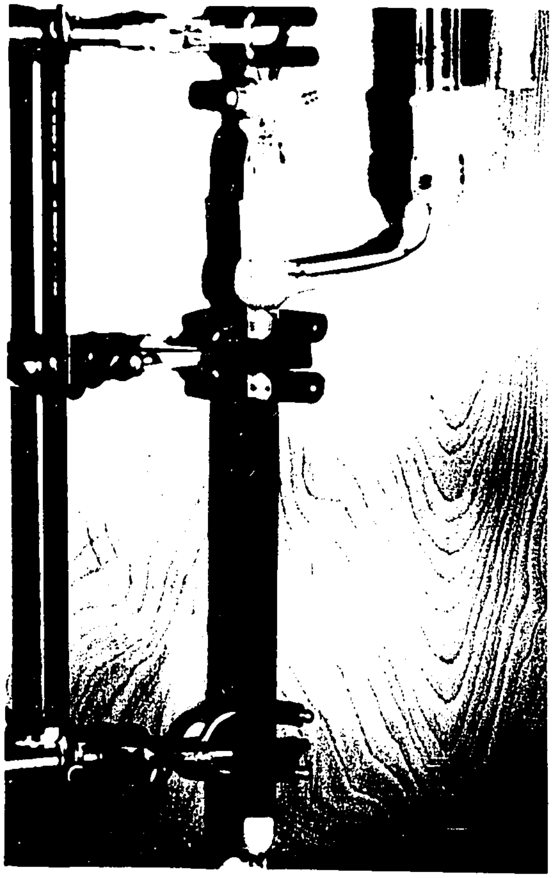

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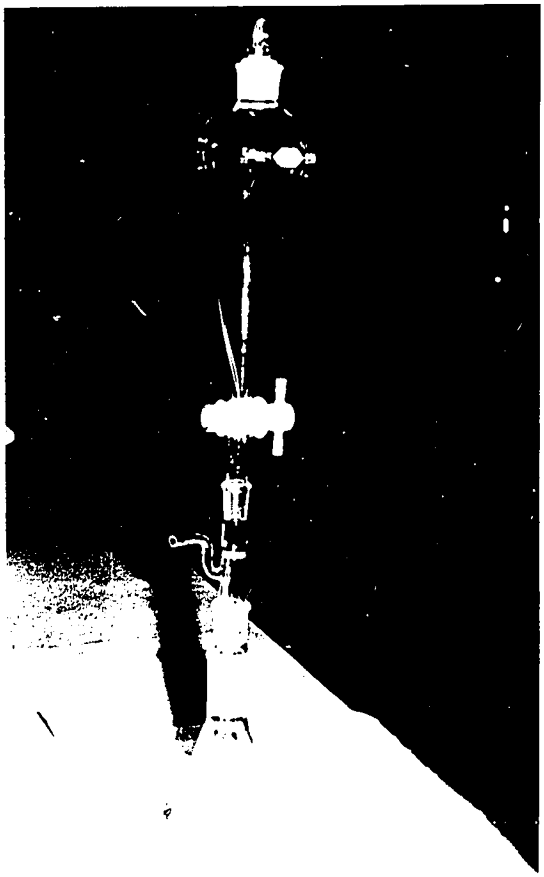


A2

The pipets were kept immersed in a 1% solution of EDTA prior to use. They were then thoroughly rinsed with tap water, deionized water and finally with absolute ethanol and dried by flushing them with dry nitrogen just before use.

3.1.5 Miscellaneous

a) Potentiometer, Leeds and Northrup Co. (cat. No. 8687).

b) Beckman Zeromatic II, pH meter.

3.2 Reagents

3.2.1 Methanol

Fisher spectranalysed grade methanol was transferred to a stoppered container which contained activated molecular-sieve granules (Linde type 3A, 1/16 in.), and allowed to stand for three weeks in order to remove water. Just before use, the resulting dried methanol was passed through a column containing a mixed-bed ion-exchange resin[19]. The column was 9 in. long and 3/4 in. in diameter and is illustrated in Plate 2. The two resins used were: (i) Fisher certified research-grade Rexyn 101 (H), organic strong-acid cation exchange, mesh size 16-50, with a total exchange capacity of 4.7 mg./g.; (ii) Baker Analysed analytical grade ion exchange strong-base resin, grade A, mesh size 16-50, with a total exchange capacity of 3.2 mg./g. Half-inch layers of each were interleaved throughout the 9-in. column.

D'Amboise[3] had shown that spectranalysed grade methanol contains significant amounts of trace metals, and that treatment of the methanol with molecular sieve granules increased the trace metals content. Therefore it was essential to eliminate these trace metals before using the methanol for chelate-exchange titrations. The mixed-bed ion-exchange resin described above sufficiently removed these trace metals. Each resin had been previously vacuum dried over P_2O_5 for three to four days. The column was then prepared by interleaving the resins as described above. Approximately 5 l. of methanol, previously dried by molecular sieve granules, was then poured through the mixed bed in order to remove the trace metals.

A special dithizone test was used in order to confirm that the purified methanol was in fact free from trace metals. This dithizone test is described in Appendix I.

The content of water in the methanol after drying it with the molecular sieve was found to be 0.27 mg. of water per ml. (Karl Fischer titration). This value did not change when the methanol was passed through the mixed-bed ion-exchange resin.

Henceforth whenever methanol is referred to it is this purified product that was used.

3.2.2 Benzene

Fisher spectranalysed grade benzene was used without further purification except that a sufficient amount of the activated molecular sieve granules (Linde Type 3A, 1/16 in.) was added to each bottle, in order to dry the benzene.

The water content of this dried benzene was determined by Kirchnerova[4]. She used a conventional Karl Fischer titration, and found the water content to be 0.035 mg. of water per ml. of benzene.

The dried benzene was found to be free of metallic impurities. The test used was the same as that described in Appendix I for benzene.

Henceforth whenever benzene is referred to it is this dried benzene that was used.

3.2.3

4,4,4-Trifluoro-1-(2-Thienyl)-1,3-Butanedione (2-Thenoyltrifluoracetone)

2-Thenoyltrifluoracetone, hereinafter referred to as HTTA, was Baker analysed reagent grade, further purified as described below.

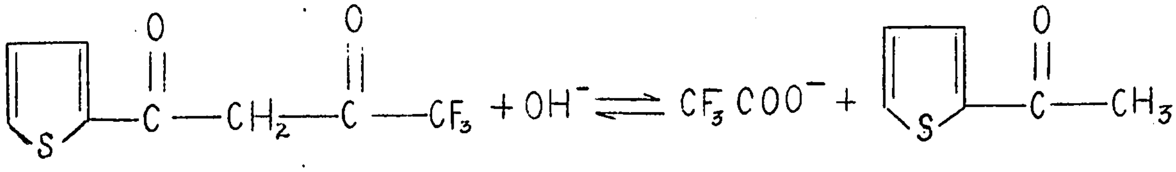
HTTA is a pale straw-yellow coloured solid, molecular weight 222.19, m.p. 42.5-43.2° C[6]. It is very soluble both in benzene and in methanol.

Usually β-diketones have been purified by vacuum sublimation. However, in the present work recrystallization proved to be satisfactory. Thus, reagent-grade HTTA was dissolved in a mixture of benzene and acetone (9:1 V/V). The acetone was A.C.S. reagent grade used without further purification. The resulting solution was heated to approximately 40° C., then a slight excess of a saturated solution of cupric acetate in water was stirred in, whereupon a precipitate of $Cu(TTA)_2$ was formed. Approximately 90% of the supernatant liquid was then evaporated without first removing the precipitate. The benzene that had evaporated was then replaced, and the mixture again evaporated, this time to about half its volume. The mixture was then cooled and filtered on a sintered-glass filter. The solid product was washed with hot water in order to remove the cupric acetate. The product was then dissolved in benzene; the benzene was then evaporated to about half its volume. The resulting mixture was cooled, filtered, and washed as before. The resulting product was again dissolved in benzene. This benzene solution was then shaken with aqueous 0.1N HCl, and the benzene phase then separated and evaporated to about a tenth of its original volume. Reagent-grade heptane was then added, and the mixture evaporated to about one-tenth its original volume. At this point crystals of HTTA had separated. The container was then immersed in an ice-water bath. The crop of HTTA crystals, approximately 5 grams, was filtered onto a fritted-glass disc, and then stored in a desiccator with silica gel, in the dark.

Assay of the purified HTTA.

The volumetric method of Reid and Calvin[7] was used. Thus, a weighed amount of HTTA was dissolved in methanol, a measured amount of aqueous 0.1 N NaOH was added, and the excess NaOH was back-titrated potentiometrically with aqueous 0.1 N HCl.

The reaction was:[7]



The assay of the purified solid HTTA was found to be 100.1 ± 0.5 (n=5) by this method. The figure 0.5 is the standard deviation. The melting point of this purified solid was found to be 44 ± 1° C. (lit. value: 42.5°C.-43.2°C.[6]).

3.2.4 Standard aqueous solution of cupric nitrate

A standard aqueous solution of cupric nitrate was used in order to standardize benzene and methanol solutions of the copper chelates and of one of the chelating agents used in the present investigation.

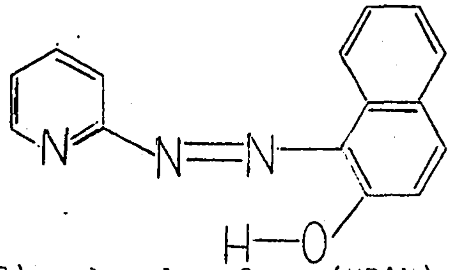
This standard aqueous solution of cupric nitrate was prepared from a weighed amount of reagent-grade copper metal, which was considered as the primary standard. The procedure is described in Appendix IV.

3.2.5
1-(2-pyridylazo)-2-naphthol

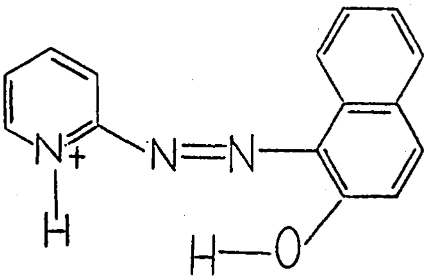
1-(2-pyridylazo)-2-naphthol, hereinafter referred to as HPAN in its molecular form, PAN in its anionic form, and (H_2PAN) in its cationic form, was Fisher certified reagent, and was used without further purification.

HPAN was first prepared by Chichibabin and Rjasanzew[8]. It is a bright-orange coloured solid, molecular weight 249.28, m.p. 137° C[10]. The melting point of the Fisher certified reagent used in the present work was 136 ± 1° C. HPAN has a tridentate ligand; it forms complexes with most metals jointly through its ortho-hydroxyl group, its azo nitrogen nearest to the phenolic ring and its heterocyclic nitrogen atom[9].

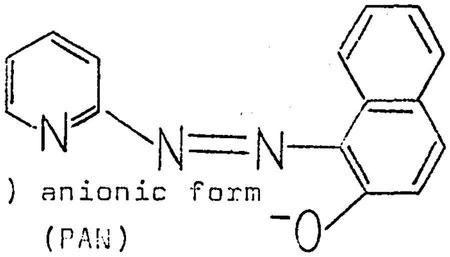
HPAN is soluble in alcohol, benzene, and in strong aqueous solutions of acids (pH 2) and alklies (pH 12)[10]; but it is practically insoluble in water and in dilute aqueous solutions of acids and alkalies. In aqueous solutions, the species in equilibrium are[10]:



2) molecular form (HPAN)



1) cationic form ($(H_2PAN)^+$)

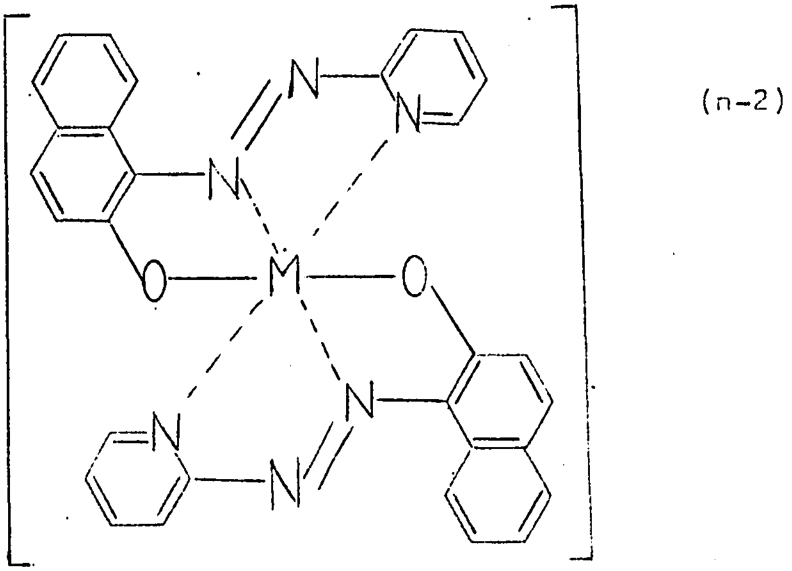


3) anionic form (PAN)

HPAN has been recommended as a complexometric indicator in direct titrations of metal ions in aqueous solutions, by standard aqueous solutions of EDTA[11,12].

The direct titration of copper with EDTA, by using HPAN as indicator, has been widely used[11,13,14].

Shibata[15] has proposed the following structure for 1:2 complexes of metal ions (M^{n+}) with PAN, in aqueous solution:



HPAN reacts slowly with most metal ions in aqueous solutions. Below pH 8 it forms a 1:1 complex with copper (II), but above pH 10 it forms a 1:2 complex[12].

Both HPAN and its copper chelate are very stable, even in dilute ethanol solutions[16].

Preparation and standardization of solutions of HPAN in benzene and methanol.

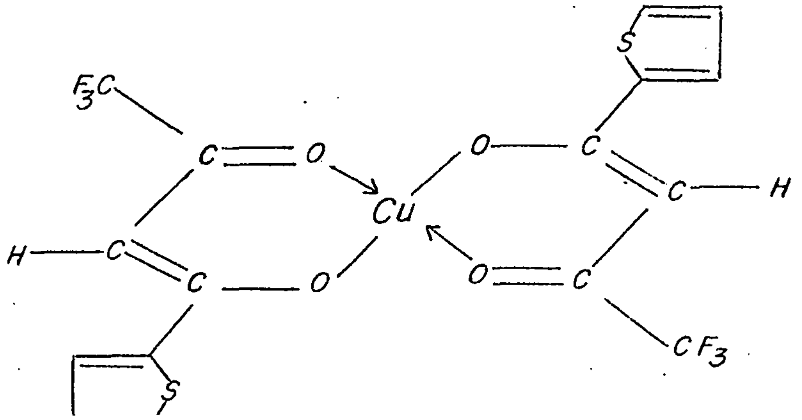
Solutions of HPAN in benzene or ethanol were freshly prepared before use. They were standardized against a standard aqueous solution of cupric nitrate as described in section 3.2.4. The standardization procedures are given in Appendix III. Briefly, one ml. of the standard $Cu(NO_3)_2$ solution was diluted with approximately 50 ml. of methanol in the 65-ml. glass titration cell of the titration assembly described on page 7. The resulting solution was then titrated with the benzene methanol solution of HPAN to be standardized. It was titrated spectrophotometrically.

3.2.6 Copper Chelates

i) Preparation and purification of the solid

a) Bis [4,4,4-Trifluoro-1-(2-Thienyl)-1,
3-butanedionato] Copper (II)

Copper (II) is coordinated with two TTA ligands by four ligand oxygen atoms, in what has been reported[17] to be a nearly square planar arrangement as follows:



Hereinafter, the symbol $Cu(TTA)_2$ refers to this square planar complex. However, proof was not provided[17] that only one isomer exists.

The preparation of the $Cu(TTA)_2$ used in this work has been described on page 16. The product was kept over silica gel in a desiccator for one week, then it was stored in the dark in a well-stoppered bottle until required for use. The melting point of this product was found to be 241± 2°C.

b) [1-(2-pyridylazo)-2-naphthol]
[4,4,4-Trifluoro-(2-Thienyl)-1,3-butanedionato]
Copper (II)

D'Amboise[3] has shown that in benzene the first ligand exchange reaction between $Cu(TTA)_2$ and HPAN is:

$$\text{A)}\quad Cu(TTA)_2 + HPAN \xrightleftharpoons{K_1} Cu(TTAPAN) + HTTA$$

where K_1 is the molar equilibrium constant:

$$3.1 \qquad K_1 = \frac{[Cu(TTA)(PAN)]\,[HTTA]}{[Cu(TTA)_2]\,[HPAN]}$$

He further showed that this mixed complex undergoes a second exchange reaction as follows:

$$\text{B)}\quad Cu(TTAPAN) + HPAN \xrightleftharpoons{K_2} Cu(PAN)_2 + HTTA$$

where K_2 is the molar equilibrium constant,

$$3.2 \qquad K_2 = \frac{[Cu(PAN)_2]\,[HTTA]}{[Cu(TTAPAN)]\,[HPAN]}$$

However, D'Amboise[3] has also shown that when benzene is the solvent, the ratio K_1 to K_2 is of the order of 10^6. Therefore, when equimolar amounts of $Cu(TTA)_2$ and HPAN are mixed in benzene, approximately 99.8% of the copper present in the system is as Cu(TTAPAN). Since HPAN and HTTA are much more soluble in benzene than are the copper chelates, the Cu(TTAPAN) can be obtained free from HTTA and HPAN by several recrystallizations from benzene. This was the method devised by D'Amboise[3] for the preparation of solid Cu(TTAPAN); the detailed procedure is given in Appendix V.

Solid Cu(TTAPAN) was a dark-brown colour. Methanol-benzene solutions of it were violet, and proved to be very stable because there was no change in absorbances of the solutions over a two-month period. The melting point of the purified dried solid was found to be 250 ± 2°C. (D'Amboise found 258°C. for his products[3]).

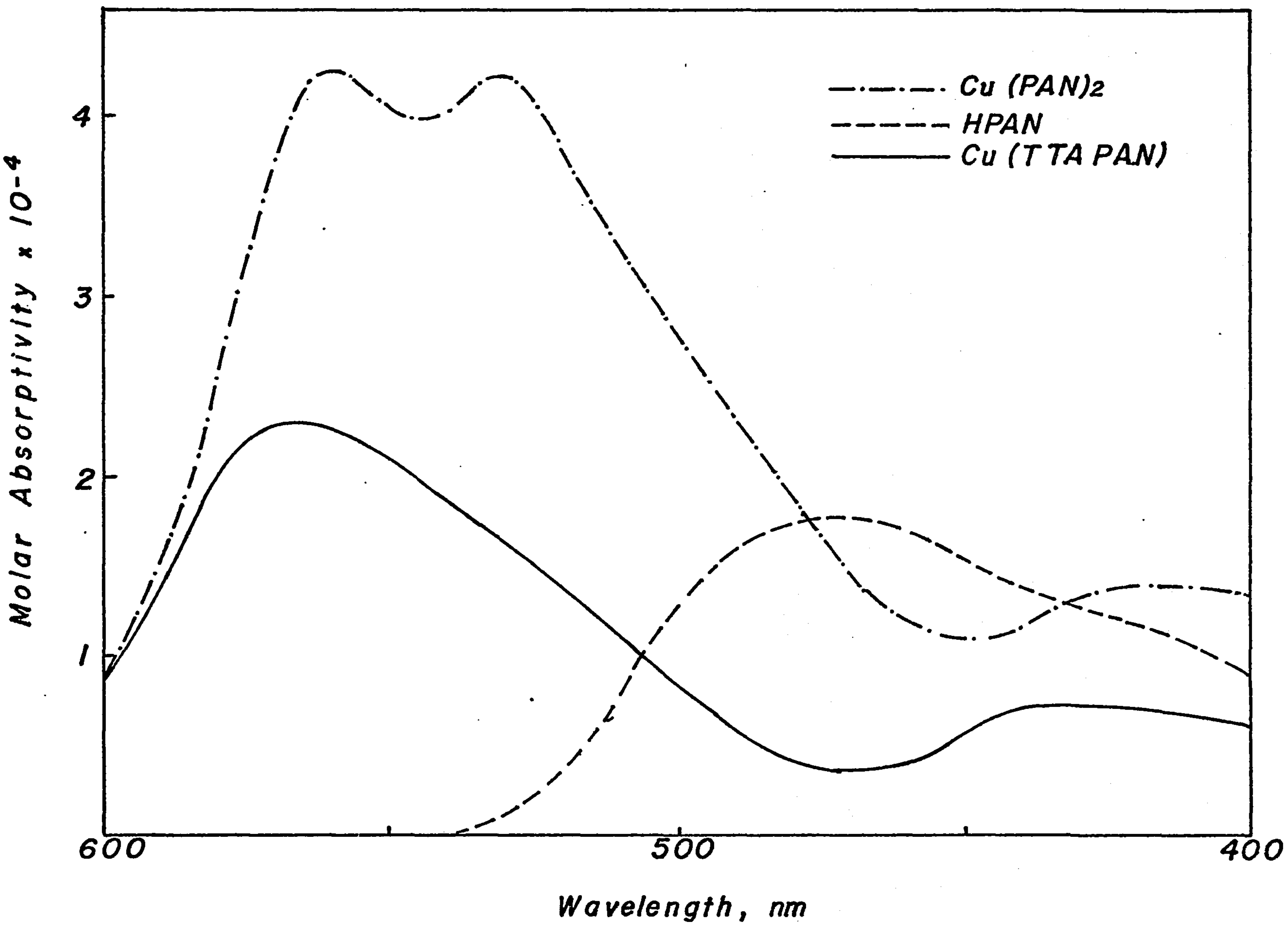
The solubility of Cu(TTAPAN) in benzene was found[3] to be approximately 8×10^{-4} M, and in methanol it was approximately 2×10^{-4} M .

The dried purified Cu(TTAPAN) was analysed for copper content and HPAN content by methods described on page 27. The results of those analyses are as follows: Copper 11.99% (expected 11.93%); PAN 46.80% (expected 46.59%).

The absorption spectrum of Cu(TTAPAN) in a benzene-methanol mixture that was 35.4 mol% in methanol was recorded in the range 400 nm. to 600 nm.; it is reproduced in Figure 1. The molar absorptivities in this wavelength range are tabulated on page 149.

FIGURE 1

The molar absorptivity curves of Cu(TTAPAN), $Cu(PAN)_2$ and HPAN in 35.4 mol% methanol in benzene, in the spectral range 400 nm. to 600 nm., at 20°C.


Cu (PAN)2
HPAN
Cu (T TA PAN)
Molar Absorptivity x 10-4
4
3
2
1
600
500
400
Wavelength, nm

c) Bis[1-(2-pyridylazo)-2-naphtholato] Copper (II)

The $Cu(PAN)_2$ used in the present work was prepared and purified by d'Amboise[3], as follows:

A solution of HPAN in methanol was prepared by dissolving 3 g. of the Fisher certified reagent in 100 ml. of methanol, previously heated to approximately 50°C. A second solution was prepared by dissolving 1.2 g. of reagent-grade $Cu(NO_3)_2 \cdot 3H_2O$ in 50 ml. of a 1:1 (V/V) methanol-water mixture. The temperature of this solution was raised to 50°C., and slowly added to the HPAN solution in methanol at 50°C. After cooling the mixture to room temperature, the resulting precipitate was filtered onto a sintered-glass filter. The resulting crystals were then dissolved in about 250 ml. of a 1:1 (V/V) benzene-hexane mixture, which was then allowed to evaporate at room temperature to approximately half of its initial volume. The resulting product was filtered as above and stored in a desiccator over P_2O_5, in the dark.

ii)
The preparation of standard solutions of the three copper chelates in methanol and benzene.

The copper chelate (Cu(TTAPAN), $Cu(TTA)_2$ and $Cu(PAN)_2$) and the solvent (benzene or methanol) were put into a dry volumetric flask. The contents were then shaken by attaching the stoppered volumetric flask to a Burrell wrist-action shaker, and shaking them for a period of up to forty-eight hours, depending on the solubility of the complex. In this way, solutions were obtained which were almost saturated. The lowest concentration was that of $Cu(PAN)_2$ in methanol, 5×10^{-5} M. The solutions of Cu(TTAPAN) and $Cu(TTA)_2$ were more concentrated.

The mixture in the volumetric flask was then filtered in the special filtration apparatus shown in Plate 1 which was dried just before use. The filtrate was then stored in a stoppered flask.

Prior to using each solution prepared in this way, the concentration of its metal chelate was determined by a spectrophotometric titration with a standard aqueous solution of EDTA. The details of this procedure are in Appendix III.

Briefly, a 1-ml. aliquot of the metal chelate in either benzene ormethanol was transferred to the 65-ml. titration cell described in connection with the titration assembly on page 7. To this 1 ml. were added about 50 ml. of methanol. A standard aqueous solution of EDTA was then titrated into this analyte, and the end point determined by spectrophotometric means.

iii)

Methods of Assay

The purity of the three copper complexes, namely $Cu(TTA)_2$, Cu(TTAPAN) and $Cu(PAN)_2$, was determined by determination of the copper content, and in the case of Cu(TTAPAN) and $Cu(PAN)_2$ by determination also of the ligand (PAN) content. For the case of $Cu(TTA)_2$ and Cu(TTAPAN), the assay method consisted in preparing a standard solution of the complex either in benzene or in methanol, and then assaying this standard solution for copper; the standard solution of Cu(TTAPAN) was also assayed for the ligand HPAN. In the case of $Cu(PAN)_2$, the solubility in the organic solvent was too low to permit the preparation of a standard solution by weighing the $Cu(PAN)_2$. Therefore, for this copper chelate the procedure used consisted in preparing an almost saturated solution and assaying it for copper and for the PAN ligand, and to rely on the ratio of these two constituents as proof of purity. However, in addition to this ratio it was possible to confirm purity by a determination of the melting point, as previously described.

a)
Determination of the copper content of the copper chelate.

A measured aliquot of the standard solution of the copper chelate in benzene or methanol was diluted by the addition of approximately 50 ml. of methanol in the 65-ml. spectrophotometric titration cell. The resulting solution was titrated spectrophotometrically by using a standard aqueous solution of EDTA that had been standardized against metallic copper. Details of the procedure are given in Appendix III.

b)
Determination of the PAN content of Cu(TTAPAN) and $Cu(PAN)_2$.

This determination was carried out by two different procedures, as follows:

b1) One of the standard solutions in methanol, used for the determination of the copper content of the chelate, was also used for the determination of the PAN content of Cu(TTAPAN) and of $Cu(PAN)_2$. Eight aliquots of this standard solution were diluted with methanol, so as to provide eight solutions, which ranged in concentration from 4×10^{-5} M to 5×10^{-6} M.

The absorbance of each solution was measured in a 1-cm. cell at 560 nm., against methanol as the spectrophotometric blank. The molar absorptivities of the copper complex in methanol were calculated from these data. The values are entered in table. 16.

To each of the eight solutions a few milligrams of EDTA powder were added. The resulting mixtures were shaken in order to ensure essentially complete displacement of the ligand PAN from the copper chelate. In order to ensure that displacement was in fact essentially complete, the absorbance of each solution was then measured at 560 nm. where Cu(TTAPAN) and Cu(PAN)$_2$ are known to absorb and where HPAN itself does not absorb. In all cases the absorbances at this wavelength were negligibly small, thereby proving that displacement of the PAN from the copper chelate was essentially complete. The HPAN remained in solution; the copper existed as the solid EDTA complex along with the excess EDTA powder.

HPAN itself absorbs with the peak at 460 nm. Therefore the HPAN content of the eight solutions was measured at 450, 460, 465 and 470 nm. The molar absorptivities of HPAN itself in methanol had previously been measured from standard solutions of HPAN in methanol. These molar absorptivities are reported in Table 1. These values were used in order to calculate the free HPAN concentration in each of the eight solutions, which in turn gave the HPAN content of the original solid. The results are entered in Table 2 for Cu(PAN)$_2$ and in Table 3 for Cu(TTAPAN).

b2) Aliquots of a standard solution of Cu(TTAPAN) in benzene previously analysed for the copper content were transferred to a set of 25-ml. volumetric flasks and diluted to volume with benzene. To each of these

Table 1

Spectrophotometric data and absorptivities of HPAN in:
1) Methanol at 450 nm., 460 nm., 465 nm., and 470 nm.
2) Benzene saturated with water at 460 nm.

Spectrophotometer — Unicam S.P. 500

Cells — silica, 1-cm. light path

Temperature = 25 ± 2°C.

1) Solvent — methanol

Soln. No.	[HPAN] M$\times10^{5}$	Absorbance 450nm	460nm	465nm	470nm	Wavelength, nm.	Mean Molar Absorptivity* x 10^{-4}	std. Dev. (n=8) x10^{-4}
1	7.109	1.179	1.250	1.247	1.226			
2	6.219	1.036	1.098	1.095	1.075			
3	5.331	0.905	0.952	0.950	0.930	450	1.656	0.010
4	4.443	0.742	0.787	0.785	0.772	460	1.756	0.007
5	3.554	0.602	0.635	0.634	0.622	465	1.752	0.007
6	2.667	0.450	0.475	0.475	0.466	470	1.718	0.005
7	1.777	0.302	0.319	0.319	0.315			
8	0.889	0.153	0.160	0.159	0.157			

2) Solvent — benzene saturated with water

Soln. No.	[HPAN] M$\times10^{5}$	Absorbance 460nm	Mean Molar Absorptivity** x 10^{-4}	Standard Deviation (n=6) x 10^{-4}
1	4.548	0.786		
2	3.790	0.660		
3	3.032	0.525	1.726	0.006
4	2.274	0.397		
5	1.516	0.263		
6	0.758	0.134		

* Mean of eight determinations, on solutions 1-8 in methanol.

** Mean of six determinations, on solutions 1-6 in benzene.

Table 2

Analysis of $Cu(PAN)_2$

(The sample was dissolved in methanol prior to analysis)

Soln. No.*	Concentration of $Cu(PAN)_2$ in methanol* M x 10^5	Absorbance of solution after removal of Cu by EDTA.!			Concentration of HPAN, calculated from cols. III-V and molar absorptivity (see Table 1), M x 10^5				Ratio of PAN to Cu in sample (Col. IX / Col. II)
		460nm	465nm	470nm	460nm	465nm	470nm	mean for 3 wavelengths	
1	1.015	0.350	0.350	0.341	1.993	1.998	1.984	1.992	1.96
2	2.200	0.763	0.761	0.746	4.344	4.345	4.341	4.343	1.97
3	1.862	0.646	0.646	0.634	3.678	3.688	3.689	3.685	1.98
4	1.523	0.528	0.525	0.516	3.006	2.997	3.003	3.002	1.97
5	0.846	0.292	0.290	0.285	1.663	1.656	1.659	1.659	1.96
6	0.677	0.236	0.235	0.229	1.344	1.342	1.333	1.340	1.98
7	0.508	0.176	0.176	0.173	1.002	1.005	1.007	1.005	1.98
8	0.423	0.149	0.147	0.143	0.848	0.839	0.832	0.840	1.99
									mean ratio = 1.97

---

* Solutions 1-8 were prepared from aliquots of a stock standard solution of the $Cu(PAN)_2$ to be analysed. The stock standard solution was prepared as described in Section 3, Subsection 3.2.6(ii). It was analysed for Cu by spectrophotometric titration with EDTA, and found to be $(4.231 \pm 0.017) \times 10^{-5}$M.

! The absorbance was due to liberated HPAN.

Table 3

Analysis of Cu(TTAPAN) for Cu and PAN by solution of a weighed amount of the solid in methanol and determination of both Cu and PAN content (see procedure bl on page 27)

Soln. No.*	Concentration of $Cu(PAN)_2$ in methanol* M x 10^5	Absorbance of solution after removal of Cu by EDTA !				Concentration of HPAN, calculated from Cols.III-VI, and molar absorptivity. (See Table 1) M x 10^5	Ratio of (PAN) to (Cu) in sample. (Col.VII/ Col.II)
		450nm	460nm	465nm	470	mean for 4 wavelengths	
1	5.472	0.892	0.944	0.944	0.920	5.354	0.98
2	4.864	0.792	0.838	0.838	0.818	4.760	0.98
3	4.256	0.690	0.733	0.731	0.718	4.178	0.98
4	3.648	0.592	0.625	0.622	0.612	3.562	0.98
5	3.040	0.496	0.522	0.519	0.510	2.975	0.98
6	1.824	0.299	0.318	0.315	0.312	1.806	0.99
7	1.216	0.197	0.210	0.210	0.206	1.198	0.99
8	0.608	0.098	0.106	0.105	0.104	0.602	0.99
							mean ratio = 0.98

Concentration of the stock Cu(TTAPAN) solution in methanol (M x 10^4)

From the weighed solid (theoretical)	From spectrophotometric titration with EDTA (n=3)	From the mean ratio given in Col. VIII
1.513	1.520±0.002	1.494±0.008

Comparison of the results			
	Cu%	Theoretical: 11.93	Found: 11.99
	PAN%	Theoretical: 46.59	Found: 45.94

* Solutions 1-8 were prepared by diluting aliquots of a stock standard solution of Cu(TTAPAN) 10-fold. This standard solution was prepared from a known weight of the solid (to give 1.513 x 10^{-4} M), and standardized with EDTA to give Col. II.

! The absorbance was due to liberated HPAN.

flasks, 6 ml. of aqueous 0.1 N HCl were added after first removing 6 ml. of the standard solution in benzene. The two-phase system was then equilibrated by shaking at room temperature, and the two phases were then allowed to separate. By this step, the copper was quantitatively transferred to the aqueous phase and the HPAN and HTTA were quantitatively left in the benzene phase.[!] The absorbance of the benzene phase was then measured at 460 nm. (which is the peak of HPAN in benzene). The concentration of HPAN in the benzene phase was then calculated by means of the following formula, which has been derived by Galik[16]:

$$3.3 \qquad [\mathrm{HPAN}] = \frac{A_{460} - A_{560} \cdot R}{a_{460}\mathrm{HPAN}} + \frac{A_{560}}{a_{560}\mathrm{CuTP}}$$

where:

a_{λ} CuTP = molar absorptity of Cu(TTAPAN) at wavelength λ

A_{λ} = absorbance at wavelength λ

$$R = \frac{a_{460}\mathrm{CuTP}}{a_{560}\mathrm{CuTP}}$$

a_{460}HPAN = the molar absorptivity of HPAN at 460 nm. in benzene saturated with aqueous 0.1 N HCl. This value is given in Table 1, and was determined independently by measuring the absorbances of standard benzene solutions of HPAN in benzene.

[!] The dissociation constant of H_2PAN^+ in water has been reported to be 1×10^{-3} [10]. The distribution ratio of HPAN between carbontetrachloride and pure water has been reported to be 1×10^{4} [10]. It seems reasonable to suppose that the distribution coefficient between benzene and water is not very different from that between carbontetrachloride and water. By using these data, it is readily shown that the HPAN remains quantitatively in the benzene phase.

The molar absorptivities of Cu(TTAPAN) in benzene at 460 nm. and at 560 nm. had already been measured by d'Amboise[3], and his values were used in the present work.

The values of the necessary measured absorbances are reported in Table 4, together with the concentrations of HPAN in all the solutions, calculated from these absorbances and equation 3.3. From these concentrations and the weight of the solid used in the preparation of the standard solution, the PAN content of the Cu(TTAPAN) was calculated, and these values are entered in Table 4. This Table also contains the values found for the copper content of the Cu(TTAPAN), as determined by the previously described spectrophotometric titration with EDTA.

An alternative procedure was also used as a check to ensure that in the above-described procedure for the determination of PAN in Cu(TTAPAN), the HPAN remained in the benzene phase after equilibration with the 6 ml. of aqueous 0.1 N HCl. Thus, a 50-ml. aliquot of the standard solution of Cu(TTAPAN) in benzene was transferred to a separatory funnel and equilibrated with 20 ml. of an aqueous solution of 0.1 N HCl. The aqueous phase was then quantitatively transferred to another separatory funnel which contained about 40 ml. of benzene. The two phases were then equilibrated. If any HPAN had remained in the aqueous phase, some would be re-extracted into the benzene. The two benzene extracts of HPAN were then combined in a 100-ml. volumetric flask and diluted to volume.

To an aliquot of a standard aqueous solution of $Cu(NO_3)_2$ in the 65-ml. cell, 50 ml. of methanol were added. The benzene extract of the HPAN was then titrated

Table 4

Analysis of Cu(TTAPAN) for Cu and PAN, by dilution of a weighed amount of solid in benzene, and determination of the copper content by spectrophotometric titration, and the HPAN content as in procedure b2 on p 28

Soln. No.*	Concentration of Cu(TTAPAN) in benzene* $M \times 10^5$	Absorbance of solution after removal of Cu by 0.1 N HCl!		Concentration of HPAN, calculated from the data in Cols. III and IV, and equation 3.3 $M \times 10^5$
		560nm	460nm	
1	4.548	0.046	0.763	4.665
2	"	0.037	0.770	4.653
3	"	0.069	0.742	4.670
4	"	0.012	0.785	4.603
5	"	0.043	0.765	4.657
6	"	0.020	0.787	4.656
7	"	0.022	0.783	4.649
8	"	0.034	0.770	4.640
9	"	0.031	0.770	4.620
10	"	0.013	0.784	4.602
11	"	0.013	0.785	4.608
12	"	0.012	0.784	4.697
13	"	0.017	0.785	4.622
14	"	0.054	0.760	4.689
15	"	0.072	0.746	4.608
16	"	0.018	0.788	4.653
17	"	0.021	0.778	4.609
18	"	0.021	0.778	4.609
				mean value = 4.640
				st.dev. = 0.030

Analysis of Cu(TTAPAN) from Cols. II and V, and amount of Cu(TTAPAN) taken:

Cu: 11.89% (theor. 11.95%)

PAN: 47.35% (theor. 46.59%)

* Solutions 1-18 were prepared by diluting 10-fold a stock standard solution of Cu(TTAPAN), which was prepared from a known weight of the solid (to give 4.565×10^{-4} M), and standardized with EDTA to give Col. II.

! The absorbance was due to liberated HPAN.

into this copper solution, as described in Appendix III. The values obtained for this particular procedure are as follows: Cu 12.08% (expected 11.93%), HPAN 47.12% (expected 46.59%).

4 — A Preliminary Study of the Chelate Exchange Between $Cu(TTA)_2$ and HPAN in Methanol-Benzene Mixtures.

The purpose of the present investigation was the evaluation of the equilibrium constants K_1' and K_2' for the following reactions

$$(A)\ Cu(TTA)_2 + HPAN \xrightleftharpoons{K_1} Cu(TTAPAN) + HTTA$$

$$(B)\ Cu(TTAPAN) + HPAN \xrightleftharpoons{K_2} Cu(PAN)_2 + HTTA$$

in methanol-benzene mixtures, by a spectrophotometric method.

D'Amboise[3] has already shown that in benzene the ratio K_1'/K_2' is of the order 10^5. When $Cu(TTA)_2$ in benzene is titrated with HPAN by the present spectrophotometric method, one break is observed in the titration graph, and it corresponds to the formation of Cu(TTAPAN). The formation of $Cu(PAN)_2$ is never seen in this titration graph because of the extremely small value of K_2. However, when methanol was the solvent, d'Amboise had shown that the ratio K_1'/K_2' was of the order 500. In that case the titration graph might be curved due to the formation of a significant amount of $Cu(PAN)_2$. Accordingly, spectrophotometric titrations of $Cu(TTA)_2$ in benzene-methanol mixtures were carried out with a standard solution of HPAN, by using the titration apparatus shown in Plate 1.

The titration procedure is described in Appendix VI. Results of titrations of $Cu(TTA)_2$ with a standard solution of HPAN in benzene, in several benzene-methanol mixtures, are given in Table 5. The $Cu(TTA)_2$ solutions

Table 5

Spectrophotometric Titration of $Cu(TTA)_2$ in methanol-benzene mixed solvents, with a standard HPAN solution in benzene.

Apparatus: Beckman Model DU spectrophotometer and titration assembly (see Plate 1).

Cell: 65-ml. glass cell with 5-cm. light path

Wavelength: 560 nm.

Temperature: 25 ± 2°C.

Methanol-benzene composition, mol% methanol	Initial concentration of $Cu(TTA)_2$, M x 10^5		
	From weight of $Cu(TTA)_2$ taken	From standardization against EDTA, using procedure in Appendix III	From titration against HPAN, using procedure in Appendix VI
8.4	3.151	3.160 ± 0.008*	3.126 ± 0.025
16.0	1.700	1.699 ± 0.009	1.702 ± 0.020
25.1	"	1.694 ± 0.005	1.703 ± 0.022
33.4	"	1.696 ± 0.006	1.708 ± 0.037
45.3	"	1.697 ± 0.007	1.701 ± 0.024
54.7	"	1.697 ± 0.007	1.696 ± 0.031
68.7	"	1.697 ± 0.008	1.731 ± 0.011
79.7	"	1.692 ± 0.006	1.761 ± 0.022

* The ± values are standard deviations for three samples.

were prepared from weighed amounts of $Cu(TTA)_2$. Column 2 in Table 5 gives the solution concentrations calculated from these weighed amounts of $Cu(TTA)_2$. The solutions were then separately standardized for copper, against a standard solution of EDTA, as described in Appendix III. The results are in Column 3 of Table 5. Finally, the same solutions were standardized against the standard solution of HPAN, as specified in Appendix VI. The results are in Column 4. Typical titration graphs are shown in Figure 2.

4.1 — Spectrophotometric absorption data for $Cu(TTA)_2$, Cu(TTAPAN), $Cu(PAN)_2$, HTTA and HPAN in benzene-methanol mixtures.

A knowledge of the absorption spectra of the chelating agents and the copper chelates was necessary in order to select the optimum wavelength for use. The relevant data have been collected together in Table 6.

4.2 — The absorption spectra of benzene-methanol solutions of mixtures of $Cu(TTA)_2$ and HPAN, in the range 400 nm. to 570 nm.

These absorption data were required in order to estimate the values of K_1 and K_2 for the two reactions written on page 36.

Stock standard solutions of $Cu(TTA)_2$, HPAN, Cu(TTAPAN) and $Cu(PAN)_2$ in benzene were prepared, and standardized as described in Appendix III.

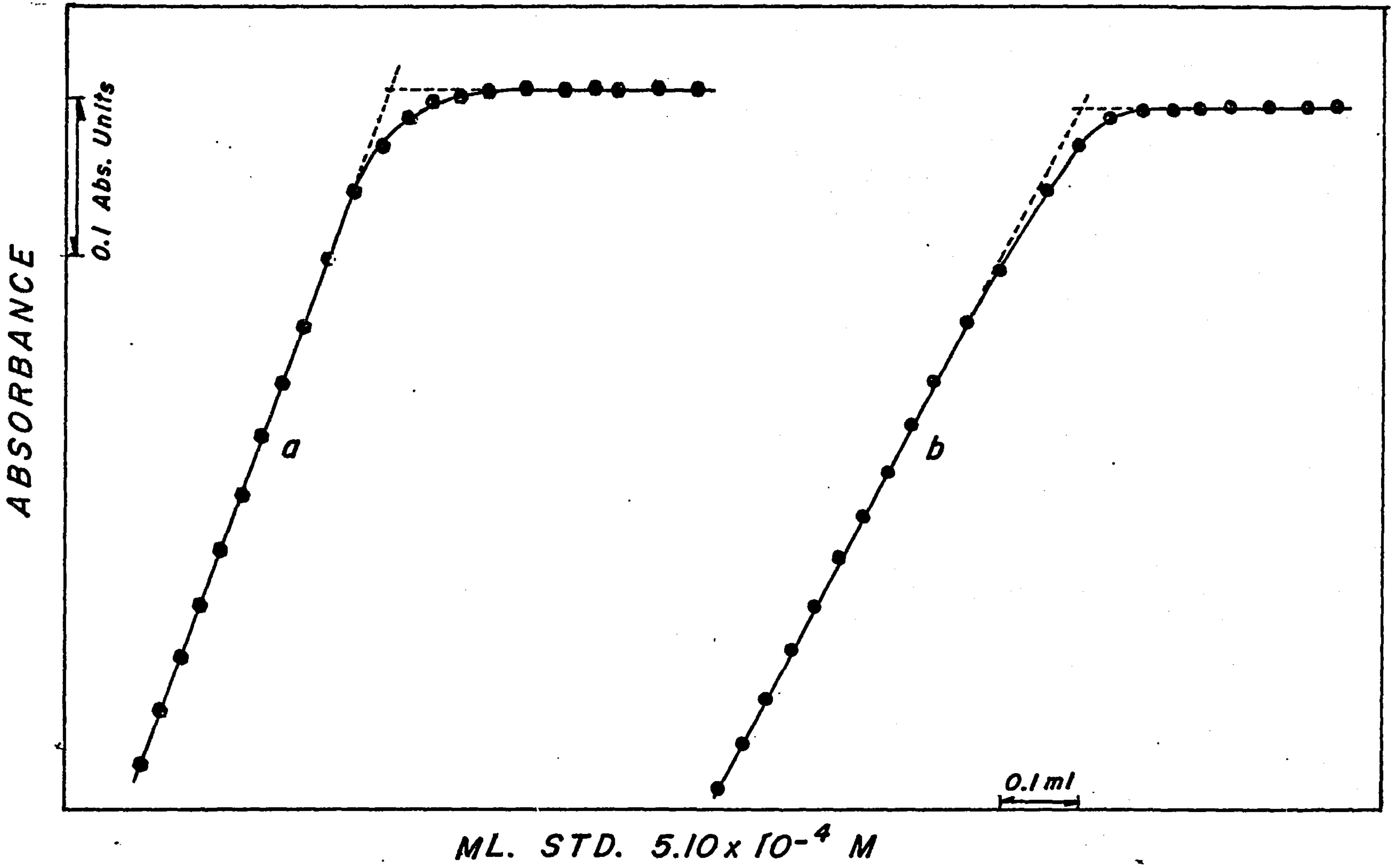
Aliquots of these stock standard solutions were

FIGURE 2

Typical titration graphs of the spectrophotometric titration of $Cu(TTA)_2$ at 25°C., with HPAN in the solvents:

a) 8.4 mol% methanol in benzene

b) 54.7 mol% methanol in benzene


0.1 Abs. Units
ABSORBANCE
a
b
0.1 ml
ML. STD. 5.10 x 10⁻⁴ M

<u>Table 6</u>

Spectrophotometric absorption data for HTTA, HPAN, $Cu(TTA)_2$, Cu(TTAPAN) and $Cu(PAN)_2$ in benzene, methanol, methanol-benzene mixtures, and other solvents.

Compound	Solvent	Absorption maxima (nm)	Ref.
$HTTA \cdot H_2O$	Aqueous acid	260, 270	18
HTTA (enol)	benzene	325	18
TTA^- (enolate ion)	aqueous alkali	340	18
HTTA	benzene, methanol	no absorption greater than 400	13
HTTA (enolate ?)	benzene-methanol (1:1 V/V)	338	18
$Cu(TTA)_2$	benzene, methanol	345, 360 (shoulder); no absorption greater than 400	This work
HPAN	benzene, methanol	} see fig. 1	This work
Cu(TTAPAN)	benzene,methanol		This work
$Cu(PAN)_2$	benzene, methanol		This work

pipetted into 25-ml. volumetric flasks, and the appropriate benzene-methanol mixture was added. The compositions of these various sets of solutions are given in Table 7.

After the solutions had been prepared they were allowed to stand for two days in stoppered volumetric flasks in the dark, in order to allow the establishment of equilibrium. D'Amboise had previously shown that equilibrium was established within an hour.[3]

The spectral transmission curves of all solutions were then recorded at 20°C. in a silica cell with a 1-cm. path length, by using the Beckman DB spectrophotometer coupled to a Sargent recorder. The cell housing of the spectrophotometer was thermostated by circulating through its water-jacket of constant temperature water from a Sargent-Welch thermostat control to ± 0.01°C. The spectrophotometric blank was 35 mol% methanol in benzene.

4.3 — Experimental results and treatment of the spectrophotometric data.

From the measured absorbances and concentrations of the solutions specified in sets 1 to 3 inclusive in Table 7, the molar absorptivities of Cu(TTAPAN), $Cu(PAN)_2$ and HPAN were calculated at 5 nm. intervals over the range 400 nm. to 600 nm. The calculation of these absorptivities was made as follows: the absorbance value was plotted against the concentration. In each case a straight line was obtained, which showed that Beer's law was obeyed for these three compounds, over the concentration range studied. The least-squares straight line was calculated (see Appendix VII). The slope of this

Table 7

Composition of solutions of $Cu(TTA)_2$, Cu(TTAPAN), $Cu(PAN)_2$, and HPAN in benzene-methanol mixtures, for spectrophotometric measurements.

Set No.	benzene-methanol mixture	Compound	Initial concentration range	Number of solutions in set
1	8.3 mol% methanol 35.4 " "	Cu(TTAPAN)	4×10^{-5} M — 3×10^{-6} M	8
2	"	$Cu(PAN)_2$	2.5×10^{-5} M — 3×10^{-6} M	8
3	"	HPAN	6×10^{-5} M — 8×10^{-6} M	8
4	"	$Cu(TTA)_2$	3×10^{-5} M	usually more than 15
		HPAN	8 x 10-5 M — 2×10^{-6} M	
5*	"	$Cu(TTA)_2$	6.4×10^{-5} M — none	usually more than 15
		HPAN	none — 6.4×10^{-5} M	

* In this set the total initial $Cu(TTA)_2$ added plus the initial HPAN added was kept constant.

least-squares fit gave the molar absorptivity. These values for the solvent 35.4 mol% methanol in benzene are given in Appendix VIII.

The absorbances of the solutions of sets 4 and 5 listed in Table 7 were also measured at 5 nm. intervals and are presented in Table 8, together with the initial concentrations of $Cu(TTA)_2$ and HPAN.

For each solution in sets 4 and 5 of this Table, an attempt was made to calculate from the absorbance data the equilibrium concentrations of the compounds involved in the reactions A and B on page 36, namely:

A) $Cu(TTA)_2 + HPAN \overset{K_1}{\rightleftharpoons} Cu(TTAPAN) + HTTA$

B) $Cu(TTAPAN) + HPAN \overset{K_2}{\rightleftharpoons} Cu(PAN)_2 + HTTA$

Let Cu_o be the initial molar concentration of $Cu(TTA)_2$, and let $(HPAN)_o$ be the initial molar concentration of HPAN. Let square brackets, $[\ ]$, denote molar concentration.

The mass-balance equations for reactions A and B are:

4.1 $Cu_o = [Cu(TTA)_2] + [Cu(TTAPAN)] + [Cu(PAN)_2]$

4.2 $[HPAN]_o = [HPAN] + [Cu(TTAPAN)] + 2[Cu(PAN)_2]$

4.3 $2Cu_o = 2[Cu(TTA)_2] + [HTTA] + [Cu(TTAPAN)]$

The mass-law equations will be written in terms of molar concentrations, i.e.,

$$K_1 = \frac{[Cu(TTAPAN)] \cdot [HTTA]}{[Cu(TTA)_2] \cdot [HPAN]}$$

$$K_2 = \frac{[Cu(PAN)_2] \cdot [HTTA]}{[Cu(TTAPAN)] \cdot [HPAN]}$$

Thus, the present derivation is a simplified one, in that all activity coefficients are considered to be unity, and no tautomeric forms, solvates or hydrates of the specified participating species are considered to co-exist.

From Beer's Law:

$$4.4 \quad A i_\lambda = a_{\lambda \, HPAN} [HPAN] + a_{\lambda \, CuTP} [Cu(TTAPAN)] + a_{\lambda \, CuP_2} [Cu(PAN)_2] + B$$

where:

$A_\lambda i$ = absorbance of solution i at wavelength λ

$a_{\lambda \, CuTP}$ = molar absorptivity of Cu(TTAPAN) at wavelength λ

$a_{\lambda \, CuP_2}$ = molar absorptivity of $Cu(PAN)_2$ at wavelength λ

B = a fit parameter. Ideally, it should be zero.

The method developed by d'Amboise[3] was used. Thus, for each solution specified in Table 7, a set of thirtyfour equations was obtained by applying to equation 4.4. the absorbance data given in Table 8, at 5 nm. intervals in the region 400 to 570 nm.

These equations were then normalized by least-squares regression analyses, and solved both for the equilibrium concentrations and their standard deviations (Appendix VII). The parameter B appeared naturally as an indication of the goodness of the fit.

From these calculations , it was found that the values of K_1 could not be calculated, because the equilibrium concentrations of $Cu(TTA)_2$ were too low; in fact, they were of the same order of magnitude as the standard deviations of Cu(TTAPAN) and HPAN. For example, in one solution the relevant equilibrium concentrations were:

$$[Cu(TTAPAN)] = (2.552 \pm 0.011) \times 10^{-5}\ M$$

$$[HPAN] = (1.429 \pm 0.004) \times 10^{-5}\ M$$

$$[Cu(TTA)_2] \sim 10^{-7}\ M$$

However, the values of K_2 could be calculated by using the same technique as that described above for K_1, by using the data for those solutions in which HPAN was in large excess. In calculating the value of K_2 in this way, use was made of the following information:

i) With HPAN in large excess the equilibrium concentration of $Cu(TTA)_2$ was sufficiently low to be neglected in the following mass-balance equations:

Table 8

Absorbance of solutions of sets 4 and 5 listed in Table 7, at 5 nm. intervals in the range 400 nm. to 570 nm. at 20°C.

	Sol. No.	Initial concentration of $Cu(TTA)_2$ M x 10^5	Initial concentration of HPAN M x 10^5	Absorbance x 10^3 wavelength, nm.				
				400	405	410	415	420
Set 4	1	2.694	0.248	56	48	43	38	35
	2	"	0.496	70	63	59	55	53
	3	"	0.910	92	87	86	84	83
	4	"	1.158	104	102	102	102	101
	5	"	1.407	118	117	118	120	119
	6	"	1.655	132	132	134	136	138
	7	"	2.069	153	156	161	167	167
	8	"	2.317	172	173	182	188	192
	9	"	2.565	187	192	201	210	213
	10	"	2.730	200	205	215	224	228
	11	"	3.061	220	236	248	259	265
	12	"	3.227	233	251	265	286	283
	13	"	3.475	265	276	290	303	311
	14	"	3.723	280	302	318	333	340
	15	"	4.302	344	360	379	396	406
	16	"	5.130	420	442	466	488	502
Set 5	1	6.062	0.673	102	88	78	70	63
	2	5.389	1.345	132	122	118	113	110
	3	5.052	1.686	148	140	139	138	137
	4	4.715	2.018	163	161	161	161	159
	5	4.378	2.358	180	181	183	185	183
	6	4.042	2.691	197	199	203	208	208
	7	3.705	3.031	210	215	224	232	235
	8	3.368	3.371	231	239	250	262	265
	9	3.031	3.704	269	280	295	308	316
	10	2.694	4.052	310	324	342	358	368
	11	2.358	4.376	349	367	388	405	418
	12	2.021	4.717	389	411	434	455	468
	13	1.684	5.049	430	456	482	505	521
	14	1.347	5.390	470	501	531	556	575
	15	0.674	6.062	554	593	631	662	685
	16	0.337	6.395	598	643	682	717	745

Table 8 (continued)

	Sol. No.	Absorbance x 10^3 wavelength, nm.										
		425	430	435	440	445	450	455	460	465	470	475
Set 4	1	33	31	30	28	26	24	21	18	17	17	17
	2	51	49	48	47	44	38	32	27	25	25	26
	3	81	80	78	77	72	63	53	44	40	41	43
	4	98	98	97	95	89	78	65	54	49	50	52
	5	118	115	114	113	105	93	77	65	58	58	73
	6	136	133	133	131	122	107	90	75	67	67	83
	7	165	164	163	160	150	132	111	94	83	84	90
	8	190	188	188	186	174	154	130	108	97	97	103
	9	211	210	210	208	197	174	148	126	114	114	122
	10	227	216	227	224	212	190	163	142	130	131	138
	11	264	265	267	267	256	235	210	190	180	180	188
	12	283	285	286	286	277	258	234	214	205	206	214
	13	313	315	318	319	310	293	272	255	247	248	255
	14	344	346	352	354	347	330	310	296	291	293	300
	15	412	418	427	431	427	415	400	392	390	393	398
	16	511	522	535	544	542	536	530	528	532	536	542
Set 5	1	58	55	53	51	47	40	32	29	29	30	32
	2	106	103	101	98	91	79	63	53	51	51	56
	3	130	129	127	124	115	108	80	66	63	63	70
	4	155	153	151	149	137	118	96	80	76	77	81
	5	181	178	178	173	160	137	111	92	88	90	96
	6	205	202	202	199	184	161	130	107	101	101	110
	7	232	230	230	227	211	183	152	126	113	113	122
	8	264	263	265	260	245	217	184	159	146	148	158
	9	317	319	323	322	312	291	266	245	236	239	247
	10	372	379	386	388	382	369	354	341	339	341	347
	11	425	434	445	453	452	447	441	439	440	443	448
	12	480	493	508	520	523	525	529	535	541	547	551
	13	537	554	571	587	597	608	621	636	648	654	656
	14	593	615	637	655	671	690	713	737	756	764	763
	15	710	740	770	797	823	859	903	946	976	983	978
	16	773	808	843	873	907	952	1006	1056	1091	1100	1092

Table 8 (continued)

	Sol. No.	Absorbance x 10^3										
		wavelength, nm.										
		480	485	490	495	500	505	510	515	520	525	530
Set 4	1	18	20	21	22	25	29	33	35	38	41	44
	2	29	32	36	41	47	54	60	65	72	78	84
	3	47	53	60	69	80	94	105	115	126	138	149
	4	58	65	74	86	100	116	131	145	159	172	189
	5	69	78	90	104	121	140	159	175	192	210	228
	6	80	92	105	121	141	165	186	205	125	245	268
	7	100	113	130	150	176	204	230	255	279	302	330
	8	114	128	145	169	197	228	259	285	312	339	370
	9	133	150	170	194	222	255	287	315	344	374	407
	10	150	166	186	212	240	273	304	330	359	387	422
	11	200	215	235	257	283	310	335	356	380	405	437
	12	225	240	258	280	303	327	349	368	390	413	445
	13	267	282	300	318	337	356	372	387	403	425	454
	14	310	325	340	357	371	383	394	403	416	435	463
	15	409	421	433	442	447	445	442	440	442	454	476
	16	549	558	565	565	554	535	509	489	478	480	496
Set 5	1	36	40	45	53	61	70	80	88	95	105	114
	2	62	71	82	98	115	133	151	168	183	201	220
	3	79	90	104	122	141	167	190	210	230	252	278
	4	93	106	123	144	169	198	224	251	275	300	328
	5	108	123	143	168	197	232	263	293	320	348	383
	6	122	140	163	191	225	266	299	330	363	396	433
	7	139	148	182	214	252	294	332	369	406	441	484
	8	172	193	221	251	287	329	367	402	437	473	519
	9	261	278	298	321	343	369	390	412	432	461	496
	10	357	369	383	395	405	409	410	413	420	434	460
	11	453	462	470	471	463	448	430	412	402	405	420
	12	554	556	555	547	525	489	450	413	388	378	382
	13	655	652	646	625	586	527	468	412	372	348	341
	14	759	751	737	705	649	567	489	412	354	318	300
	15	965	949	916	862	772	647	522	406	312	249	208
	16	1072	1047	1009	940	827	677	525	390	277	202	168

Table 8 (continued)

	Sol. No.	Absorbance x 10^3							
		wavelength, nm.							
		535	540	545	550	555	560	565	570
Set 4.	1	47	50	53	55	58	60	60	60
	2	90	95	102	106	110	113	115	115
	3	162	172	183	191	198	205	211	210
	4	203	218	231	242	252	261	267	267
	5	246	264	280	295	306	317	324	325
	6	290	310	329	345	359	371	380	380
	7	358	383	405	426	445	460	471	471
	8	400	430	455	480	500	518	532	535
	9	440	471	500	525	548	567	582	584
	10	455	488	518	544	566	587	601	602
	11	470	504	534	560	585	605	619	620
	12	475	508	537	564	590	610	625	627
	13	483	516	546	573	598	618	632	631
	14	492	523	551	578	602	623	635	634
	15	503	533	560	587	610	632	644	640
	16	518	545	570	597	620	640	652	646
Set 5	1	123	131	138	143	150	153	156	156
	2	239	255	272	284	295	375	312	311
	3	300	320	339	355	371	383	391	390
	4	355	381	403	424	441	456	465	465
	5	415	442	468	493	515	532	541	542
	6	469	503	535	563	588	608	621	620
	7	525	563	598	630	658	684	697	697
	8	560	598	636	670	698	723	742	744
	9	532	568	600	631	658	680	697	698
	10	489	514	542	570	594	615	632	634
	11	438	460	483	504	525	543	556	556
	12	395	410	428	446	463	477	488	487
	13	346	356	368	382	396	408	415	413
	14	298	301	308	320	329	338	444	441
	15	190	181	180	183	187	191	191	186
	16	123	110	103	103	103	103	103	98

$$4.5 \quad Cu_o = [Cu(TTAPAN)] + [Cu(PAN)_2]$$

$$4.6 \quad [HPAN]_o = [HPAN] + [Cu(TTAPAN)] + 2\,[Cu(PAN)_2]$$

$$4.7 \quad [HTTA] = [HPAN]_o - [HPAN]$$

These equations for use in calculating K_2 are the counterpart of those of equations 4.1 to 4.3 used for the calculation of K_1.

ii) In addition, the absorbance equation was used:

$$4.4 \quad A_{\lambda}^{i} = a_{\lambda HPAN}[HPAN] + a_{\lambda CuTP}[Cu(TTAPAN)] + a_{\lambda CuP_2}[Cu(PAN)_2] + B$$

Then for each solution specified in Table 7, a set of thirty-seven equations was obtained by applying to equation 4.4 the absorbances given in Table 8 at 5 nm. intervals in the range 400 nm. to 570 nm. As before, this treatment led to values of equilibrium concentrations with their standard deviations for HPAN, Cu(TTAPAN) and $Cu(PAN)_2$. From the three standard deviations, namely those for HPAN, Cu(TTAPAN) and $Cu(PAN)_2$, the percentage standard deviation was calculated by the formula

$$\% \mathcal{E} = \frac{\sigma}{\bar{x}} \times 100.$$

The lowest $\% \mathcal{E}$ of the three concentrations was then noted by inspection, and the particular compound it corresponded to was used for the further calculations. The concentration found for this particular compound was then substituted into equations 4.5, 4.6 and 4.7, together with the data for Cu_o and $HPAN_o$, and these three equations were then solved for the equilibrium concentrations of HPAN, Cu(TTAPAN), $Cu(PAN)_2$ and HTTA. Therefrom, a value of K_2 was obtained.

In this way a value for K_2 was obtained for each of the solutions specified in Table 7. These values of K_2 are tabulated in Table 9. From the seven values of K_2 in that table, a mean value of 0.101 was obtained, with a standard deviation for six degrees of freedom of 0.029. These values are for the particular benzene-methanol mixture having 35.4 mol.% of methanol at 20°C.

Table 9

Molar equilibrium concentrations of Cu(TTAPAN), $Cu(PAN)_2$, HPAN and HTTA for the solutions having an initial molar concentration of HPAN in excess, and the values of K_2 calculated therefrom.

Solvent: 35.4 mol% of methanol in benzene.

Temperature: 20°C.

Cu_o M x 10^5	$[HPAN]_o$ M x 10^5	Equilibrium concentrations, M x 10^5						K_2
		HTTA	$Cu(PAN)_2$	Cu(TTAPAN)	St. Dev.	HPAN	St. Dev.	
2.694	4.052	2.799	.105	2.589	0.017	1.253	-	0.110
2.358	4.376	2.530	.172	2.186	0.014	1.846	-	0.093
2.021	4.717	2.264	.243	1.778	-	2.453	0.012	0.079
1.684	5.049	1.948	.264	1.420	-	3.101	0.011	0.086
2.694	5.723	2.800	.106	2.588	0.016	.926	-	0.081
"	4.302	2.836	.142	2.552	0.011	1.466	-	0.093
"	6.123	2.868	.174	2.520	0.013	3.255	-	0.164

5 — The chelate exchange reactions of Cu(TTAPAN) with HTTA and HPAN in methanol-benzene mixtures.

5.1 — Introduction

A method which would allow the evaluation of K_1 and K_2 for reactions A and B in methanol-benzene mixtures was developed by d'Amboise[3], and it was applied in the present investigation.

The method consisted of spectrophotometrically following the equilibrium concentrations of Cu(TTAPAN) and/or $Cu(PAN)_2$ in reactions A and B, namely:

$$\text{A) } Cu(TTAPAN) + HTTA \overset{K_1^{-1}}{\rightleftharpoons} Cu(TTA)_2 + HPAN$$

$$\text{B) } Cu(TTAPAN) + HPAN \overset{K_2}{\rightleftharpoons} Cu(PAN)_2 + HTTA$$

Thus, sets of solutions in methanol-benzene mixtures were prepared, in which the initial concentration of Cu(TTAPAN) was kept constant, and the initial concentration of HTTA or of HPAN was changed.

The method requires that: i) only Cu(TTAPAN) and $Cu(PAN)_2$ absorb at the wavelengths selected for the absorbance measurements; ii) both Cu(TTAPAN) and $Cu(PAN)_2$ in methanol-benzene mixtures obey Beer's law for the range of concentration studied; iii) the order of magnitude of the molar absorptivities of Cu(TTAPAN) and $Cu(PAN)_2$ was such that at an appropriate wavelength one can be detected in the presence of a known amount of the other; iv) in reacting Cu(TTAPAN) with HTTA in methanol-benzene mixtures according to reaction (A) the HPAN formed did not react significantly with Cu(TTAPAN) present in equilibrium in the solution, to form Cu(PAN)$_2$ according to reaction B; v) in reacting Cu(TTAPAN) with HPAN in methanol-benzene mixtures, the HTTA formed did not react significantly with Cu(TTAPAN) present in equilibrium in solution, to form Cu(TTA)$_2$ according to reaction (A).

These various requirements were met in the present investigation. Thus, in Section 4 it was shown that Cu(TTAPAN) and Cu(PAN)$_2$ in 35.4 mol% of methanol in benzene obey Beer's law in the range of concentrations used. It is shown later in this section that these complexes also obey Beer's law for all methanol-benzene compositions investigated.

The spectral range 540 nm. to 580 nm. was selected for the absorbance measurements because in this range only Cu(TTAPAN) and Cu(PAN)$_2$ absorb significantly (see Figure 1). Furthermore, in this range the molar absorptivities of the two complexes in methanol-benzene mixtures were found to be different enough to permit quantitative observation of one in the presence of the other.

D'Amboise[3] had previously shown that requirements (iv) and (v) are met. He did so by using his values of K_1' and K_2' for reactions A and B respectively in pure methanol and in pure benzene, to calculate the equilibrium concentrations of the species that co-exist where Cu(TTAPAN) is allowed to react with HTTA or HPAN in these solvents. These conclusions by d'Amboise have been confirmed in the present work. Thus, the values of K_1' and K_2'

found in this work are used in Section 5.3.4 to show that requirements (iv) and (v) were met in the present systems.

5.2 — Procedures

5.2.1 — Preparation of stock standard solutions of Cu(TTAPAN), $Cu(PAN)_2$, HTTA and HPAN in benzene or methanol

The materials have already been described in Section 3.2.

Stock standard solutions of Cu(TTAPAN) and $Cu(PAN)_2$ in benzene or methanol, were prepared by equilibrating excess solid with solvent and filtering with the apparatus illustrated in plate 2. Then, the filtrate was diluted with solvent to approximately twice its initial volume to yield a concentration of approximately 4×10^{-4} M and 2×10^{-4} M for Cu(TTAPAN) in benzene and methanol respectively, and of approximately 2×10^{-4} M and 4×10^{-5} M for $Cu(PAN)_2$ in benzene and methanol respectively. Prior to use, the solutions were standardized by spectrophotometric titration with a standard aqueous solution of EDTA (Appendix III).

Stock standard solutions of HPAN in benzene or methanol were prepared by dissolution of 0.01 gram of the solid in 100-ml. volumetric flask, with the solvent. The resulting solution was then standardized by spectrophotometric titration against a standard aqueous solution of $Cu(NO_3)_2$ (Appendix III).

Stock standard solutions of HTTA were prepared just before use, by dissolution of a carefully weighed amount of the purified and dried solid with benzene or methanol in a 100-ml. volumetric flask, to yield a concentration of approximately 0.1 M. A second stock solution of HTTA in benzene or methanol was prepared by transferring a 10-ml. aliquot from this 0.1 M solution into another 100-ml. volumetric flask, which was then diluted to volume with the solvent at 25°C.

5.2.2 — Preparation of solutions for determinations of molar absorptivities of Cu(TTAPAN) and $Cu(PAN)_2$ in methanol-benzene mixtures, and for spectrophotometric investigations on the chelate exchange reactions of Cu(TTAPAN) with HTTA or HPAN in methanol-benzene mixtures, at 25°C.

The general procedure for the preparation of the above solutions has been given in Section 4.2on page 38. Thus, aliquots of the stock standard solutions given in Section 5.2.1 were pipetted in 25-ml. volumetric flasks, and the appropriate benzene-methanol mixture was added. The compositions of these various sets of solutions are given in Table 10 (this table is the counterpart of Table 7). The methanol-benzene mixtures used in the spectrophotometric investigation of the exchange reaction between Cu(TTAPAN) and HTTA at 25 ±2°C. were in mol% of methanol: 8.38, 16.0, 23.0, 35.4, 40.9, 55.2, 59.4, and 76.7; for the exchange reaction between Cu(TTAPAN) and HPAN at 25 ±2°C., 16.0, 35.4, 41.0, 50.9, 59.4, 76.7, and 89.8 mol% methanol in benzene were used.

After the solutions had been prepared, they were allowed to stand for three days, in stoppered volumetric

Table 10

Composition of solutions in methanol, benzene, or methanol-benzene mixtures[!], prepared from the stock standard solutions of Cu(TTAPAN), $Cu(PAN)_2$, HTTA and HPAN in benzene or methanol, and used for the spectrophotometric study of the exchange reactions between Cu(TTAPAN) and HPAN or HTTA, at 15°C., 25°C., and 35°C.

Set	Number of solutions prepared	Compound(s)	Concentration range, M
A	10-15	Cu(TTAPAN)	app. 3×10^{-5}
		HTTA	1×10^{-1} to 1×10^{-4}
B	10-15	Cu(TTAPAN)	app. 2.5×10^{-5}
		HPAN	2×10^{-4} to 1×10^{-6}
C	6-8	Cu(TTAPAN)	4.5×10^{-5} to 5×10^{-6}
D	6-8	$Cu(PAN)_2$	2.5×10^{-5} to 2.5×10^{-6}
[*]E	3	Cu(TTAPAN)	app. 3×10^{-5}
[*]F	3	Cu(TTAPAN)	app. 2.5×10^{-5}

[!] The methanol-benzene mixtures used in the spectrophotometric investigation of Cu(TTAPAN) with HTTA and HPAN have been given in Section 5.2.2.

[*] The initial concentrations of Cu(TTAPAN) in sets E and F were the same as in sets A and B respectively.

flasks in the dark, in order to allow the establishment of equilibrium.

The fact that three days were sufficient to ensure equilibrium was proved in a separate experiment as follows: spectrophotometric measurements of solutions prepared as described in set A of Table 10 were made after two days and also after being stored in the dark for two months. The results are in Table 11.

5.2.3 — Spectrophotometric Measurements

The absorbances of all sets of solutions with composition listed in Table 10, were measured at 25±2°C. in 1-cm. silica cells, at the selected wavelengths in the spectral range 540 nm. to 580 nm., by using the Unicam S.P. 500 spectrophotometer. The spectrophotometric blank was always the particular methanol-benzene mixture used as solvent in the sample for measurements.

5.2.4 — Procedure for the spectrophotometric investigation of the exchange reactions between Cu(TTAPAN) and HTTA or HPAN, in benzene, methanol and methanol-benzene mixtures, at 15°C. and 35°C.

The solutions were prepared as in Section 5.2.2, except that in the case of the chelate exchange reaction between Cu(TTAPAN) and HTTA the solvents used were pure benzene and 40.9 mol% methanol in benzene, and in the case of the chelate exchange reaction between Cu(TTAPAN) and HPAN the solvents used were 40.9 mol% methanol in benzene and pure methanol. The composition of the solutions used in this investigation are also given in Table 10.

Table 11

Proof of equilibrium of solutions Cu(TTAPAN) and HTTA in methanol-benzene mixtures at 25°C.

Sol. No.	Initial Concentration		Absorbance at 550nm x 10^3		Ratio of Col.IV to Col.V	Absorbance at 560nm x 10^3		Ratio of Col.VII/VIII
	Cu(TTAPAN) Mx10^5	HTTA Mx10^3	After 2 days	After 2 months		After 2 days	After 2 months	
1	3.085	19.42	195	199	0.98	206	212	0.97
2	"	14.56	220	217	1.01	235	232	1.01
3	"	9.708	262	262	1.00	278	279	1.00
4	"	4.854	332	332	1.00	355	353	1.01
5	"	3.883	356	358	0.99	380	382	0.99
6	"	2.912	382	389	0.98	409	415	0.99
7	"	1.942	421	434	0.97	448	461	0.97
8	"	0.970	474	486	0.98	508	519	0.98
9	"	0.728	491	496	0.99	526	528	1.00
10	"	0.485	515	528	0.98	551	564	0.98
11	"	0.427	548	552	0.99	586	590	0.99
				mean=	0.99		mean=	0.99
				st.dev.=	0.01		st.dev.=	0.01

The absorbances were measured as follows: constant-temperature water from a Sargent-Welch thermostat (control to $\pm 0.1^{o}C.$) was circulated through the water jacket of the cell compartment of the Unicam S.P. 500 spectrophotometer. The temperature of the 1-cm. silica cell containing the sample of the solution whose absorbance was to be measured, was measured by using a copper-constantan thermocouple. It was connected to the volt potentiometer described in Section 3.1 and with one end placed tightly between the sample-cell and the cell holder, and with the reference end immersed in an ice-water bath; repetitive measurements were made during the experiments.

The 25-ml. volumetric flasks containing the solutions for measurements were immersed in the water bath of another Sargent-Welch thermostat (control to $\pm 0.01^{o}C.$, thermomonitor controlled), which was set at the same temperature as the cell compartment of the spectrophotometer. After allowing them to stand for four hours, they were removed and quickly dried with absorbent paper. Immediately a sample of the solution was transferred to the 1-cm. sample-cell. The temperature was measured after two minutes and then the absorbance was measured at each selected wavelength. The spectrophotometric blank was always the methanol-benzene mixture being used for the sample solution.

5.3 — Results and Treatment of the Data

5.3.1 — The exchange reaction between Cu(TTAPAN) and HTTA in methanol-benzene mixtures, at $25 \pm 2^{o}C$.

i) Equation to calculate K_1 for reaction (A)

The species that co-exist in the exchange reaction of Cu(TTAPAN) with HTTA in methanol-benzene mixtures are: Cu(TTAPAN), $Cu(TTA)_2$, HTTA and HPAN. Of these compounds, only Cu(TTAPAN) absorbs in the spectral range used, namely 540 nm. to 580 nm. (see Figure 1). Thus, if the known concentration of the added Cu(TTAPAN) is kept constant for all the solutions prepared as in set A and listed in Table 10, the exchange reaction can be followed spectrophotometrically by changing the initial known concentration of HTTA in these solutions. The molar absorptivity of Cu(TTAPAN) in the methanol-benzene mixture at the chosen wavelengths was also required.

The molar absorptivities of Cu(TTAPAN) in methanol-benzene mixtures at the wavelengths selected, were determined by a least-squares fit of the data , from the measured absorbances and the known concentrations of the solutions of set C in Table 10. The values obtained for all methanol-benzene solvent mixtures studied in the spectral range given above, are entered in Table 12. Beer's law was obeyed for all of these solutions in the range of concentrations studied; a plot of absorbance versus concentration is given in Figure 3 for 35.4, 59.0, and 76.7 mol% methanol in benzene.

A rigorous equation is now derived, in order to treat the absorbance data in Table 13. Let round brackets, (), denote activities, and square brackets, [ ], molar concentration. Let γ_A denote the molar activity coefficient for species A. Then for reaction (A)

$$\text{(A)}\quad Cu(TTA)_2 + HPAN \rightleftharpoons Cu(TTAPAN) + HTTA$$

$$\text{(5.1)}\quad K_1 = \frac{[Cu(TTAPAN)]\cdot(HTTA)}{[Cu(TTA)_2]\cdot[HPAN]} \times r$$

Table 12

Molar absorptivity of Cu(TTAPAN) in methanol-benzene mixtures, in the spectral range 540 nm. to 580 nm., at 25 ± 2°C.

The solutions used are set C of Table 10.

Solvent; mol% methanol in benzene	Least-squares value of molar absorptivity and st. dev., x 10^{-4}											
	wavelength in nm.											
	540		550		554		560		564		565	
8.38	1.888	0.009	2.081	0.006	-	-	2.215	0.008	-	-	2.252	0.010
16.0	-	-	2.024	0.011	-	-	2.150	0.013	-	-	-	-
23.0	1.879	0.006	2.069	0.002	-	-	2.204	0.006	-	-	2.229	0.010
35.4	1.847	0.018	2.040	0.020	-	-	2.176	0.021	-	-	-	-
40.9	1.835	0.010	2.037	0.008	-	-	2.182	0.007	2.209	0.006	-	-
50.9	1.877	0.008	2.052	0.007	-	-	2.174	0.007	-	-	-	-
55.2	1.877	0.007	2.055	0.009	-	-	2.178	0.006	-	-	-	-
59.4	-	-	2.088	0.011	-	-	2.231	0.008	-	-	-	-
76.7	1.895	0.005	2.079	0.006	2.123	0.007	2.167	0.006	-	-	-	-
89.8	1.913	0.004	2.091	0.005	2.147	0.006	2.174	0.008	-	-	-	-

Table 12 (continued)

Solvent, mol% methanol in benzene	Least-squares value of molar absorptivity and st. dev., x 10^{-4}						N*
	wavelengths in nm.						
	566		570		580		
8.38	-	-	2.242	0.008	1.896	0.013	8
16.0	2.182	0.013	2.152	0.013	-	-	8
23.0	-	-	2.198	0.007	1.811	0.007	9
35.4	-	-	-	-	-	-	-
40.9	-	-	2.183	0.017	1.788	0.023	10
50.9	-	-	2.068	0.011	-	-	7
55.2	-	-	2.114	0.012	1.686	0.017	6
59.4	-	-	-	-	-	-	-
76.7	-	-	2.013	0.010	-	-	8
89.8	-	-	1.920	0.011	-	-	7

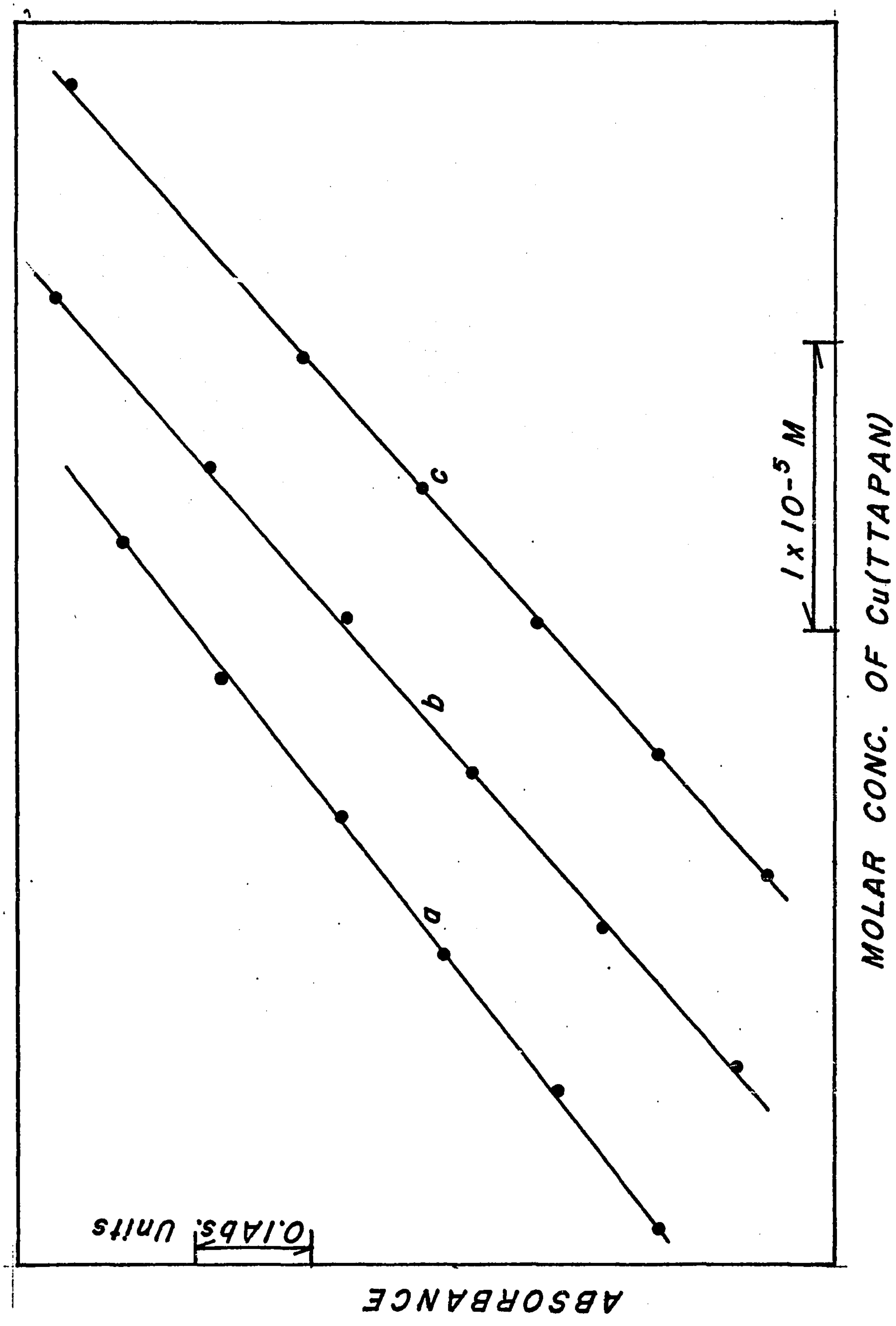
* No. of solutions used for least-squares fit.

FIGURE 3

Beer's law plot for Cu(TTAPAN) in (a) 35.4 mol% methanol, (b) 76.7 mol% methanol and (c) 59.0 mol% methanol in benzene

Note: (i) The concentration range for Cu(TTAPAN) in these solvents was approximately 5×10^{-6} M to 2×10^{-5} M

(ii) Each of the three graphs on extrapolation passed through the origin.


a
b
c
0.1Abs. Units
1 x 10^{-5} M
MOLAR CONC. OF Cu(TTAPAN)
ABSORBANCE

(5.2) where: $$r = \frac{\gamma_{Cu(TTAPAN)}}{\gamma_{Cu(TTA)_2} \cdot \gamma_{HPAN}}$$

It was shown on page 62 that Cu(TTAPAN) obeys Beer's law in the benzene-methanol solvents. Further, the absorbances in Table 13 are for Cu(TTAPAN). Therefore:

(5.3) $$A = a \cdot [Cu(TTAPAN)]$$

(5.4) $$A_o = a \cdot [Cu(TTAPAN)]_o$$

where a is the molar absorptivity of Cu(TTAPAN); and subscript zero denotes the initial value before addition of HTTA to the solution of Cu(TTAPAN).

Now the data in Table 13 refer to equilibrium solutions that resulted from mixing Cu(TTAPAN) and HTTA. Therefore at equilibrium,

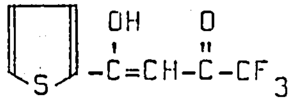
(5.5) $$[HPAN] = [Cu(TTA)_2]$$

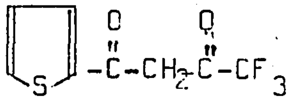
Then from equations (5.1), (5.3), (5.4) and (5.5),

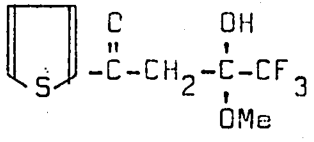
$(5.6)_a$ $$\frac{K_1}{r} = \frac{A/a\ (HTTA)}{\left\{[Cu(TTAPAN)]_o - \frac{A}{a}\right\}^2}$$

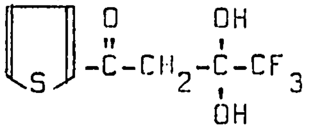
$(5.6)_b$ $$\frac{K_1}{r} = \frac{A/a\ (HTTA)}{\left(\frac{A_o - A}{a}\right)^2}$$

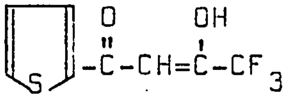
It is necessary to express (HTTA) in terms of $[HTTA]_T$, the stoichiometric concentration of HTTA added, since only the later value is given in Table 13. Now HTTA in solution is considered to exist in several forms (7,20,21,22),

enol,  , denoted here by HTTA

keto,  , denoted here by HTTA'

methanolate,  , denoted here by HTTA'.S

hydrate,  , denoted here by HTTA'.w

The enol isomer  is known to be present in only very small amounts, (22,25).

In addition, the enol is a weak acid, dissociating to H^+ and TTA^-, with a dissociation constant Ka, depending on the solvent and the pH[22]. In dry benzene, 95% of the HTTA is reported to exist in the enol form[7,20], whereas in benzene saturated with water 11% of the HTTA is present as ketohydrate[20].

The methanol-benzene mixtures used in the present work also contained water in the concentration range 1×10^{-3} M (for benzene) to 2×10^{-2} M (for methanol). Moreover, Adam.. and Larsen[24], who have studied the kinetics of ligand exchange between metal chelates and β-diketones, have shown that only the exchange of the enol form is important.

Let the equilibrium constants be

$$(5.7)\quad K_k = \frac{(HTTA')}{(HTTA)}$$

$$(5.8)\quad K_s = \frac{(HTTA'.S)}{(HTTA')\ (S)}$$

where (S) is the activity of methanol in the benzene-methanol solvent.

$$(5.9)\quad K_w = \frac{(HTTA'.w)}{(HTTA')\ (w)}$$

where (w) is the activity of the very low concentrations (approximately 0.02 M) of water in the mixed solvent.

$$(5.10)\quad K_a = \frac{(TTA^-)(H^+)}{(HTTA)} = \frac{(TTA^-)^2}{(HTTA)}$$

then since

$$(5.11)\quad [HTTA]_i = [HTTA] + [HTTA'] + [HTTA'.S] + [HTTA'.w] + [TTA^-] + [Cu(TTA)_2]$$

where $[HTTA]_i$ is the initial stoichiometric concentration of HTTA. On substituting equations (5.7)-(5.10), into equation (5.11),

$$(5.12)\quad (HTTA) = \frac{[HTTA]_T - [Cu(TTA)_2]}{\varphi}$$

where

$$(5.13)\quad \varphi = \left[\frac{1}{\gamma_{HTTA}} + \frac{K_k}{\gamma_{HTTA'}} + \frac{K_k K_s (S)}{\gamma_{HTTA'.S}} + \frac{K_k K_w (w)}{\gamma_{HTTA'.w}} + \frac{K_a^{1/2}}{(HTTA)^{\frac{1}{2}}}\right]$$

then equation (5.6) becomes:

$$(5.14)_a \quad \frac{K_1\varphi}{r} = \frac{(A/a)\cdot\left[[HTTA]_i - [Cu(TTAPAN)]_o + A/a\right]}{\left\{Cu(TTAPAN)_o - A/a\right\}^2}$$

$$(5.14)_b \quad \frac{K_1\varphi}{r} = \frac{(A/a)\cdot\left[[HTTA]_i - \frac{A_o - A}{a}\right]}{\left(\frac{A_o - A}{a}\right)^2}$$

From the data on Table 13, and the absorbance values in Appendix IX, the R.H.S. of equation $(5.14)_a$, i.e. $K_1\varphi/r$, was evaluated for each equilibrium solution at each wavelength. The results are reported in Table 13, and representative sets of these data are plotted in Figures 4 to 6. Inspection shows that these plots (and the data) exhibit a plateau, with abnormally high values of $K_1\varphi/r$ at the extremities, particularly at the lowest values of $[HTTA]_i$. The matter is dealt with in the Discussion Section.

5.3.2 — The exchange reaction between Cu(TTAPAN) and HPAN in methanol-benzene mixtures, at 25 ± 2°C.

The chelate exchange reaction (B) $Cu(TTAPAN) + HPAN = Cu(PAN)_2 + HTTA$ in benzene-methanol mixtures at 25 ± 2°C. was followed spectrophotometrically over the range 540-580 nm., in order to calculate the molar equilibrium constant K_2:

$$(5.15) \quad K_2 = \frac{[Cu(PAN)_2]\cdot(HTTA)}{[Cu(TTAPAN)]\cdot[HTTA]} \times p$$

Table 13

Values of the function $\frac{K_1\varphi}{r}$ of equation (5.14)a, for the chelate exchange reaction $Cu(TTA)_2 + HPAN \rightleftharpoons Cu(TTAPAN) + HTTA$ in benzene-methanol mixtures, at 25 ± 2°C.

Absorbance values used are in Appendix IX.

Sol. No.	Solvent: mol% methanol	Initial conc. of Cu(TTAPAN) M x 10^5	Initial stoichiometric conc. of HTTA M x 10^4	$K_1\varphi/r$ wavelength, nm.					
				540	550	560	565	570	580
1	8.38	3.085	388.3	798	788	785	788	781	783
2	"	"	291.2	767	762	767	761	761	776
3	"	"	194.2	765	746	746	748	744	743
4	"	"	145.6	680	677	681	680	688	666
5	"	"	97.08	718	717	714	714	705	701
6	"	"	48.54	635	646	650	656	656	654
7	"	"	38.83	637	649	652	648	642	641
8	"	"	29.12	625	636	650	658	659	699
9	"	"	19.42	627	640	655	651	645	689
10	"	"	9.708	615	641	663	670	677	693
11	"	"	7.281	599	611	636	653	636	625
12	"	"	4.854	574	621	646	662	658	787
13	"	"	2.427	584	639	660	693	650	773

Table 13 (continued)

Sol. No.	Solvent: mol% methanol	Initial conc. of Cu(TTAPAN) M x 10^5	Initial stoichiometric conc. of HTTA M x 10^4	$K_1\varphi/r$ wavelength, nm.					
				540	550	560	565	570	580
1	23.0	3.085	291.2	542	531	532	536	535	548
2	"	"	194.2	522	505	503	505	506	507
3	"	"	145.6	504	490	489	493	501	505
4	"	"	97 .08	488	475	476	478	475	485
5	"	"	48.54	466	456	463	466	477	492
6	"	"	38.83	461	465	461	468	472	480
7	"	"	29.12	471	472	473	489	485	511
8	"	"	19.42	463	458	465	469	473	486
9	"	"	9.708	445	451	464	479	483	515
10	"	"	7.281	436	454	461	475	489	519
11	"	"	4.854	437	448	480	505	516	589
12	"	"	2.427	473	490	522	526	549	676

				550	560	566	570
1	16.0	3.166	277.3	588	585	595	605
2	"	"	246.5	591	594	602	609
3	"	"	184.9	574	583	599	613
4	"	"	154.1	558	567	576	586
5	"	"	123.2	521	529	545	555

Table 13 (continued)

Sol. No.	Solvent: mol% methanol	Initial conc. of Cu(TTAPAN) M x 10^5	Initial stoichiometric conc. of HTTA M x 10^4	$K_1\varphi/r$ wavelength, nm.			
				550	560	566	570
6	16.0	3.166	92.44	539	551	556	564
7	"	"	61.62	530	545	562	574
8	"	"	30.81	548	546	548	567
9	"	"	24.65	529	546	565	582
10	"	"	18.49	538	553	572	586
11	"	"	12.32	534	570	588	619
12	"	"	6.162	555	587	604	641

				550	560	565	570
1	35.4	3.165	277.3	387	393	390	398
2	"	"	246.5	381	388	396	397
3	"	"	184.9	375	384	383	390
4	"	"	154.1	383	378	383	392
5	"	"	123.2	367	378	379	383
6	"	"	92.44	357	367	370	375
7	"	"	61.62	354	369	377	383
8	"	"	30.81	356	374	380	386
9	"	"	24.65	351	373	378	387
10	"	"	18.49	355	373	378	382
11	"	"	12.32	350	382	390	399
12	"	"	6.162	336	399	400	399

Table 13 (continued)

Sol. No.	Solvent: mol% methanol	Initial conc. of Cu(TTAPAN) M x 10^5	Initial stoichiometric conc. of HTTA M x 10^4	$K_1\varphi/r$ wavelength, nm.		
				550	560	570
1	35.4	3.754	420.1	435	433	445
2	"	"	280.0	419	422	435
3	"	"	196.0	407	411	428
4	"	"	140.0	389	398	416
5	"	"	84.01	391	395	420
6	"	"	56.01	393	405	440
7	"	"	28.00	413	427	482
8	"	"	11.20	424	461	573
9	"	"	8.401	405	450	550
10	"	"	5.601	443	472	575
11	"	"	2.520	505	589	854
12	"	"	1.400	594	725	1.237

Sol. No.	Solvent: mol% methanol	Initial conc. of Cu(TTAPAN) M x 10^5	Initial stoichiometric conc. of HTTA M x 10^4	$K_1\varphi/r$ wavelength, nm.					
				540	550	560	564	570	580
1	40.9	3.085	194.2	430	410	400	405	399	396
2	"	"	145.6	411	391	388	389	388	390
3	"	"	97.08	401	385	376	378	373	381
4	"	"	48.54	389	373	370	369	370	371
5	"	"	38.83	397	378	373	374	366	363
6	"	"	29.12	389	372	371	374	370	379
7	"	"	19.42	399	386	373	378	371	387

Table 13 (continued)

Sol. No.	Solvent: mol% methanol	Initial conc. of Cu(TTAPAN) M x 10^5	Initial stoichiometric conc. of HTTA M x 10^4	$K_1\varphi/r$ wavelength, nm. 540	550	560	564	570	580
8	40.9	3.085	9.708	403	391	392	395	390	403
9	"	"	7.281	402	383	383	385	375	382
10	"	"	4.854	409	392	387	402	399	418
11	"	"	2.427	429	414	402	409	419	423

				540	550	560	570	580
1	55.2	3.085	194.2	332	321	323	322	305
2	"	"	145.6	325	314	317	312	295
3	"	"	97.08	310	302	307	303	285
4	"	"	72.80	309	301	301	297	280
5	"	"	48.54	306	299	303	302	280
6	"	"	38.83	308	301	303	296	275
7	"	"	27.91	303	300	303	301	273
8	"	"	24.27	306	299	305	302	268
9	"	"	19.42	307	303	309	301	260
10	"	"	9.708	309	309	318	321	275
11	"	"	7.281	319	309	319	320	291
12	"	"	4.854	342	339	359	374	311
13	"	"	3.641	323	340	349	361	291
14	"	"	2.427	340	346	392	406	318

Table 13 (continued)

Sol. No.	Solvent: mol% methanol	Initial conc. of Cu(TTAPAN) $M \times 10^5$	Initial stoichiometric conc. of HTTA $M \times 10^4$	$K_1\varphi/r$ wavelength, nm.		
				540	550	560
1	59.4	3.646	147.5	233	229	233
2	"	"	132.8	237	229	228
3	"	"	118.0	233	217	220
4	"	"	103.3	238	232	230
5	"	"	88.51	238	228	227
6	"	"	73.76	234	232	233
7	"	"	59.01	240	230	233
8	"	"	51.63	232	236	230
9	"	"	44.26	239	226	227
10	"	"	29.50	241	230	227
11	"	"	14.75	241	235	234
12	"	"	7.376	210	243	237

				540	550	560	570	580
1	76.7	3.085	194.2	266	256	255	255	248
2	"	"	145.6	250	238	245	247	252
3	"	"	97.08	243	236	240	240	235
4	"	"	48.54	229	222	228	234	230
5	"	"	38.83	233	225	231	242	226
6	"	"	29.12	226	221	234	239	238

Table 13 (continued)

Sol. No.	Solvent: mol% methanol	Initial conc. of Cu(TTAPAN) M x 10^5	Initial stoichiometric conc. of HTTA M x 10^4	$K_1\varphi/r$ wavelength, nm.				
				540	550	560	570	580
7	76.7	3.085	19.42	246	237	247	254	264
8	"	"	9.708	245	239	269	286	291
9	"	"	7.281	242	233	261	273	269
10	"	"	4.854	233	233	266	290	269
11	"	"	2.427	247	243	292	307	292

where

$$(5.16)\quad p = \frac{\gamma_{Cu(PAN)_2}}{\gamma_{Cu(TTAPAN)} \cdot \gamma_{HPAN}}$$

and where round brackets denote activity, and square brackets concentration. The initial concentration of Cu(TTAPAN) was kept constant, and that of added HPAN was varied (set B, Table 10). However, unlike reaction (A), the absorbances of Cu(TTAPAN) and of $Cu(PAN)_2$ had to be taken into account in reaction (B). Consequently their molar absorptivities had to be obtained. However, all the other information used in the derivation of the equation which allowed the calculation of $K_1 \varphi/r$ is applied in the present case.

The molar absorptivities of $Cu(PAN)_2$ in the methanol-benzene mixtures used were obtained as usual, from the concentrations and measured absorbances of the solutions prepared as in set D given in Table 10, in the spectral range selected, at $25 \pm 2^{o}C$. These values are entered in Table 14. In all cases it was found that Beer's law was obeyed.

A rigorous equation similar to equation5.14for reaction (A) is now derived for reaction (B).

$$(5.17)\quad [Cu(TTAPAN)]_i = [Cu(TTAPAN)] + [Cu(PAN)_2]$$

$$(5.18)\quad [HPAN]_i = [HPAN] + [Cu(PAN)_2]$$

and

$$(5.19)\quad [HTTA]_T = (HTTA)\varphi = [Cu(PAN)_2]$$

Table 14

Molar absorptivity of $Cu(PAN)_2$ in methanol-benzene mixtures, in the spectral range 540 nm. to 580 nm., at 25 ± 2°C.

The solutions used are set C of Table 10.

Solvent; mol% methanol in benzene	Least-squares value of molar absorptivity and standard deviation, x 10^{-4}										N*
	wavelength in nm.										
	540		550		554		560		570		
16.0	3.892	0.008	3.945	0.007	-	-	4.058	0.011	3.425	0.015	6
35.4	3.858	0.035	3.964	0.032	-	-	4.044	0.028	-	-	6
41.0	3.880	0.011	4.008	0.011	-	-	4.044	0.014	3.224	0.020	6
50.9	3.865	0.007	3.995	0.010	-	-	4.010	0.013	3.188	0.029	6
59.4	-	-	4.037	0.011	-	-	-	-	-	-	6
76.7	3.717	0.018	3.871	0.008	3.927	0.010	3.810	0.015	2.858	0.005	6
89.8	3.751	0.006	3.833	0.028	3.849	0.035	3.658	0.032	2.574	0.008	6

* No. of solutions for least-squares fit.

where subscript i denotes initial concentration, subscript T denotes total (stoichiometric) concentration, and φ is defined by equation (5.13).

$$(5.20)\quad A = a_{Cu(TTAPAN)}\left[Cu(TTAPAN)\right] + a_{Cu(PAN)_2}\left[Cu(PAN)_2\right]$$

$$A_o = a_{Cu(TTAPAN)}\left[Cu(TTAPAN)\right]_i$$

where A is the measured absorbance of the solution specified in set B of Table 10, a_L denotes the molar absorptivity of species L, and A_o is the absorbance which a given solution would have if HPAN had not been added (set F of Table 10).

Then it is readily shown that:

$$(5.21)\quad Cu(PAN)_2 = \frac{A - A_o}{a_{Cu(PAN)_2} - a_{Cu(TTAPAN)}} \equiv \theta$$

which for convenience is represented by θ

Substitution of equations (5.17), (5.18), (5.19), (5.20) and (5.21) into equation (5.15) gives

$$(5.22)\quad \frac{K_2\varphi}{p} = \frac{\theta^2}{\left(\left[Cu(TTAPAN)\right]_i - \theta\right)\left(\left[HPAN\right]_i - \theta\right)}$$

which may be rearranged to give:

$$(5.23)\quad \frac{K_2\varphi}{p} = \frac{\dfrac{A}{[Cu(TTAPAN)]_i - \theta} - a_{Cu(TTAPAN)}}{a_{Cu(PAN)_2} \cdot \left(\dfrac{[HPAN]_i}{\theta} - 1\right)}$$

For each methanol-benzene mixture used as solvent for the exchange reaction of Cu(TTAPAN) with HPAN, listed on page 67, and for each wavelength selected in the spectral range 540 nm. to 565 nm.[!], the right-hand side of equation 5.23 was calculated for each concentration of total HPAN added to the solutions in set B of Table 10. The value of $[Cu(TTAPAN)]_i$ was also known, the values of A and A_o were measured, and the values of the molar absorptivities of Cu(TTAPAN) and $Cu(PAN)_2$ were obtained from measured absorbances and concentrations of solutions in sets C and D respectively (Table 10).

The measured absorbances A and A_o are given in Appendix X. The molar absorptivities of Cu(TTAPAN) and $Cu(PAN)_2$ in the methanol-benzene mixtures used are given in Tables 12 and 14 respectively. From these data, a set of values of $\frac{K_2\varphi}{p}$ was calculated for each wavelength. These values are entered in Table 15.

[!] Absorbances values beyond 565 nm. were not recorded. The error in setting the wavelength was relatively large beyond 565 nm., because around this wavelength the absorption curves were rising steeply.

Table 15

Values of the function $K_2\varphi/p$ of equation (5.23), for the chelate exchange reaction

$$\mathrm{Cu(TTAPAN)} + \mathrm{HPAN} \rightleftharpoons \mathrm{Cu(PAN)_2} + \mathrm{HTTA}$$

in benzene-methanol mixtures, at 25 ± 2°C.

Absorbance values used are in Appendix X.

Sol. No.	Solvent; mol% methanol	Initial conc. of Cu(TTAPAN) $M \times 10^5$	Initial stoichiometric conc. of HPAN $M \times 10^5$	$K_2\varphi/p \times 10^3$ wavelength, nm.		
				550	560	566
1	16.0	2.652	12.16	56	62	38
2	"	"	11.30	48	52	31
3	"	"	10.43	47	50	32
4	"	"	8.688	47	49	30
5	"	"	7.819	34	41	28
6	"	"	6.950	46	53	35
7	"	"	5.213	45	51	34
8	"	"	4.344	47	52	36
9	"	"	3.475	51	56	39
10	"	"	2.607	35	38	25
11	"	"	1.738	58	68	44
12	"	"	0.869	37	42	29
				540	550	560
1	35.4	2.652	12.16	94	78	79
2	"	"	10.43	89	73	73
3	"	"	8.688	90	75	79
4	"	"	6.950	83	75	81
5	"	"	6.082	79	72	70
6	"	"	5.213	85	76	76
7	"	"	4.344	79	73	75
8	"	"	3.475	79	74	78
9	"	"	2.607	79	81	82
10	"	"	1.738	87	83	86
11	"	"	0.869	85	85	94

Table 15 (continued)

Sol. No.	Solvent; mol% methanol	Initial conc. of Cu(TTAPAN) M × 10^5	Initial stoichiometric conc. of HPAN M × 10^5	$K_2\varphi/p \times 10^3$ wavelength, nm.		
				540	550	560
1	41.0	3.032	11.60	110	90	82
2	"	"	10.63	104	94	86
3	"	"	9.668	107	93	90
4	"	"	8.701	102	93	86
5	"	"	7.734	100	99	92
6	"	"	6.760	94	90	92
7	"	"	5.801	98	89	95
8	"	"	4.834	103	100	97
9	"	"	3.867	100	96	97
10	"	"	1.934	97	93	100
11	"	"	0.967	104	105	116
12	"	"	0.677	97	100	110
				540	550	560
1	50.9	3.032	11.60	141	115	120
2	"	"	10.63	141	124	129
3	"	"	9.668	128	113	114
4	"	"	8.701	128	118	123
5	"	"	7.734	131	122	109
6	"	"	6.768	117	124	112
7	"	"	5.801	130	122	121
8	"	"	4.834	116	117	114
9	"	"	3.867	113	119	119
10	"	"	0.967	118	131	119
11	"	"	0.677	130	127	152

Table 15 (continued)

Sol. No.	Solvent; mol% methanol	Initial conc. of Cu(TTAPAN) M x 10^5	Initial stoichiometric conc. of HPAN M x 10^5	$K_2\varphi/p$ x 10^3 wavelength, nm.
				550
1	59.4	1.822	10.99	193
2	"	"	10.08	159
3	"	"	9.162	149
4	"	"	8.246	149
5	"	"	7.330	145
6	"	"	6.413	150
7	"	"	5.497	133
8	"	"	4.581	102
9	"	"	3.665	103
10	"	"	2.749	134
11	"	"	1.832	132
12	"	"	0.961	135
				550
1	59.4	1.822	12.44	118
2	"	"	11.20	130
3	"	"	8.708	126
4	"	"	7.464	126
5	"	"	6.220	123
6	"	"	5.598	125
7	"	"	4.976	123
8	"	"	2.488	122
9	"	"	1.866	133
10	"	"	1.244	150
11	"	"	0.622	169

Table 15 (continued)

Sol. No.	Solvent; mol% methanol	Initial conc. of Cu(TTAPAN) M x 10^5	Initial stoichiometric conc. of HPAN M x 10^5	$K_2\varphi/p \times 10^3$ wavelength, nm.			
				540	550	554	560
1	76.7	2.110	11.71	374	311	295	320
2	"	"	9.760	348	310	289	324
3	"	"	8.784	314	283	257	301
4	"	"	7.808	303	281	272	295
5	"	"	6.832	303	300	267	285
6	"	"	5.856	292	287	283	288
7	"	"	4.880	291	275	263	269
8	"	"	3.904	251	252	245	243
9	"	"	2.928	340	348	331	361
10	"	"	1.952	305	309	330	325
11	"	"	0.976	343	383	342	353
				540	550	554	560
1	89.8	3.032	11.60	406	443	406	405
2	"	"	10.63	369	427	463	438
3	"	"	9.668	350	397	413	399
4	"	"	8.701	400	453	455	455
5	"	"	7.734	330	368	395	398
6	"	"	6.768	371	428	416	429
7	"	"	5.801	339	386	397	431
8	"	"	4.834	353	400	363	398
9	"	"	3.867	336	424	396	456
10	"	"	1.934	317	377	416	419
11	"	"	0.967	292	535	417	407
12	"	"	0.677	318	398	417	482

5.3.3. The exchange reaction of Cu(TTAPAN) with HPAN and HTTA in methanol, benzene and methanol-benzene mixtures, at 15°C. and 35°C.

The equations 5.14 and 5.23, which allowed calculation of $\frac{K_1\varphi}{r}$ and $\frac{K_2\varphi}{p}$ at 25°± 2°C. for reactions (A) and (B), were also used to calculate these quantities at 15°C. and 35°C.

In Section 5.2.4 , the procedures have been described for measuring the absorbances of these solutions at 15°C. and 35°C., having the compositions specified in Tables 10, 18 and 19. The known initial concentrations of the reactants Cu(TTAPAN), HTTA and HPAN in these solutions were for 25°C. However, it was unnecessary to correct these concentrations for the change in volume of the solution in going from 25°C. to 35°C. or from 25°C. to 15°C., because these volume changes would equally affect the value both of the numerator and of the denominator of the R.H.S. of equations 5.1 and 5. 15.

The molar absorptivities of Cu(TTAPAN) and $Cu(PAN)_2$ were obtained by measuring absorbances at 15°C. and 35°C., but the concentration of solute was for 25°C. It was necessary to calculate the molar absorptivities in this way because corrections for change in concentration due to volume change with temperature had not been made for the other variables in equations 5.14 and 5.23, as explained in the preceding paragraph. These values of molar absorptivities, in the spectral range used, are entered in Tables 16 and 17, for Cu(TTAPAN) and $Cu(PAN)_2$ respectively.

Table 16

Molar absorptivity of Cu(TTAPAN) in pure methanol, pure benzene and in 40.9 mol% methanol in benzene, at 15°C. and 35°C.

The solutions used are set C of Table 10.**

Temperature °C.	Solvent; mol% methanol in benzene	Least-squares value of molar absorptivity and standard deviation x 10^{-4}												N*
		wavelength in nm.												
		540		550		560		564		570		580		
15	0.0	1.907	0.024	2.127	0.020	2.243	0.006	-	-	2.301	0.006	2.046	0.013	7
	40.9	1.938	0.012	2.152	0.010	2.266	0.010	2.272	0.008	2.198	0.015	1.776	0.018	6
	100.0	1.985	0.007	2.146	0.006	2.186	0.007	-	-	1.832	0.020	-	-	9
35	40.9	1.883	0.013	2.084	0.009	2.188	0.011	2.182	0.006	2.097	0.012	1.676	0.015	6
	100.0	1.921	0.007	2.077	0.003	2.089	0.004	-	-	1.735	0.010	-	-	9
	0.0	1.903	0.025	2.083	0.018	2.193	0.010	-	-	2.222	0.008	1.924	0.015	7

** The concentration of Cu(TTAPAN) in these solutions was for 25°C.

* No. of solutions for least-squares fit.

Table 17

Molar absorptivity of $Cu(PAN)_2$ in pure methanol and in 40.9 mol% methanol in benzene, at 15°C. and 35°C. The solutions used are set D of Table 10.**

Temp. °C.	Solvent; mol% methanol in benzene	Least-squares value of molar absorptivity and standard deviation $\times 10^{-4}$; wavelength in nm.						N*
		540		550		560		
15°C.	40.9	-	-	4.056	0.013	4.092	0.015	
	100.0	3.523	0.023	3.715	0.023	3.400	0.021	7
35°C.	40.9	-	-	3.986	0.012	3.186	0.012	
	100.0	3.458	0.025	3.570	0.023	3.183	0.011	7

* No. of solutions for least-squares fit.

** The concentration of $Cu(PAN)_2$ in these solutions was for 25°C.

Reactions (A) and (B) at 35°C. and 15°C. were studied in the following solvents: for the exchange reaction for Cu(TTAPAN) with HPAN pure methanol, and 40.9 mol% methanol in benzene were the solvents. For the exchange reaction of Cu(TTAPAN) with HTTA pure benzene, and 40.9 mol% methanol in benzene were the solvents. The molar absorptivities of Cu(TTAPAN) and $Cu(PAN)_2$ were of course also measured in these solvents.

5.3.3(i) Calculated values of the function $\frac{K_1\varphi}{r}$ of equation 5.14, in pure benzene and in 40.9 mol% methanol-benzene, at 15°C. and 35°C.

In Table 18 are entered the absorbances A and A_{∞} (defined in Section 5.3.1), found at 15°C. and 35°C. for reaction (A). The composition of the solutions are specified in Tables 10 and 18. These absorbance values, together with the molar absorptivities of Cu(TTAPAN) listed in Table 16, were used directly in equation 5.14 in order to calculate $\frac{K_1\varphi}{r}$. The values so obtained are given for each wavelength in Table 18.

5.3.3(ii) Calculated values of the function $\frac{K_2\varphi}{p}$ of equation 5.23 in pure benzene and 40.9 mol% methanol in benzene, at 15°C. and 35°C.

The measured absorbances of solutions of known $[Cu(TTAPAN)]_i$ and $[HPAN]_i$ in sets B and F of Table 10, together with the molar absorptivities of Cu(TTAPAN) and

Table 18

Spectrophotometric data and calculated values of the function $K_1\varphi/r$ of equation (5.14) for the chelate exchange reaction

$$Cu(TTA)_2 + HPAN \rightleftharpoons Cu(TTAPAN) + HTTA$$

in pure benzene and in 40.9 mol% methanol in benzene, at 15°C. and 35°C.

Temperature = 15°C.

Solvent	Sol. No.	$[Cu(TTAPAN)]_i$ M x 10^5	$[HTTA]_i$ M x 10^3	Absorbance x 10^3 wavelength, nm.						$K_1\varphi/r$ wavelength, nm.					
				540	550	560	570	580		540	550	560	570	580	
pure benzene	1	4.548	864.3	266	297	318	326	287		1212	1214	1251	1248	1225	
	2	"	648.2	305	338	361	370	325		1192	1176	1208	1205	1175	
	3	"	518.6	338	375	400	410	360		1192	1178	1210	1207	1173	
	4	"	432.1	364	405	432	442	390		1183	1176	1210	1202	1180	
	5	"	345.7	398	441	469	478	422		1190	1169	1197	1176	1154	
	6	"	172.9	492	551	586	600	526		1150	1157	1206	1196	1136	
	7	"	129.6	530	592	629	648	568		1150	1156	1195	1215	1145	
	8	"	82.11	582	652	692	712	627		1118	1142	1183	1200	1142	
	9	"	64.82	608	678	725	748	658		1115	1113	1209	1249	1173	
	10	"	56.18	620	694	742	763	670		1084	1106	1208	1224	1132	
	11	"	43.21	650	724	772	792	698		1131	1119	1214	1212	1139	
	12	"	34.57	668	748	796	815	716		1105	1138	1228	1206	1098	
	13	"	21.61	700	782	840	865	755		1026	1040	1253	1300	1080	
	14	"	12.96	730	825	878	898	790		952	1115	1262	1209	1057	
	15	"	4.321	786	878	945	964	850		970	997	1620	1395	1150	
				540	550	560	564	570	580	540	550	560	564	570	580
40.9 mol% methanol in benzene	1	3.085	194.2	187	199	212	214	207	167	626	598	603	619	623	620
	2	"	145.6	201	217	232	233	226	180	518	494	508	514	527	501
	3	"	97.08	240	262	279	282	276	222	531	516	532	546	560	528
	4	"	46.45	304	332	353	355	346	278	468	454	476	589	499	465
	5	"	38.83	328	358	382	385	375	298	505	473	501	515	548	508
	6	"	29.12	355	389	415	419	408	328	507	480	518	545	558	540
	7	"	19.42	395	434	461	466	455	366	571	533	588	607	636	608
	8	"	9.708	441	486	519	524	512	412	621	564	643	705	637	675
	9	"	7.281	449	496	528	534	522	424	439	402	437	478	497	429
	10	"	4.854	480	528	564	569	555	445	599	547	681	770	846	626
	11	"	2.427	503	552	590	597	584	470	456	402	510	543	652	521

Table 18 (continued)

Temperature = 35°C.

Solvent	Sol. No.	$[Cu(TTAPAN)]_i$ M x 10^5	$[HTTA]_i$ M x 10^3	Absorbance x 10^3 wavelength, nm. 540	550	560	564	570	580	$K_1\varphi/r$ wavelength, nm. 540	550	560	564	570	580
pure benzene	1	4.548	864.3	206	224	239		246	214	779	770	787		808	814
	2	"	648.2	240	264	279		286	251	757	763	768		784	803
	3	"	518.6	270	297	315		321	278	751	758	769		778	778
	4	"	432.1	295	325	346		352	308	745	755	772		779	796
	5	"	345.7	328	362	385		390	339	747	760	778		777	784
	6	"	172.9	425	470	500		510	440	720	742	765		781	772
	7	"	129.6	462	513	546		555	478	699	733	760		769	755
	8	"	82.11	520	578	615		625	540	680	723	756		766	758
	9	"	64.82	548	609	650		660	568	670	717	764		772	750
	10	"	56.18	565	626	672		680	587	668	708	780		775	763
	11	"	43.21	594	659	702		716	608	661	711	760		790	707
	12	"	34.57	615	684	728		742	636	643	708	758		788	738
	13	"	21.61	657	731	779		789	673	619	700	771		769	682
	14	"	12.96	692	772	828		838	715	565	674	816		807	692
	15	"	4.321	754	845	894		908	772	494	718	784		821	597
40.9 mol% methanol in benzene	1	3.085	194.2	167	179	190	192	184	146	356	336	343	351	349	345
	2	"	145.6	180	194	205	206	198	157	307	292	295	300	300	295
	3	"	97.08	222	242	255	257	248	195	314	304	307	313	317	305
	4	"	48.45	280	305	325	326	315	246	281	269	280	285	290	271
	5	"	38.83	305	334	355	357	345	272	292	282	293	302	307	294
	6	"	29.12	335	366	388	390	376	296	302	288	299	308	311	294
	7	"	19.42	376	412	448	442	427	338	326	311	368	349	358	341
	8	"	9.708	428	470	500	503	488	384	332	315	344	365	390	350
	9	"	7.281	436	478	508	510	490	385	282	264	287	301	301	267
	10	"	4.854	469	515	548	552	536	422	338	314	357	394	439	376
	11	"	2.427	495	543	578	580	560	442	301	270	320	348	371	313

$Cu(PAN)_2$ at 15°C. and 35°C. given in Tables 16 and 17, were used in equation 5.23. For each solution composition in Cu(TTAPAN) and HPAN, and for each wavelength, a value of $K_2\psi/p$ was calculated. These values are entered in Table 19.

5.3.4. The disproportionation of Cu(TTAPAN) into $Cu(TTA)_2$ and $Cu(PAN)_2$, in methanol-benzene mixtures.

The proof referred to in Section 5.1, that requirements (iv) and (v) were met in the present systems, is as follows:

The complexes $Cu(PAN)_2$ and $Cu(TTA)_2$ are formed simultaneously on reacting Cu(TTAPAN) with HTTA or HPAN according to reactions (A) and (B).

$$\text{(A)}\quad \text{Cu(TTAPAN)}\quad \text{HTTA} \xrightleftharpoons{K_1^{-1}} \text{Cu(TTA)}_2\quad \text{HPAN}$$

$$\text{(B)}\quad \text{Cu(TTAPAN)}\quad \text{HPAN} \xrightleftharpoons{K_2} \text{Cu(PAN)}_2\quad \text{HTTA}$$

An overall reaction is the disproportionation of Cu(TTAPAN) according to reaction (C).

$$\text{(C)}\quad 2\text{Cu(TTAPAN)} \xrightleftharpoons{K_2/K_1} \text{Cu(TTA)}_2 + \text{Cu(PAN)}_2$$

where

$$(5.24)\quad \frac{K_2}{K_1} = \frac{\left[\text{Cu(TTA)}_2\right]\left[\text{Cu(PAN)}_2\right]}{\left[\text{Cu(TTAPAN)}\right]^2}$$

In solutions of Cu(TTAPAN) to which HTTA or HPAN

Table 19

Spectrophotometric data and calculated values of the function $K_2\varphi/p$ of equation (5.23) for the chelate exchange reaction

$$\mathrm{Cu(TTAPAN)} + \mathrm{HPAN} \rightleftharpoons \mathrm{Cu(PAN)_2} + \mathrm{HTTA}$$

in pure methanol and in 40.9 mol% methanol in benzene, at 15°C. and 35°C.

Solvent	Sol. No.	$[\mathrm{Cu(TTAPAN)}]_i$ M × 10^5	$[\mathrm{HPAN}]_i$ M × 10^5	Absorbance!! × 10^3 wavelength, nm.		$K_2\varphi/p$ × 10^3 wavelength, nm.	
Temp.=15°C.				540	550	540	550
pure methanol	1	2.432	10.70	288	282	710	575
	2	"	9.810	278	272	654	536
	3	"	8.918	278	272	736	602
	4	"	8.026	265	262	664	579
	5	"	7.134	258	258	684	629
	6	"	6.243	248	248	685	633
	7	"	5.351	245	245	805	744
	8	"	4.459	226	226	750	698
	9	"	3.567	209	210	779	740
	10	"	2.675	187	190	833	826
	11	"	1.784	148	150	766	755
	12!	"	-	482	525	-	-

Table 19 (continued)

Solvent	Sol. No.	$[Cu(TTAPAN)]_i$ M × 10^5	$[HPAN]_i$ M × 10^5	Absorbance!! × 10^3 wavelength, nm.		$K_2\varphi/p$ × 10^3 wavelength, nm.	
Temp.=15°C.				550	560	550	560
40.9 mol% methanol in benzene	1	3.032	13.18	279	270	105	110
	2	"	12.17	272	262	106	110
	3	"	11.16	262	255	105	112
	4	"	10.14	240	241	100	106
	5	"	9.128	243	236	106	112
	6	"	8.114	228	224	102	111
	7	"	7.099	218	212	105	111
	8	"	6.085	202	197	103	109
	9	"	5.071	188	183	106	112
	10	"	4.057	171	167	108	116
	11	"	3.043	153	150	117	126
	12	"	2.028	127	125	125	137
	13!	"	-	631	670	-	-
Temp.=35°C.				540	550	540	550
pure methanol	1	2.432	10.70	272	262	523	502
	2	"	9.810	260	252	470	465
	3	"	8.918	258	248	510	487
	4	"	8.026	245	238	464	465
	5	"	7.134	242	234	512	503
	6	"	6.243	225	219	456	460
	7	"	5.351	222	216	532	536
	8	"	4.459	202	198	482	500
	9	"	3.567	185	182	489	513
	10	"	2.675	168	167	551	601
	11	"	1.784	131	132	479	548
	12!	"	-	458	498	-	-

Table 19 (continued)

Solvent	Sol. No.	[Cu(TTAPAN)]$_i$ M x 10^5	[HPAN]$_i$ M x 10^5	Absorbance!! x 10^3 wavelength, nm.		$K_2\varphi/p$ x 10^3 wavelength, nm.	
Temp.=35^{o}C.				550	560	550	560
	1	3.032	13.18	260	244	93	87
	2	"	12.17	252	235	92	85
	3	"	11.16	241	227	90	85
	4	"	10.14	228	212	86	79
	5	"	9.128	215	198	82	74
40.9 mol% methanol in benzene	6	"	8.114	204	191	81	77
	7	"	7.099	192	178	81	74
	8	"	6.085	177	167	78	75
	9	"	5.071	162	153	77	74
	10	"	4.057	149	140	82	77
	11	"	3.043	132	125	86	83
	12	"	2.028	112	107	96	96
	13!	"	-	619	654	-	-

! The absorbance values for this solution are A_o values.

!! The absorbance values given are $\Delta A = (A - A_o)$.

has not been added

$$(5.25)\quad \frac{K_2}{K_1} = \frac{[\mathrm{Cu(PAN)_2}]^2}{[\mathrm{Cu(TTAPAN)}]^2}$$

The highest value of the ratio K_2/K_1 studied in the present work was for 76.7 mol% methanol in benzene, in which case a value of 1.3×10^{-3} was obtained. In that case, for a solution of Cu(TTAPAN) in 76.7 mol% methanol in benzene,

$$\frac{[\mathrm{Cu(PAN)_2}]}{[\mathrm{Cu(TTAPAN)}]} = 0.036$$

The mass-balance equation for solutions of Cu(TTAPAN) to which HTTA or HPAN has not been added, is

$$(5.26)\quad [\mathrm{Cu(TTAPAN)}]_i = 2[\mathrm{Cu(PAN)_2}] + [\mathrm{Cu(TTAPAN)}]$$

and Beer's law for this solution is

$$(5.20)\quad A = a_{\mathrm{Cu(TTAPAN)}}[\mathrm{Cu(TTAPAN)}] + \\ + a_{\mathrm{Cu(PAN)_2}}[\mathrm{Cu(PAN)_2}]$$

in the range where $\mathrm{Cu(TTA)_2}$ does not absorb, but Cu(TTAPAN) and $\mathrm{Cu(PAN)_2}$ do absorb.

In the spectral range studied, $a_{\mathrm{Cu(PAN)_2}} \simeq 2a_{\mathrm{Cu(TTAPAN)}}$. Therefore, for a solution of Cu(TTAPAN), equation (5.20) becomes:

$$A \simeq a_{Cu(TTAPAN)} \left\{ [Cu(TTAPAN)] + 2[Cu(PAN)_2] \right\}$$

which, on using equation (5.26), becomes:

$$(5.27) \quad A \simeq a_{Cu(TTAPAN)} \; [Cu(TTAPAN)]_i$$

The ratio of the molar absorptivities $a_{Cu(PAN)_2}/a_{Cu(TTAPAN)}$ in the spectral range 540 nm. to 580 nm. is not exactly 2. From the absorptivities in Appendix VIII it is seen that this ratio varies with the wavelength; but in all cases it was in the range 1.8-2.2. The validity of equation (5.27) is shown by the fact that the Beer's law plots in Figure 3 are straight lines.

Now in 76.7 mol% methanol in benzene, the ratio K_2/K_1 is 0.036. Thus, Cu(TTAPAN) alone in this solvent will disproportionate to the extent of 4%, into $Cu(TTA)_2$ and $Cu(PAN)_2$. However, equation (5.27), together with the fact that the ratio of absorptivity of Cu(TTAPAN) to absorptivity of $Cu(PAN)_2$ is within 20% of 2, shows that none of the spectrophotometric data used in the present investigation would be significantly affected by this disproportionation, with the exception of the molar absorptivity of Cu(TTAPAN) at wavelengths where $a_{Cu(TTAPAN)}/a_{Cu(PAN)_2} \neq 2$. The small error introduced into this molar absorptivity would be important only when the absorptivity is used in an absolute sense. It automatically is cancelled out when this molar absorptivity is used in order to calculate K_1 and K_2.

6 — Discussion

6.1 — The variation of $K_1\varphi/r$ with concentration of HTTA

Values of $K_1\varphi/r$ for the system Cu(TTAPAN)-HTTA at 25°C. are given in Table 13; the basic concentration and absorbance data for that table are in Appendix IX.

In these experiments, a somewhat wide range of initial concentrations of HTTA was used, in order to study the effect, if any, of high and low concentrations of HTTA on the value of $K_1\varphi/r$.

Inspection of the values in Table 13, and of figures 4-6, does indicate a decided tendency for abnormally high values of $K_1\varphi/r$ to be obtained at the lowest and also at the highest concentrations of $[\mathrm{HTTA}]_i$. This tendency did not depend on the wavelength, in the range 540 nm. to 580 nm.

D'Amboise has shown very recently that the presence of dissolved water in benzene produced values of $K_1\varphi/r$ that were measurably too large when low (2-5 x 10^{-3} M) values of $[\mathrm{HTTA}]_i$ were used, and that the effect varied with the water concentration. A reason for this effect may be as follows: the addition of water to a benzene-methanol solution of HTTA results in the formation of some keto-hydrate, with a resulting drop in the concentration of free HTTA. Since

$$(5.13)\ \varphi = \left[\frac{1}{\gamma_{\mathrm{HTTA}}} + \frac{K_k}{\gamma_{\mathrm{HTTA'}}} + \frac{K_k K_s (S)}{\gamma_{\mathrm{HTTA'.S}}} + \frac{K_k K_w (w)}{\gamma_{\mathrm{HTTA'w}}} + \left(\frac{Ka}{(\mathrm{HTTA})}\right)^{\frac{1}{2}}\right]$$

FIGURE 4

The variation of $K_1\varphi/r$ with initial concentration of HTTA in 16.0 mol% methanol in benzene, at 25°C.

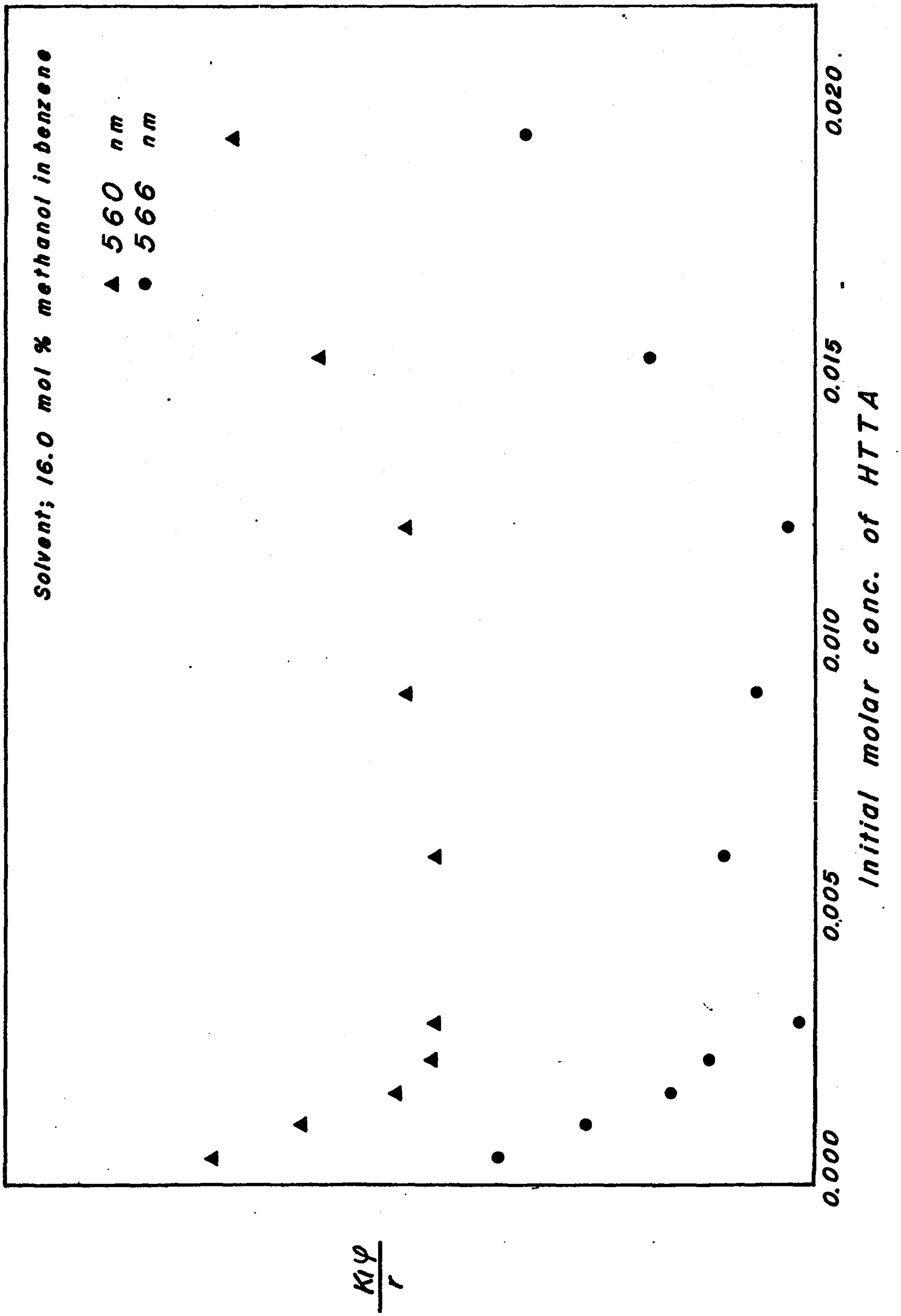

Solvent; 16.0 mol % methanol in benzene
▲ 560 nm
● 566 nm
0.000
0.005
0.010
0.015
0.020
Initial molar conc. of HTTA
K1φ/r

FIGURE 5

The variation of $K_1\varphi/r$ with initial concentration of HTTA in 55.2 mol% methanol in benzene, at 25°C.

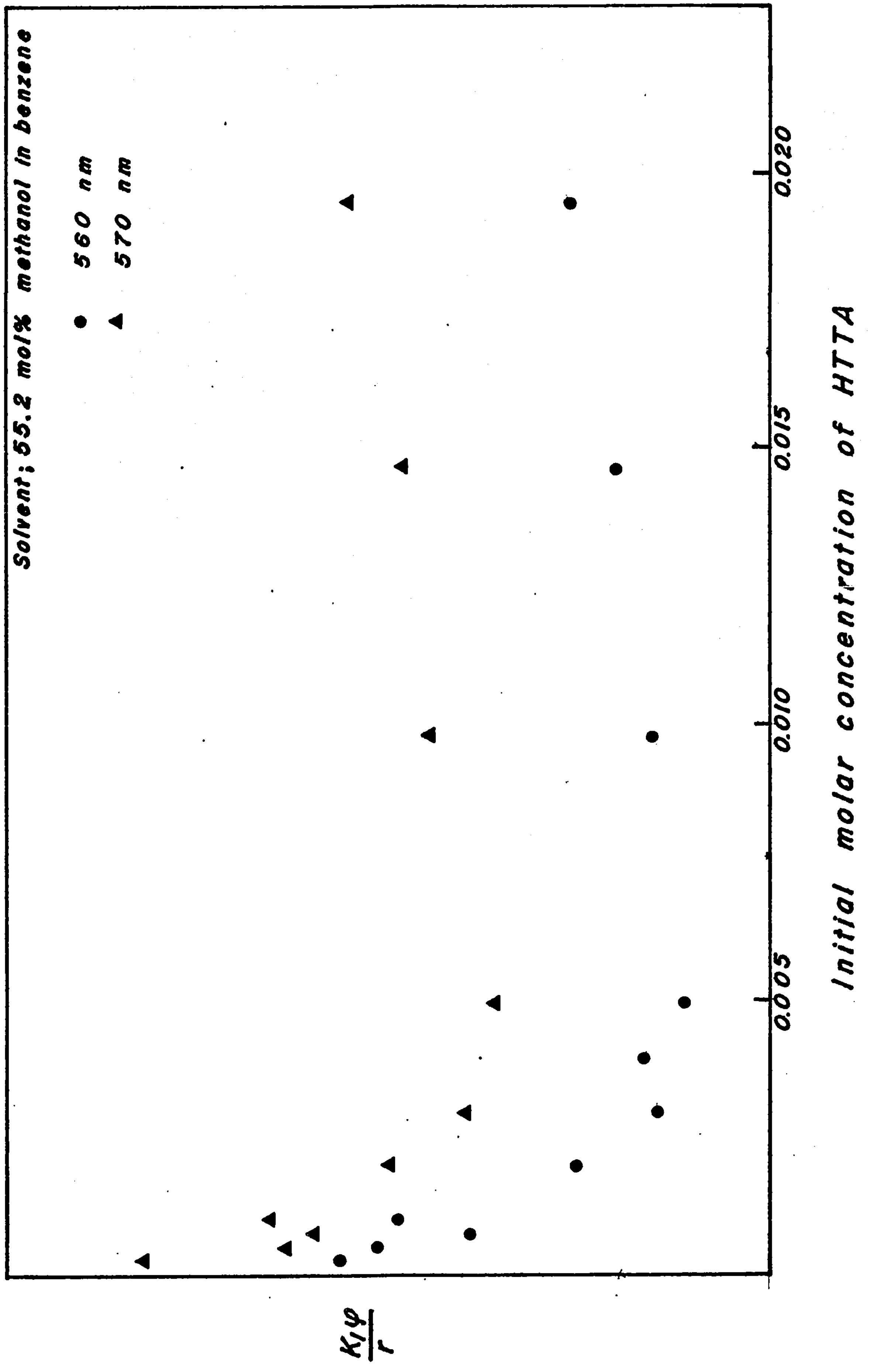
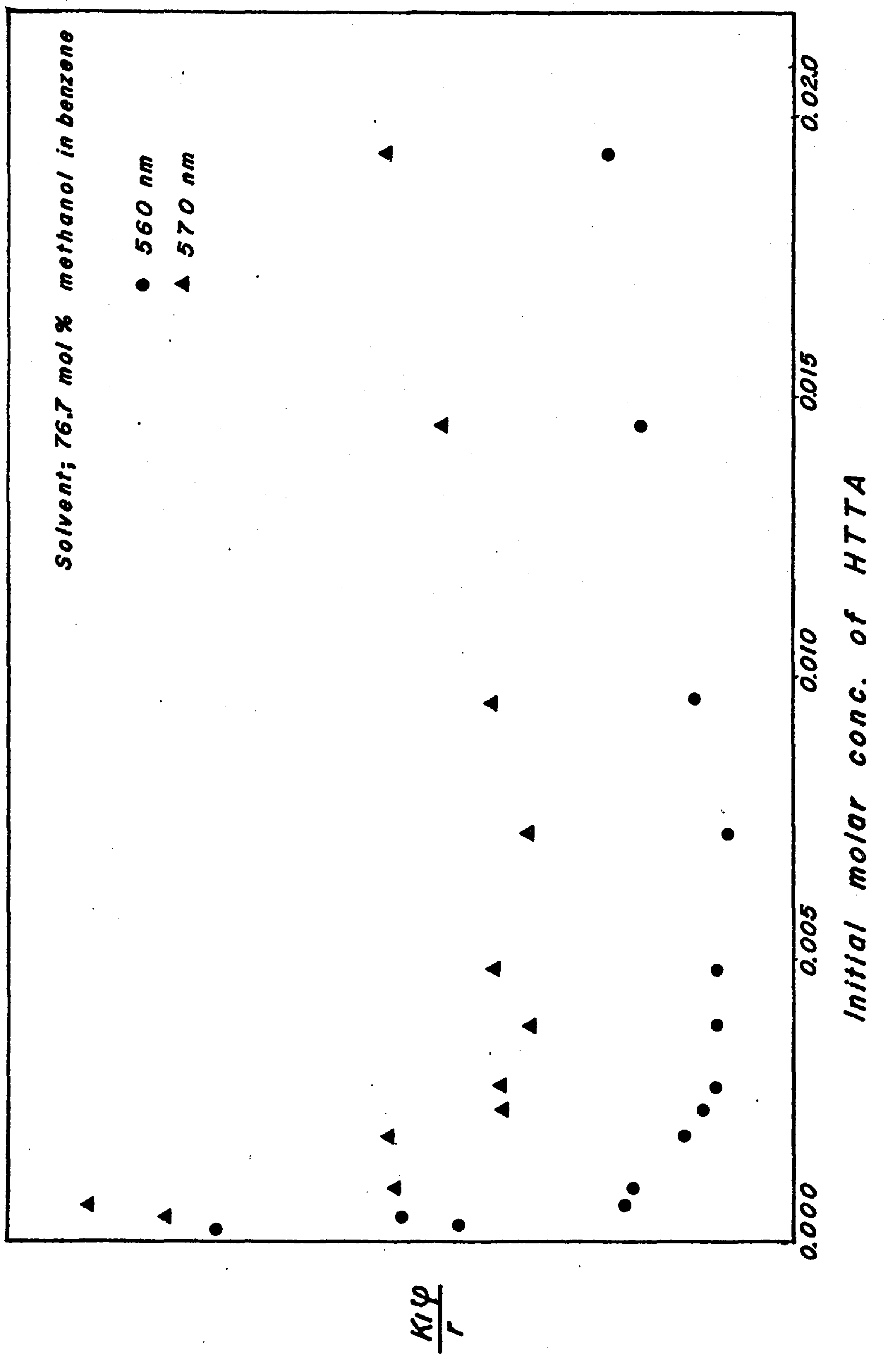

Solvent; 55.2 mol% methanol in benzene
● 560 nm
▲ 570 nm
0.005
0.010
0.015
0.020
Initial molar concentration of HTTA
$\frac{K_I\psi}{r}$

FIGURE 6

The variation of $K_1\varphi/r$ with initial concentration of HTTA in 76.7 mol% methanol in benzene, at 25°C.


Solvent; 76.7 mol % methanol in benzene
● 560 nm
▲ 570 nm
0.000
0.005
0.010
0.015
0.020
Initial molar conc. of HTTA
$\frac{K_1\varphi}{r}$

a drop in (w), the water activity in the solvent, will produce a drop in φ, and so in $K_1\varphi/r$. This drop becomes smaller, the larger the value of $[HTTA]_i$. Since K_kK_w is unknown for the present solvents, quantitative treatments are not possible at present.

In the present systems the initial water content varied from 1×10^{-3} M for benzene, to 2×10^{-2} M for methanol. Handling of these solutions in undried air may have increased these values somewhat. Therefore the values of $K_1\varphi/r$ at the lowest concentrations of $[HTTA]_i$ are likely to be in error due to the hydrate formation.

Furthermore, the term $[Ka/(HTTA)]^{\frac{1}{2}}$ in equation (5.13) may affect φ significantly at low values of $[HTTA]_i$. This is especially the case in high-methanol solvents because the enolization constant $[(HTTA)/(HTTA')]$ is expected to be low in methanol. The value of Ka in methanol-benzene mixtures is unknown, so quantitative treatment is not possible. However, the value of Ka in water has been reported[7] to be 5×10^{-5}; and K_k in water has been reported[7] to be 62.5. Then for water, the value of $[Ka/(HTTA)]^{\frac{1}{2}}$, for $(HTTA) = 1 \times 10^{-5}$ M, would be 1.7; and for $(HTTA) = 1 \times 10^{-2}$ M, it would be 0.007.

For these two known reasons for $K_1\varphi/r$ being abnormally high, namely hydrate formation and ionization of HTTA, it was considered correct to reject those values of $K_1\varphi/r$ in Table 13, for solutions less than 0.485×10^{-3} M in $[HTTA]_i$.

Inspection of Table 13 also shows that the values of $K_1\varphi/r$ appear to be consistently high at the highest concentrations of $[HTTA]_i$. To test this apparent trend, the

53.5

values of $K_1\varphi/r$ in that table were averaged for a given solvent mixture, over the several wavelengths and over all values of $[HTTA]_i$ except that those below 0.485×10^{-3}M were rejected. The resulting mean values of $K_1\varphi/r$ are in Col. 2 of Table 20. Col. 3 contains the value of $K_1\varphi/r$ at the highest value of $[HTTA]_i$, which is listed in Col. 4. Adjacent columns contain the corresponding values, for slightly lower concentrations of $[HTTA]_i$.

The question now is whether or not there is a reasonable basis for rejecting these apparently high values of $K_1\varphi/r$ at the higher values of $[HTTA]_i$. First, for a given solvent mixture, K_1 itself will remain constant with changes in $[HTTA]_i$. Second, the systems were shown by the data of Table 11 to be in equilibrium, by comparison of the absorbances at 25°C., measured after two days and after two months. Third, it has already been shown that all the requirements listed in Section 5.1 for the use of equation (5.14) to the present systems, have been met. The terms which must be significantly affected[!] by high values of $[HTTA]_i$ are φ and r.

Now

$$5.2 \qquad r = \frac{\gamma_{Cu(TTAPAN)}}{\gamma_{Cu(TTA)_2}\,\gamma_{HPAN}}$$

In the present solutions, the initial concentration of Cu(TTAPAN) was of the order 1×10^{-5} M. Therefore the

---

[!] It is realized that terms affected by high values of $[HTTA]_i$ are going to be affected also at lower values. However, what is sought here is a term which is measurably affected at the highest values of $[HTTA]_i$ but negligibly so at lower values.

Table 20

Comparison of average values of K_1, with values for highest concentrations of $[HTTA]_i$, for the exchange reaction $Cu(TTA)_2 + HPAN \rightleftharpoons Cu(TTAPAN) + HTTA$ in benzene-methanol mixtures at 25°C.

Source of data: Table 13

Sol. Nos.	$K_1\varphi/r$ mean	$K_1\varphi/r$ for highest $[HTTA]_i$	Higher $[HTTA]_i$ M x 10^1	$K_1\varphi/r$ for second highest $[HTTA]_i$	second highest $[HTTA]_i$ M x 10^1	$K_1\varphi/r$ for 3rd highest $[HTTA]_i$	3rd highest $[HTTA]_i$ M x 10^1	mol% MeOH in benzene
1-13	686	788	0.388	767	0.291	751	0.194	8.38
1-12	570	593	0.277	599	0.246	592	0.184	16.0
1-12	487	537	0.291	508	0.194	497	0.146	23.0
1-12	379	392	0.277	390	0.247	383	0.185	35.4
1-12	438	438	0.420	425	0.280	415	0.196	35.4
1-11	387	407	0.194	393	0.146	382	0.097	40.9
1-14	307	321	0.194	313	0.146	301	0.097	55.2
1-12	232	232	0.147	231	0.133	223	0.118	59.4
1-11	246	256	0.194	246	0.146	240	0.097	76.7

equilibrium concentrations of Cu(TTAPAN), $Cu(TTA)_2$, and HPAN were too small for the value of r to be significantly different from unity for all the solutions.

Inspection of equation (5.13) shows that the activity coefficients, (w), and (HTTA) all affect φ. For a given solvent, K_k, K_s and K_w will be constant. For the high concentrations of methanol used in the solvent mixtures, (S) is also essentially constant. The consequence of variations in (w) and in (HTTA) have already been dealt with. There remain the activity coefficients. The value of γ_{HTTA} has been reported[23] in benzene, where 95% of the $[HTTA]_i$ exists as the enol[7,20], to follow the relationship

$$(6.1) \quad \gamma_{HTTA} = 1 - 0.24\,[HTTA]^{0.48}$$

Their reference state evidently was an infinitely dilute solution.

Unfortunately, the activity coefficients of all the equilibrium forms of HTTA are not known in the mixed solvents of the present work. However, it is considered advisable on the basis of equation (6.1) to reject the values of $K_1\varphi/r$, for values of $[HTTA]_i$ above 0.0154 M.

After rejecting from Table 13 values of $K_1\varphi/r$ for values of $[HTTA]_i$ below 0.485×10^{-3} M, and above 0.0154 M, the remaining values of $K_1\varphi/r$ for a given solvent mixture were averaged over the several wavelengths, and over the remaining range of $[HTTA]_i$ values. These mean values and their standard deviations are in Table 21. They are the final values for the present investigation.

Table 21

Final mean values of $\frac{K_1\varphi}{r}$ averaged over all wavelengths, for the exchange reaction

$$Cu(TTA)_2 + HPAN \rightleftharpoons Cu(TTAPAN) + HTTA$$

in methanol-benzene mixtures at 25°C.

Source of data: Table 13, with values of K_1 rejected when 0.485×10^{-3} M $>$ $[HTTA]_i > 0.154 \times 10^{-1}$ M.

Sol. Nos.	$K_1\varphi/r$ mean	s.d.	N	methanol, mol% in benzene	$K_1\varphi/r$ mean for $[HTTA]_i$ in Col. IX	s.d.	N	$[HTTA]_i$ M x 10^3
4-12	660	19	6	8.38	667	63	6	0.243
4-12	562	20	4	16.0	597*	35	4	0.616
3-11	479	18	6	23.0	539	72	6	0.243
4-12	376	13	4	35.4	384*	31	4	0.616
4-10	444	45	3	35.4	852	108	3	0.140
2-10	385	8	6	40.9	416	10	6	0.243
2-12	305	13	5	55.2	360	37	5	0.243
1-12	232	2	3	59.4	230*	18	3	0.737
2-10	245	10	5	76.7	276	29	5	0.243

* These values were not discarded when calculating K_1 of Col. II.

As described previously, values of $K_1\varphi/r$ for values of $[HTTA]_i$ less than 0.485×10^{-3} M were discarded on the grounds of hydrate formation and ionization. For interest, Col. 6 of Table 21 contains some of these discarded values averaged for a given solvent over the several wavelenghts, and Col. 9 contains the corresponding values of $[HTTA]_i$. Comparison of Cols. 2 and 6 shows that indeed all the discarded values are higher than the final means.

Inspection of the data given in Table 15 shows that, unlike the case of $K_1\varphi/r$, abnormally high values of $K_2\varphi/p$ do not occur. The conditions that led to the high values for $K_1\varphi/r$ were absent in the case of $K_2\varphi/p$. Thus, in the exchange reaction of Cu(TTAPAN) with HPAN (reaction B), the concentration of HTTA formed was very small, much smaller than the concentration of water in the methanol-benzene mixtures. The value of (w) in the expression for φ (equation 5.13) would then be essentially unaffected by the HTTA formed. Moreover, the activity coefficients of the several species of HTTA can be considered to be equal to unity, because of their small concentrations. There remains $[Ka/(HTTA)]^{\frac{1}{2}}$ as the only term that could influence the value of φ, and therefore of $K_2\varphi/p$. All that can be said at present is that φ must change in value as $[HPAN]_i$ is changed. The reason is that for constant $[Cu(TTAPAN)]_i$ an increase in $[HPAN]_i$ leads to an increase in the value of HTTA formed, which in turn leads to a change in $[Ka/(HTTA)]^{\frac{1}{2}}$. However, this change is too small to observe in the present work, due to the scatter in the data.

From the data given in Table 15, and for each methanol-benzene mixture used, a mean value of $K_2\varphi/p$ at 25°C. was calculated, the average being over all wavelengths used and over all concentrations of $[HPAN]_i$ for a given methanol-benzene mixture. These grand means and their standard deviations are entered in Table 23. The standard deviation in each case was calculated from the deviation of the grand mean from the individual means for each $[HPAN]_i$ at each wavelength.

From the data given in Table 18, and for the solvents pure benzene and 40.9 mol% methanol in benzene, a mean value of $K_1\varphi/r$ at 15°C. and at 35°C. was calculated; these grand means and their s.d. are entered in Table 22. Values of $K_1\varphi/r$ for $[HTTA]_i$ below 0.485 M, and above 0.0154 were rejected.

From the data given in Table 19, and for the solvents pure methanol and 40.9 mol% methanol in benzene, a mean value of $K_2\varphi/p$ at 15°C. and at 35°C. was calculated. These grand means and their s.d. are entered in Table 24.

Table 22

Final mean values of $K_1\varphi/r$ averaged over all wavelengths, for the exchange reaction

$$Cu(TTA)_2 + HPAN \rightleftharpoons Cu(TTAPAN) + HTTA$$

in benzene, and in 40.9 mol% methanol in benzene, at 15°C. and 35°C.

Source of data: Table 18, with values of $K_1\varphi/r$ rejected when

$$0.485 \times 10^{-3}\ M > [HTTA]_i > 0.150 \times 10^{-1}\ M$$

Soln. No.	Solvent	$K_1\varphi/r$ at 15°C.		$K_1\varphi/r$ at 35°C.		N
		mean	s.d.	mean	s.d.	
7-15	Pure benzene	1154	41	728	34	5
2-10	40.9 mol% methanol in benzene	546	35	314	10	6

Table 23

Final mean values of $K_2\varphi/p$ averaged over all wavelengths, for the exchange reaction

$$Cu(TTAPAN) + HPAN \rightleftharpoons Cu(PAN)_2 + HTTA$$

in methanol-benzene mixtures, at 25 ± 2°C.

Source of data: Appendix X.

Sol. No.	Solvent; mol% methanol in benzene	$K_2\varphi/p \times 10^3$	
		mean	
1-12	16.0	43	9
1-12	35.4	80	4
1-12	41.0	97	3
1-11	50.9	123	3
1-11	59.4	136	4
1-11	76.7	303	11
1-12	89.8	402	36

Table 24

Final mean values of $K_2\varphi/p$ averaged over all wavelengths, for the exchange reaction

$$Cu(TTAPAN) + HPAN \rightleftharpoons Cu(PAN)_2 + HTTA$$

in methanol-benzene mixtures, at 15°C. and 35°C.

Source of data: Table 19

Sol. No.	Solvent	$K_2\varphi/p$ at 15°C.	$K_2\varphi/p$ at 35°C.	N
1-11	pure methanol	0.700 ± 0.034	0.500 ± 0.003	2
1-12	40.9 mol% methanol in benzene	0.111 ± 0.003	0.061 ± 0.004	2

6.2 — The reasons for the variation of $K_1\varphi/r$ and $K_2\varphi/p$ with the mol% methanol in the methanol-benzene mixtures.

Inspection of Table 21 shows that the value of $K_1\varphi/r$ decreases with an increase in the methanol content of the benzene-methanol mixtures. This decrease is shown graphically in Figure 7. Inspection of Table 23 shows that $K_2\varphi/p$ increases with an increase in the methanol content of the benzene-methanol mixtures, and this increase is shown graphically in Figure 8. Explanations were sought for the decrease in $K_1\varphi/r$ and the increase in $K_2\varphi/p$, with an increase in the methanol content of the solvent. The values of $K_1\varphi/r$ are considered first.

The values of K_1 for reaction A at 25°C. in the methanol-benzene mixtures could not be calculated, because φ and r were unknown. However, approximate values of φ in pure benzene and in pure methanol could be calculated, because literature data were available for these two solvents. In addition, the ratio $r_{benzene}/r_{methanol}$ (abbreviated r_b/r_m) was estimated from solubility values measured by d'Amboise, of Cu(TTAPAN), $Cu(TTA)_2$ and HPAN both in methanol and in benzene. These estimates of φ and of r_b/r_m are now described.

The function φ is defined in equations (5.13) and (5.12) as

$$\varphi = \frac{1}{\gamma_{HTTA}} + \frac{K_k}{\gamma_{HTTA'}} + \frac{K_kK_w(w)}{\gamma_{HTTA'.w}} + \frac{K_kK_S(S)}{\gamma_{HTTA'.S}} + $$

$$+ \left(\frac{Ka}{(HTTA)}\right)^{\frac{1}{2}} = \frac{[HTTA]_i - [Cu(TTA)_2]}{(HTTA)}$$

FIGURE 7

The variation of $K_1\varphi/r$ with mol% methanol in the methanol-benzene mixtures used as solvents, at 25°C.

Note: (i) The values of $K_1\varphi/r$ are the final means, given in Table 21

(ii) The values of $K_1\varphi/r$ in pure benzene and in pure methanol were obtained by d'Amboise[3]

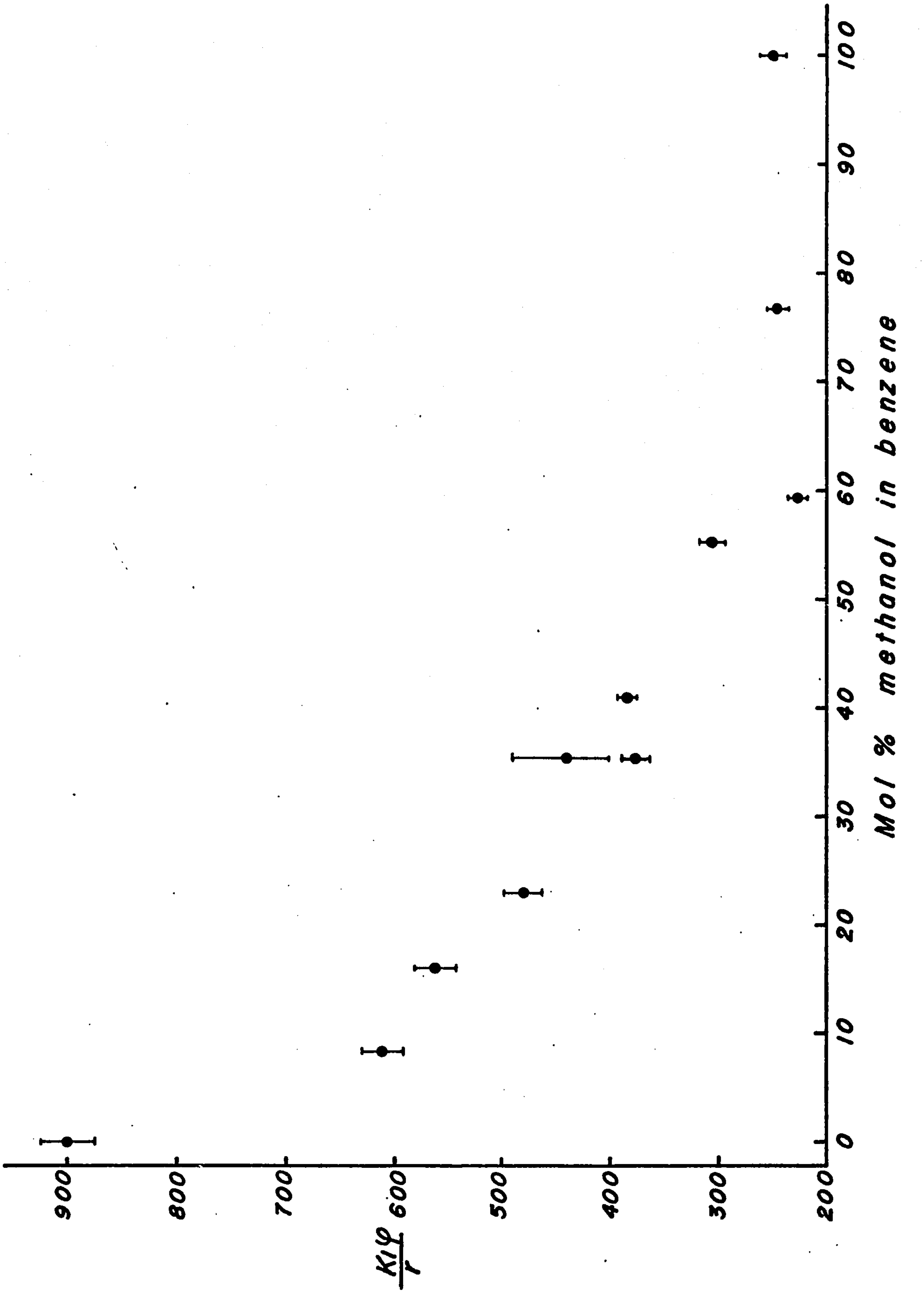
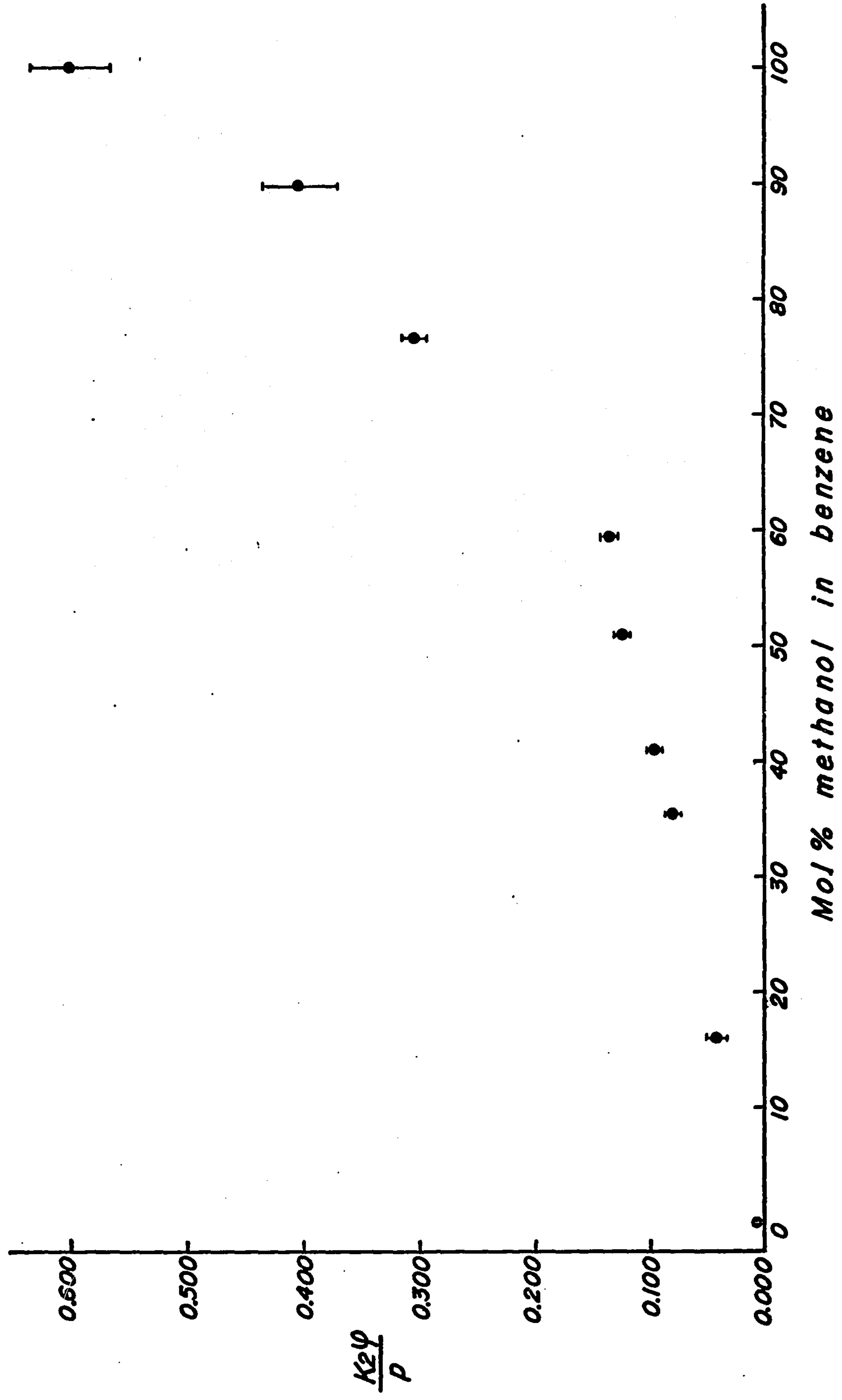

0
10
20
30
40
50
60
70
80
90
100
Mol % methanol in benzene
200
300
400
500
600
700
800
900
KIφ / r

FIGURE 8

The variation of $K_2\varphi/p$ with mol% methanol in the methanol-benzene mixtures used as solvents, at 25°C.

Note: (i) The values of $K_2\varphi/p$ are final means, given in Table 23

(ii) The values of $K_2\varphi/p$ in pure methanol and in pure benzene were obtained by d'Amboise[3]



K2φ/P
0.600
0.500
0.400
0.300
0.200
0.100
0.000
0
10
20
30
40
50
60
70
80
90
100
Mol % methanol in benzene

It has been reported[7,20] that in benzene 95% of the HTTA exists as the enol. Therefore, in that solvent, the value of φ will be approximately $1/\gamma_{HTTA}$. However, inspection of equation (5.12) shows that as the methanol content of the mixed solvent increases, the value of φ would be expected to increase due to the formation of the several species described in Section 5.3.1. For example, the formation of these species would automatically reduce the value of (HTTA) in equation (5.12) and therefore φ would increase. In addition, as the methanol content of the mixed solvent was increased, (S) and therefore φ would be increased. Furthermore, it has been pointed out [27] that while there is internal hydrogen-bond formation in the enol form, the equilibrium from enol to keto, hetohydrate and ketomethamolate is shifted towards these keto forms in solvents which have a considerable hydrogen-bond capacity, such as methanol; this is an additional reason for the increase in φ with an increase in methanol content of the solvent. The ratio $[HTTA]/[HTTA]_{TOTAL}$, which equals $1/\varphi\gamma_{HTTA}$ for a solution of HTTA in solvent, has been measured in several alcohols by Wakahayashi et al[26]. They used NMR measurements on 0.5 M solutions of HTTA in several normal alcohols, but not in methanol. In order to obtain an estimate of the value of $[HTTA]/[HTTA]_{TOTAL}$ in methanol, their values were plotted as a function of the size of the alkyl group in the normal alcohols used, and this graph was then extrapolated back to the alkyl group CH_3. The extrapolated value found was 0.2 for $[HTTA]/[HTTA]_{TOTAL}$. Therefore, the corresponding value of $\varphi\gamma_{HTTA}$ would be 5.

In summary, it seems reasonable to consider that in the present systems $\varphi\gamma_{HTTA}$ went from a value of approximately 1 in pure benzene to 5 in pure methanol.

The next factor to be considered in the term $K_1\varphi/r$

was the value of r in going from benzene through the mixed solvents to methanol. It was possible to obtain a crude estimate of the value of the ratio r in benzene to r in methanol, as follows:

It is readily shown for a saturated solution of solute L in benzene (subscript b) and in methanol (subscript m), that

$$(6.1) \quad \mu^{o}_{L,b} - \mu^{o}_{L,m} = -RT \ln \frac{\gamma_{L,b} m_{L,b}}{\gamma_{L,m} m_{L,m}}$$

where $\mu^{o}_{L,b}, \mu^{o}_{L,m}$	denote the chemical potential of L in its standard state in benzene, and in methanol respectively.
$m_{L,b}, m_{L,m}$	denote the molal concentration of L in a saturated solution in benzene, and in methanol respectively.
$\gamma_{L,b}, \gamma_{L,m}$	denote the activity coefficient of L in its saturated solution in benzene, and in methanol respectively.

By choosing for all solvents the standard state of L to be the conventional hypothetical 1-molar solution of L in benzene, equation 6.1 becomes

$$(6.2) \quad \frac{\gamma_{L,b}}{\gamma_{L,m}} = \frac{m_{L,m}}{m_{L,b}}$$

By the definition of r in equation 5.2, and by also using equation 6.2,

$$(6.3)\quad \frac{r_b}{r_m} = \frac{\dfrac{\mathcal{M}_{Cu(TTAPAN),b}}{\mathcal{M}_{Cu(TTAPAN),m}}}{\dfrac{\mathcal{M}_{Cu(TTA)_2,b}}{\mathcal{M}_{Cu(TTA)_2,m}} \times \dfrac{\mathcal{M}_{HPAN,b}}{\mathcal{M}_{HPAN,m}}}$$

The solubilities of Cu(TTAPAN), $Cu(TTA)_2$, $Cu(PAN)_2$ and HPAN in pure methanol and pure benzene have been measured by d'Amboise[3], and they are given in Table 25. On using these data in equation (6.3), a value of 0.43 was obtained for the ratio r_b/r_m. Accordingly, the term r would cause the function $K_1\varphi/r$ to decrease in value, on going from benzene to methanol. It is important to notice here that unlike the complexes Cu(TTAPAN) and $Cu(PAN)_2$, the complex $Cu(TTA)_2$ is much more soluble in methanol than in benzene. This is in agreement with the fact that methanol can readily hydrogen-bond to the oxygen atom of the square planar chelate $Cu(TTA)_2$[21]. Therefore, while the complexes Cu(TTAPAN) and $Cu(PAN)_2$ probably, due to steric effects, are not much more solvated in methanol than they are in benzene, the complex $Cu(TTA)_2$ is expected to be more soluble in methanol than in benzene. Thus, a large part of the increase in the value of r on going from benzene to methanol occurs because the complex $Cu(TTA)_2$ is more solvated in methanol than it is in benzene. It is recognized that the use of solubility values, which in some cases are high, can lead only to a crude estimate of r_b/r_m, since the solutions are very unlikely to be ideal ones.

The estimated values of the ratio $(\varphi\gamma_{HTTA})_b/(\varphi\gamma_{HTTA})_m$ and of the ratio r_b/r_m for the two solvents benzene and methanol were then compared with the results obtained for the function $K_1\varphi/r$ of equation 5.14 in the present systems. The values of this function were determined by d'Amboise[3],

Table 25

Solubilities of $Cu(TTA)_2$, $Cu(PAN)_2$, Cu(TTAPAN) and HPAN, in methanol and benzene, at 20°C.

Compound	Solubility in mols./litre at 20°C. (3)	
	Solvent	
	Benzene	Methanol
Cu(TTAPAN)	8.6×10^{-4}	1.9×10^{-4}
$Cu(PAN)_2$	3.0×10^{-4}	6.6×10^{-5}
$Cu(TTA)_2$	1.8×10^{-2}	8.0×10^{-2}
HPAN	2.0×10^{-1}	2.4×10^{-2}

in pure benzene and in pure methanol; he found the values 900 and 250 respectively (see Figure 7).

Therefore

$$\frac{(K_1\varphi/r)_b}{(K_1\varphi/r)_m} = \frac{900}{250}$$

Whereas a concentration quotient

$$^{c}K_1 = \frac{[\quad][\quad]}{[\quad][\quad]}$$

will change from solvent to solvent , it is supposed that all the factors that produce this change have been accounted for in φ and r.

Then,

$$(6.4) \quad \frac{(\varphi_b/\varphi_m)}{(r_b/r_m)} = 3.6$$

By using the above calculated estimates of $(\varphi\gamma_{HTTA})_b/(\varphi\gamma_{HTTA})_m$ and of r_b/r_m,

$$(6.5) \quad \frac{(\varphi_b/\varphi_m)}{(r_b/r_m)} \times \frac{\gamma_{HTTA,b}}{\gamma_{HTTA,m}} = \frac{1}{5} \times \frac{1}{0.43}$$

On substituting equation (6.4) into equation (6.5),

$$(6.6) \quad \frac{\gamma_{HTTA,m}}{\gamma_{HTTA,b}} = 7.7$$

The change in value of $K_2\varphi/p$ (equation 5.23) on going from benzene to methanol was interpreted in the same way as the change in $K_1\varphi/r$. Thus, the value of the ratio P_b/P_m

(with subscript b denoting benzene, and m methanol) was estimated from the solubility data given in Table 25 to be approximate 120. The value of the ratio $\varphi_b \times \gamma_{HTTA,b}/\varphi_m \times \gamma_{HTTA,m}$ has already been estimated for use in $K_1\varphi/r$, to be 0.2. Therefore, as a rough estimate,

$$(6.7)\quad \frac{\varphi_b/\varphi_m}{P_b/P_m} \cdot \frac{\gamma_{HTTA,b}}{\gamma_{HTTA,m}} \simeq \frac{1}{600}$$

Now d'Amboise^3 has found that

$$(6.8)\quad \frac{(K_2\varphi/p)_b}{(K_2\varphi/p)_m} = \frac{0.007}{0.600}.$$

Then, on assuming that all the factors that affect the value of the concentration quotient

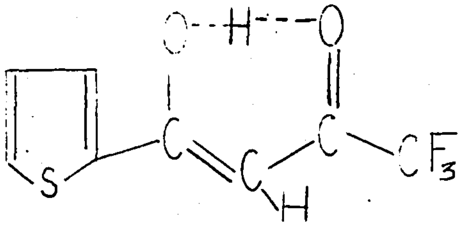
$$^cK_2 = \frac{[\quad][\quad]}{[\quad][\quad]}$$

on going from one solvent to another have been taken into account in φ and r,

$$(6.9)\quad \frac{\varphi_b/\varphi_m}{P_b/P_m} = \frac{0.007}{0.600}$$

From equations (6.7) and (6.9), $\left(\gamma_{HTTA,m}/\gamma_{HTTA,b}\right) = 7$.

The solubilities of HTTA in benzene and in methanol have not been measured, and so a direct comparison of the solubility ratio with the value 7 (for reaction B) and 7.7 (for reaction A) is not possible. The derived ratios (7.7, 7) suggest that HTTA (enol form) would be more soluble, and hence more solvated in benzene than in methanol. It is known[25] that in non-polar solvents the HTTA (enol) has an intra-hydrogen bond.



However, the estimates of r_b/r_m and of P_b/P_m, and therefore of $\tilde{\gamma}_{HTTA,m}/\tilde{\gamma}_{HTTA,b}$ assume that the solubility data in Table 25 can be used to estimate r and p. For saturated solutions that are very dilute, solubility ratios should give good estimates of activity-coefficient ratios. But when the saturated solutions are more concentrated they are more unlikely to be ideal. In that case solubility ratios will not give a good estimate of activity-coefficient ratios of very dilute solutions.

In addition, it is to be remembered that $\tilde{\gamma}_{HTTA,m}$, which occurs in the expression $\varphi_m \tilde{\gamma}_{HTTA,m}$ is the activity coefficient of HTTA (enol) in a 0.5 molar solution in methanol. The reason is that Wakayayashi et al[26] used 0.5 molar solutions in their NMR studies which led to the value of $[HTTA]/[HTTA]_T$, and therefore to $\varphi_m \tilde{\gamma}_{HTTA,m} = 5$. However, the HTTA solutions used in the present work were 0.04 molar or less.

Therefore the present discussions of $K_1\varphi/r$ and $K_2\varphi/p$ must be regarded as merely exploratory, insofar as actual values of φ/r and φ/p are concerned.

Claims to Original Research

1) The apparent molar equilibrium constants K_1' and K_2' for reactions (A) and (B)

$$(A) \quad Cu(TTA)_2 + HPAN \rightleftharpoons Cu(TTAPAN) + HTTA$$

$$(B) \quad Cu(TTAPAN) + HPAN \rightleftharpoons Cu(PAN)_2 + HTTA$$

in methanol-benzene mixtures were successfully evaluated by using spectrophotometric data in conjunction with algebraic equations which were derived for the purpose. These apparent equilibrium constants K_1' and K_2' were obtained at $15^oC.$, $25^oC.$ and $35^oC.$

2) The factors which caused K_1' and K_2' not to be thermodynamic constants (K_1 and K_2 being the thermodynamic constants) were identified as the relevant activity coefficients, and also the fact that the HTTA existed as enol, keto, ion, and solvates in the solutions.

3) The practical titration of $Cu(TTA)_2$ by HPAN used as a volumetric reagent in organic solvent, was studied in benzene, in methanol and in mixtures of the two. The end-point was sharp only in benzene. It became less distinct as the methanol content was increased, due to the increase in the value of K_2' with the methanol content.

Suggestions for Further Work

1) In this work it was found that in order to evaluate the thermodynamic equilibrium constants K_1 and K_2 for reactions (A) and (B) in methanol, benzene or their mixtures, it would be necessary to calculate the terms φ, r and p for the solutes in these solvents. Investigation of all the chemical species as well as the determination of the relevant equilibrium constants involved are necessary, as well as evaluation of the various activity coefficients.

2) It would be useful to study the present systems in a different solvent or mixture of solvents, in which the reaction of $Cu(TTA)_2$ with HPAN would be faster than in benzene and yet, the values of $K_2\varphi/p$ would be too small to cause reaction (B) to occur to a significant extent, during titrations of $Cu(TTA)_2$ with HPAN.

3) In Tables 22 and 24, it can be seen that both $K_1\varphi/r$ and $K_2\varphi/p$ increase with a decrease of temperature. Explanation for this fact was not sought in the present work, due to the fact that values of K_1 and K_2 themselves could not be obtained without much additional data. It could be of interest to investigate the dependence of K_1 and of K_2 on temperature.

Appendix I

Dithizone Test for the Metal Content of the Solvents.

i) Methanol

The dithizone used was reagent grade, and was not further purified.

A 2.5×10^{-4} M solution of dithizone in purified methanol was used.

It had been observed that when dithizone solution was added to methanol that contained trace metals, two peaks were observed, one at 590 nm. and the other at 450 nm. Dithizone alone has two peaks at these wavelengths. However, the ratio of the absorbance at 590 nm. to that at 450 nm. decreased with increasing concentration of copper (II) for a fixed concentration of dithizone. These facts were used in order to test the purified methanol for the presence of trace metals. Thus, the purified methanol to be tested was treated with the dithizone solution sufficient to give one absorbance of about 0.5 to 1. The ratio of the absorbance at 590 nm. to that at 450 nm. was then determined. The same solution was then diluted with a known volume of the purified methanol under test and the ratio of absorbances was again measured. This procedure was repeated for several dilutions of the original solution with the methanol under test and the ratios of the absorbances at 590 nm. to that at 450 nm. were tabulated. If the ratios remained constant for all dilutions of the original solution, the methanol was considered sufficiently free of trace metals to be used for chelate-exchange titrations. Otherwise, it was recycled through the purification process.

ii) Benzene

The spectra of dithizone and its metal chelates in benzene have been studied by many authors[15]. Dithizone has two peaks, one at 618 nm. and the other at 450 nm. The metal dithizonates, however, have just one peak, between 450 nm. and 550 nm., depending on the metal. Accordingly, a test for the presence of trace metals in benzene was carried out by performing dilutions of a solution of dithizone in benzene with the benzene under test, and measuring the absorption spectra of all these solutions. The benzene was considered free from trace metals when the following two criteria were met: (i) No band between 450 nm. and 550 nm. was observed; (ii) the ratio of the absorbance at 618 nm. to that at 450 nm. did not change with dilutions of the benzene solution of dithizone with more benzene.

Appendix II

General spectrophotometric-titration procedures.

The spectrophotometric-titration procedures used the apparatus described in Section 3.1.1. They have been described by Gray[1].

Briefly, in using the Unicam S.P. 500 spectrophotometer, a warm-up period of one hour for the spectrophotometer and ten minutes for the tungsten lamp was necessary in order to ensure stable absorbance readings. The 65-ml. titration cell, cleaned and dried by the process described on page 11, was positioned in the cell compartment. Approximately 50 ml. of methanol was then transferred to the cell. The wavelength was set either at 460 nm. or 560 nm., depending on the system being studied. The sensitivity potentiometer of the apparatus was set at the midway position, stirring was started, and the spectrophotometer was adjusted to zero absorbance. An aliquot of the solution to be titrated was then pipetted into the titration cell. The platinum-needle delivery tip was attached to the Koch micro-buret filled with the titrant, and was pushed through the silicone-rubber system. The tip of the needle was always under the surface of the solution. Then increments of the titrant were added and the absorbance measured after each addition. The increments added, and the equilibration period, depended on the particular titration.

As was found by Gray, close temperature control was unnecessary, and all experiments were conducted at room temperature.

The titration graph was a plot of the measured absorbances against ml. of titrant added, and the end point was determined by inspection, by extrapolation of the straight-line portions of the graph, to their intersection point.

Appendix III

Standardization of stock solutions of Cu(TTAPAN), Cu(PAN)$_2$, Cu(TTA)$_2$ and HPAN in methanol or benzene by spectrophotometric titration.

The general procedure given in Appendix II was used.

i) Standardization of stock solution of HPAN in methanol or benzene, against standard aqueous Cu(NO$_3$)$_2$ solution.

The stock solution of HPAN in methanol or benzene was used as titrant in the buret, even though it was the solution to be standardized. The concentration of this solution was known to be approximately 5 x 10^{-4} M. The aliquot of the aqueous Cu(NO$_3$)$_2$ solution transferred to the titration cell to be titrated with the HPAN contained approximately 16 mg. of copper. Methanol was then added.

In the titration, Cu(PAN NO$_3$) was formed; it had an absorbance maximum at 560 nm. Accordingly, the absorbance at this wavelength was recorded as a function of titrant added. Naturally the absorbance increased with addition of titrant. The end point was well defined, unless the methanol used contained dissolved trace metals. In that case the titration graph was curved, and the end point could not be detected. Incidentally, this fact was also used as a test for trace metals in methanol.

An equilibration period of approximately one minute was allowed after each addition, prior to taking the absorbance measurement.

A typical titration graph is given in Figure 9.

ii) Standardization of stock aqueous EDTA solution, against standard aqueous $Cu(NO_3)_2$ solution.

The stock aqueous solution of EDTA to be standardized was used as titrant in the buret. It was prepared by dissolution of a weighed amount of the solid in deionized water, to give a solution approximately 4×10^{-4} M. It was stored in a polyethylene bottle.

The methanol was added as a solvent into the titration cell. This methanol was buffered to pH 10 by an ammonia-ammonium chloride buffer mixture, before adding the standard aqueous solution of $Cu(NO_3)_2$.

The volumes of methanol and standard copper solution were such that the copper in the titration cell was approximately 5×10^{-5} M. The wavelength was set at 560 nm. The spectrophotometer was then adjusted to zero absorbance referred to the analyte prior to its titration.

Standard solution of HPAN in methanol was added, sufficient to allow complexation of all Cu(II) present in the titration cell. This complexation consisted in the formation of $Cu(PAN\ NO_3)$.

Addition of increments of the aqueous EDTA standard solution (the titrant) resulted in the replacement of the PAN and NO_3^- ligands from the mixed copper complex. This displacement was followed spectrophotometrically by the decrease in absorbance at 560 nm., which was where the $Cu(PAN\ NO_3)$ had a peak.

The first titration was not counted. Thus, after its end point another aliquot of the standard aqueous solution of $Cu(NO_3)_2$ was added to the titration cell and titrated as before. In this way, the results were not affected by trace metals dissolved in the methanol and buffer solution used. The number of titrations performed in the same methanol solution were then only limited to the volume of the cell itself.

An equilibration period of approximately one minute was allowed after each addition, prior to taking the absorbance measurements.

A typical titration graph is given in Figure 9.

iii) Standardization of Cu(TTAPAN), $Cu(PAN)_2$ and $Cu(TTA)_2$ solutions in methanol or benzene by spectrophotometric titration with a standard aqueous solution of EDTA.

The steps followed in the standardizations of Cu(TTAPAN), $Cu(PAN)_2$ and $Cu(TTA)_2$ solutions in methanol or benzene by spectrophotometric titration with the above standard aqueous solution of EDTA, were the same as in the standardization of this aqueous solution of EDTA itself with the standard aqueous solution of $Cu(NO_3)_2$, given in part (ii) in the present section, except that in the case of Cu(TTAPAN) and $Cu(PAN)_2$ no HPAN was added; these complexes also have a well defined peak at 560 nm. (see Figure 1).

An equilibration period of approximately one minute was allowed after each addition, prior to taking the absorbance measurement.

A typical titration graph is given in Figure 9.

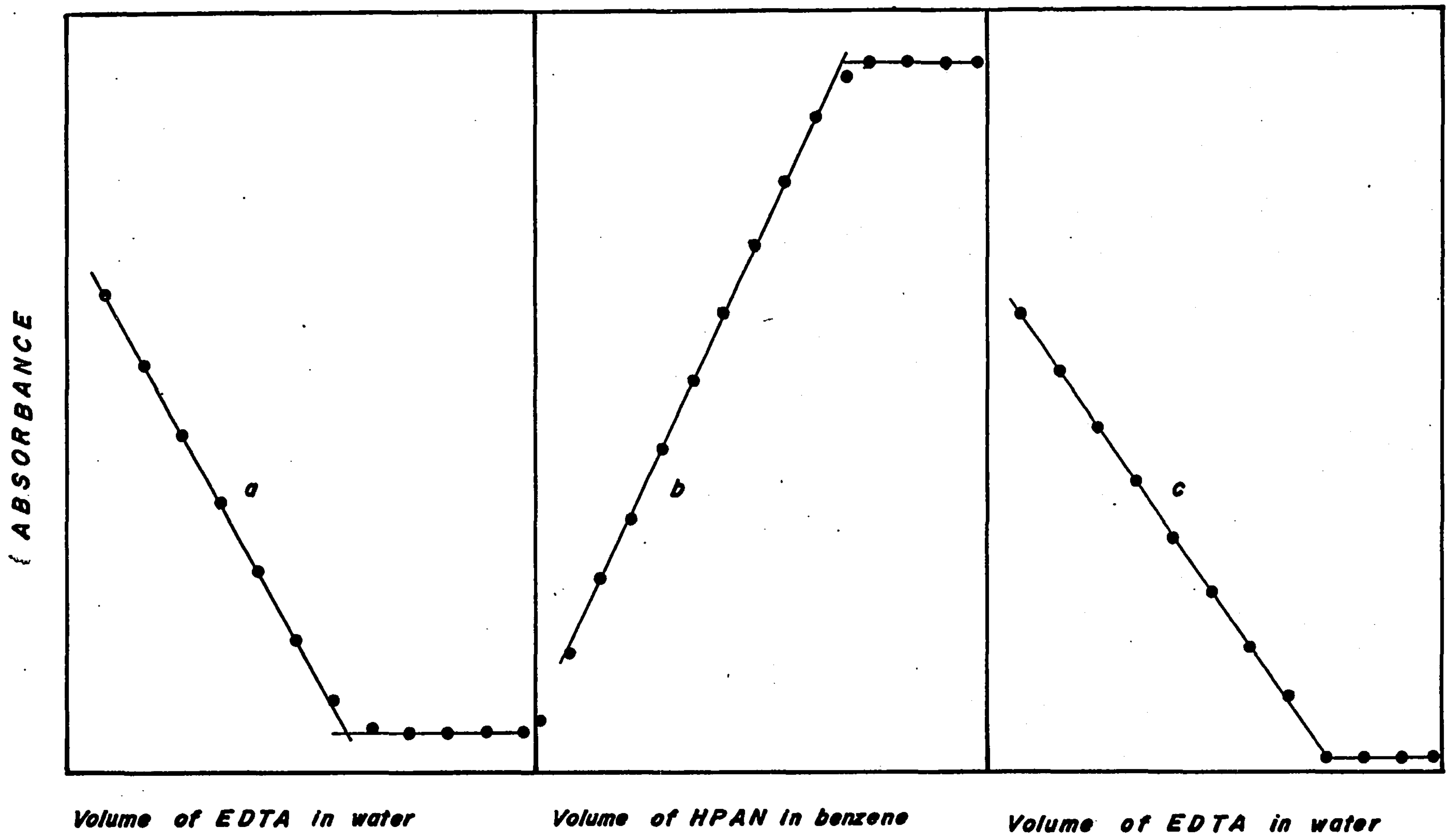
FIGURE 9

Typical titration graphs for the chelate-exchange titration at 25°C. of

a) $Cu(NO_3)_2$ in methanol, versus EDTA in water

b) $Cu(NO_3)_2$ in methanol, versus HPAN in benzene

c) Cu(TTAPAN) in methanol, versus EDTA in water


ABSORBANCE
a
b
c
Volume of EDTA in water
Volume of HPAN in benzene
Volume of EDTA in water

Appendix IV

Preparation of a stock standard aqueous solution of $Cu(NO_3)_2$

The procedures for the preparation of stock standard solution of cupric nitrate used have been described by Gray[1].

Fisher certified A.C.S. analytical-grade copper metal was used. The stock standard solution was prepared by accurately weighing 0.166 g. of this analytical-grade copper metal into 100-ml. beaker. The copper was then dissolved in 1:1 nitric acid and the solution evaporated to moist dryness. The residue was taken up with 5 ml. of water and the solution was evaporated as near to dryness as possible without forming basic insoluble copper salts. The residue was then taken up in deionized water, quantitatively transferred to a calibrated 100-ml. volumetric flask and made up to the mark.

Appendix V

The Preparation of Cu(TTAPAN) According to the Method of d'Amboise[3].

A weighed amount of crystalline $Cu(TTA)_2$, purified as described on page 20, was dissolved in benzene. An equimolar amount of HPAN was added and the temperature of the solution was raised to 45°C. The solution was then thoroughly mixed. Half of the benzene was then allowed to evaporate at a temperature slightly above room temperature, and the solution was then placed in an ice-water bath. The resulting crystals were filtered onto a sintered-glass filter and then dissolved in benzene, and recrystallized as before, by evaporation of benzene, cooling of the solution, and filtration. The purified Cu(TTAPAN) product was dried in a vacuum desiccator over P_2O_5 for a week, then transferred to another desiccator containing silica gel and it was stored there until used.

Appendix VI

Spectrophotometric Titration of Cu(TTA)$_2$ in Methanol-Benzene Mixtures with a Standard HPAN Solution in Benzene.

The Beckman Model D.U. spectrophotometer, and titration assembly described on page 7 and illustrated in Plate 1, were used. The general procedures for spectrophotometric titrations are given in Appendix II.

Stock solutions of Cu(TTA)$_2$ in benzene were prepared and standardized by the method described on page 20. HPAN solutions in benzene were standardized as in Appendix III.

The Koch micro-buret was rinsed and filled with the standard HPAN solution in benzene. An appropriate aliquot of standard Cu(TTA)$_2$ solution was pipetted into the 65-ml. titration cell, such that after dilution to about 50 ml. and the addition of HPAN necessary for the conversion of Cu(TTA)$_2$ to Cu(TTAPAN), the absorbance at 560 nm. was between 0.6 and 0.8.

Methanol and benzene were pipetted into the titration cell which contained the aliquot of Cu(TTA)$_2$ to be titrated. The proportion of methanol and benzene depended on the particular experiment.

The micro-buret was positioned, the wavelength adjusted to 560 nm., the spectrophotometer adjusted to zero absorbance for the solution to be titrated, and the titration started. The absorbance of the Cu(TTAPAN) formed was followed. An interval of 5-10 minutes was needed in order to achieve equilibrium after each addition of titrant.! In solvents with a large concentration of methanol, the reaction was faster. The titration graph was a plot of absorbance versus ml. of titrant added, and the end point was determined by inspection, from the intersection of the extrapolation of the two straight-line portions of the graph.

The results of the titrations of Cu(TTA)$_2$ in several methanol-benzene mixtures with HPAN are given in Table 5.

! Equilibrium in the sense that no variation in absorbance was detected after that period.

Appendix VII

1) REGRE 1: Least-squares fit for
   $y = mx + b$

2) PRABC5: Least-squares fit for
   $Z = A_1x_1 + A_2x_2 + A_3x_3 + B$

3) SPECR3: Least-squares fit of
   a Beer's Law plot

1) [illegible]

```
C    PROGRAM REGR1-
C      THIS PROGRAM CALCULATES THE REGRESSION COEFFICIENTS FOR  A STAIGHT LINE
C      Y = MX + B     IT GIVES M AND B AND THEIR STANDARD DEVIATIONS
C      N IS THE NUMBER OF EXPERIMENTAL POINTS. IT IS GIVEN FIRST IN A FIELD
C      OF (I3). THEN THE POINTS X(I), Y(I) ARE GIVEN IN FIELDS (5(2E8.3)).
      DIMENSION X(100),  Y(100)
      READ(5,1) N
    1 FORMAT(I3)
      READ(5,2) (X(I), Y(I), I = 1,N)
    2 FORMAT(5(2E8.3))
      SUMX = 0.
      SUMY = 0.
      SUMXY = 0.
      SUMX2 = 0.
      SUMY2 =0.
      DO 3 I= 1,N
      SUMX = SUMX + X(I)
      SUMY = SUMY + Y(I)
      SUMXY = SUMXY + (X(I)*Y(I))
      SUMX2 = SUMX2 + (X(I)**2)
    3 SUMY2 = SUMY2 + (Y(I)**2)
      XM = SUMX/N
      YM = SUMY/N
      SX2 = SUMX2 - (XM*SUMX)
      SY2 = SUMY2 -(YM*SUMY)
      SXY = SUMXY - (XM*SUMY)
      BM = SXY/SX2
      AB = YM - (BM*XM)
      SSD = SY2 -(BM*SXY)
      VARY = SSD/(N-2)
      VARM =  SQRT((VARY/SX2)**2)
      STDVM = SQRT(VARM)
      STDVB = SQRT((SUMX2*VARM)/N)
      WRITE(6,14)
   14 FORMAT(1H0,//25X,'SIMPLE REGRESSION ANALYSIS',//20X,'EQUATION:  Y
     1 = MX  + B ',//10X,'EXPERIMENTAL RESULTS',//15X,'Y',15X,'X',/)
      WRITE(6,5) (Y(I), X(I), I = 1,N)
    5 FORMAT(1H0,10X,E12.4,5X,E12.4)
      WRITE(6,17) BM, AB
   17 FORMAT(1H0,20X,'THE REGRESSION LINE IS :',//35X,'Y = (',E15.6,')*X
     1  (',E15.5,')',//)
      WRITE(6,7) STDVM, STDVB
    7 FORMAT(1H0,15X,'STDVEV ON THE SLOPE M IS: ',E12.4,//15X,'STD DEV O
     1N THE INTERCEPT B IS: ',E12.4,//)
      WRITE(6,12) XM,SX2, SXY,YM,SY2, SSD
   12 FORMAT(1H0,20X,'XM = ',E12.4,10X,'SX2 = ',E12.4,10X,'SXY = ',E12.4
     1,//20X,'YM = ',E12.4,10X,'SY2 = ',E12.4,10X,'SSD = ',E12.4,/)
  333 CONTINUE
      WRITE(6,111)
  111 FORMAT(1H0,45X,'END OF COMPILATION')
      END
```

2. BRABC5

```
C   PROGRAM TO CALCULATE THE REGRESSION COEFFICIENTS AND THEIR VARIANCE
C          EQUATION     Z =   A1 * X1   + A2 * X2   +   A3 * X3   + B
C        N IS THE NUMBER OF POINTS USED IN ONE SET
C      M IS THE NUMBER OF SETS OF DATA
      DIMENSION Z(100), X1(100), X2(100), X3(100)
      READ(5,2) N,M
    2 FORMAT(2I3)
      READ(5,33) (X1(I), X2(I), X3(I), I=1,N)
   33 FORMAT(5(3F5.0))
      DO 19 J=1,M
      READ(5,3) (Z(I), I=1,N)
    3 FORMAT(20F4.3)
      SOX1  = 0.
      SOX2  =0.
      SOX3= 0.
      SOZ  = 0.
      SOX12  = 0.
      SOX22  = 0.
      SOX32  = 0.
      SOX1X2  = 0.
      SOX1X3  = 0.
      SOX2X3  = 0.
      SOX1Z  = 0.
      SOX2Z  = 0.
      SOX3Z  = 0.
      SSD  = 0.
      DO 4   I = 1, N
      SOX1  = SOX1  +  X1(I)
      SOX2  = SOX2  + X2(I)
      SOX3  = SOX3  + X3(I)
      SOZ  =  SOZ  + Z(I)
      SOX12  =  SOX12  +  (X1(I)**2)
      SOX22  =  SOX22  +  (X2(I)**2)
      SOX32  =  SOX32  +  (X3(I)**2)
      SOX1X2  =  SOX1X2  +  (X1(I)*X2(I))
      SOX1X3  =  SOX1X3  +  (X1(I)*X3(I))
      SOX2X3  =  SOX2X3  +  (X2(I)*X3(I))
      SOX1Z  =  SOX1Z  +  (X1(I)*Z(I))
      SOX2Z  =  SOX2Z  +  (X2(I)*Z(I))
      SOX3Z  =  SOX3Z  +  (X3(I)*Z(I))
    4 CONTINUE
      X1M  =  SOX1/N
      X2M  =  SOX2/N
      X3M  =  SOX3/N
      ZM  =  SOZ/N
      SX12  =  SOX12  -  (X1M*SOX1)
      SX22  =  SOX22  -  (X2M*SOX2)
      SX32  =  SOX32  -  (X3M*SOX3)
      SX1X2  =  SOX1X2  -  (X2M*SOX1)
      SX1X3  =  SOX1X3  -  (X3M*SOX1)
      SX2X3  =  SOX2X3  -  (X3M*SOX2)
      SZX1  =  SOX1Z  -  (ZM*SOX1)
      SZX2  =  SOX2Z  -  (ZM*SOX2)
      SZX3  =  SOX3Z  -  (ZM*SOX3)
```

2) PRABC5 (continued)

```
      D1 = (SX22*SX32) - (SX2X3**2)
      D2 = (SX1X3*SX2X3)- (SX32*SX1X2)
      D3 = (SX1X2*SX2X3) - (SX22*SX1X3)
      D = (D1*SX12) + (D2*SX1X2) + (D3*SX1X3)
      C11 = D1/D
      C22 = ((SX12*SX32) - (SX1X3**2))/D
      C33 = ((SX12*SX22) - (SX1X2**2))/D
      C12 = D2/D
      C13 = D3/D
      C23 = ((SX1X3*SX1X2) - (SX12*SX2X3))/D
      A1 = (C11*SZX1)  + (C12*SZX2)  + (C13*SZX3)
      A2 = (C12*SZX1) + (C22*SZX2) + (C23*SZX3)
      A3 = (C13*SZX1) + (C23*SZX2) + (C33*SZX3)
      B = ZM - (A1*X1M) - (A2*X2M) - (A3*X3M)
    5 CONTINUE
      DO 6 I = 1,N
    6 SSD = SSD + ((Z(I) -(A1*X1(I)) - (A2*X2(I)) - (A3*X3(I)) - B)**2)
      VARE = SSD/(N-4)
      STDVE = SQRT(VARE)
      VARA1 = C11*VARE
      VARA2 = C22*VARE
      VARA3 = C33*VARE
      COV12 = C12*VARE
      COV13 = C13*VARE
      COV23 = C23*VARE
      STDA1 = SQRT(VARA1)
      STDA2 = SQRT (VARA2)
      STDA3 = SQRT(VARA3)
      VARB = VARE/N
      STDB = SQRT(VARB)
    7 CONTINUE
      WRITE(6,8)
    8 FORMAT(1H1,40X,'EQUATION   -   Z = A1*X1 + A2*X2  + A3*X3  + B ',/
     1//20X,'EXPERIMENYAL  DATA',/17X,'Z',23X,'X1',22X,'X2',22X,'X3')
      WRITE(6,9) (Z(I), X1(I), X2(I), X3(I), I = 1,N)
    9 FORMAT(1H0,4(10X,E12.4,3X))
      WRITE(6,10)  A1, A2, A3, B
   10 FORMAT(1H ,20X,'CALCULATED RESULTS -  LEASTS SQUARES FIT',///,15X,
     1'A1 = ',E12.4,/15X,'A2 = ',E12.4,/15X,'A3 = ',E12.4,/15X,'B = ',E1
     22.4)
      WRITE(6,11) SX12,SX22, SX32,SX1X2,SX1X3,SX2X3,SZX1,SZX2,SZX3
   11 FORMAT(1H ,30X,'SX12 = ',E12.4,4X,'SX22 = ',E12.4,4X,'SX32 = ',E12
     1.4,//30X,'SX1X2 = ',E12.4,4X,'SX1X3 = ',E12.4,4X,'SX2X3 = ',E12.4,
     2//30X,'SZX1 = ',E12.4,4X,'SZX2 = ',E12.4,4X,'SZX3 = ',E12.4)
      WRITE(6,12) C11,C22,C33,C12,C13,C23,D
   12 FORMAT(1H ,30X,'C11 = ',E12.4,4X,' C22 = ',E12.4,4X,'C33 = ',E12.4
     1,//30X,'C12 = ',E12.4,4X,'C13 = ',E12.4,4X,'C23 = ',E12.4,//30X,'D
     2 = ',E12.4)
      WRITE(6,13)  SSD, VARE, STDVE
   13 FORMAT(1H ,40X,'STATISTICAL DATA'/30X,'SSD = ',E12.4,4X,'VARE = ',
     1E12.4,4X,'STDVE = ',E12.4)
      WRITE(6,14) VARA1,VARA2,VARA3,STDA1,STDA2,STDA3,COV12,COV13,COV23
   14 FORMAT(1H ,30X,'VARA1 = ',E12.4,4X,'VARA2 = ',E12.4,4X,'VARA3 = ',
     1E12.4,/30X,'STDA1 = ',E12.4,4X,'STDA2 = ',E12.4,4X,'STDA3 = ',E12.
     24,/30X,'COV12 = ',E12.4,4X,'COV13 = ',E12.4,4X,'COV23 = ',E12.4)
      WRITE(6,15) VARB, STDB
   15 FORMAT(1H ,30X,'VARB = ',E12.4,10X,'STDB = ',E12.4,////50X,'END OF
     1 COMPILATION')
   19 CONTINUE
      END
```

3) SPECTR3

```
C     PROGRAM SPECTR3
C      L IS THE NUMBER OF SETS OF DATA    FIELD I2
C      N IS THE NUMBER OF WAVELEMGTHS USED TO CALCULATE THE SPECTRA
C     M IS THE NUMBER OF CONCENTRATION USED
      DOUBLE PRECISION  C(10), A(100,10), LAMDA(100), ABSO(100), AINT(10
     10), PERA(100)
      READ(5,70) L
   70 FORMAT(I2)
      DO 71 J1 = 1,L
      READ(5,1) N,M
    1 FORMAT(2I4)
      READ(5,2) (LAMDA(I), I=1,N)
    2 FORMAT(25I3)
      READ(5,3) ((A(I,J),J=1,M),I=1,N)
    3 FORMAT(20F4.3)
      READ(5,4) (C(J), J = 1,M)
    4 FORMAT(10E8.3)
      SOMC = 0.
      SOMCAR = 0.
      SUM = 0.
      SOMAC = 0.
      SOMAB = 0.
      DO 6 J=1,M
      SOMC = SOMC + C(J)
    6 SOMCAR = SOMCAR + (C(J)**2)
      D = (M*SOMCAR)-(SOMC**2)
      DO 7 I=1,N
      DO 8 J=1,M
      SOMAB = SOMAB + A(I,J)
      SOMAC = SOMAC + (A(I,J)*C(J))
    8 CONTINUE
      ABSO(I) = (M*SOMAC-SOMAB*SOMC)/D
      AINT(I) = ((SOMAB*SOMCAR)-(SOMC*SOMAC))/D
      DO 28 J=1,M
   28 SUM = SUM + (ABSO(I)*C(J) + AINT(I) - A(I,J))**2
      SOMAB = 0.
      SOMAC = 0.
      ERR = (SUM/D)**2
      ERR2 = SQRT(ERR)
      PERA(I) = 100.*(SQRT(ERR2))/ABSO(I)
    7 SUM = 0.
      IF (J1-1)   99,99,100
   99 CONTINUE
      WRITE (6,20)
   20 FORMAT(1H1,///,15X,'EXPERIMENTAL  RESULTS',//)
      WRITE(6,22) (LAMDA(I), (A(I,J), J= 1,M),I=1,N)
   22 FORMAT(1H ,10X,I3,4X,8F10.3)
      WRITE(6,23) (C(J), J = 1,M)
   23 FORMAT(1H0,///,8X,8E12.4,//)
  100 WRITE(6,14)
   14 FORMAT(1H1,///,15X,'CALCULATED SPECTRA',///7X,'LAMBDA   ABSORPTIVI
     1TIES    INTERCEPT')
      WRITE(6,16) (LAMDA(I),ABSO(I),PERA(I), AINT(I), I=1,N)
   16 FORMAT(1H ,8X,I3,4X,F6.0,3X,F5.2,7X,F8.3)
   71 CONTINUE
      WRITE(6,17)
   17 FORMAT(1H ,/////,25X,'****END OF COMPILATION****')
      END
```

APPENDIX VIII

Table 26

Molar absorptivities of Cu(TTAPAN), Cu(PAN)$_2$ and of HPAN in 35.4 mol% methanol in benzene, at 5 nm. intervals in the spectral range 400 nm. to 600 nm.

The No. of solutions for the least-squares fit was 8.

Wave-length in nm.	Least-squares values of molar absorptivity and % standard deviation!					
	Cu(TTAPAN)		Cu(PAN)$_2$		HPAN	
400	6510.	0.75	13649.	0.25	9542.	1.06
405	6807.	0.27	14211.	0.26	10232.	0.12
410	7174.	0.27	14248.	0.29	10935.	0.17
415	7518.	0.26	14101.	0.23	11476.	0.14
420	7646.	0.18	13926.	0.36	11944.	0.11
425	7584.	0.26	13784.	0.44	12439.	0.06
430	7491.	0.32	13503.	0.37	13033.	0.14
435	7535.	0.28	12749.	0.44	13667.	0.18
440	7442.	0.30	11791.	0.64	14189.	0.17
445	5923.	0.44	11029.	0.68	14794.	0.18
450	6038.	0.63	10797.	0.66	15533.	0.13
455	5007.	0.48	11274.	0.51	16504.	0.19
460	4116.	0.34	12231.	0.54	17394.	0.27
465	3676.	0.24	13588.	0.36	17995.	0.23
470	3702.	0.31	15144.	0.28	18151.	0.30
475	4022.	0.35	16986.	0.25	17993.	0.30
480	4561.	0.26	19117.	0.33	17605.	0.32
485	5228.	0.20	21582.	0.21	17081.	0.35
490	5111.	0.38	23961.	0.23	16332.	0.45
495	7148.	0.40	26247.	0.25	15056.	0.38
500	8371.	0.41	28293.	0.15	13141.	0.49
505	9795.	0.28	30456.	0.16	10478.	0.65
510	11155.	0.23	32941.	0.18	7869.	0.73
515	12344.	0.19	35635.	0.24	5460.	1.04
520	13625.	0.13	38535.	0.26	3443.	0.94
525	14825.	0.17	40597.	0.29	3341.	2.82
530	16270.	0.24	41274.	0.35	1921.	1.28
535	17543.	0.26	40825.	0.27	1037.	1.29
540	18851.	0.20	40222.	0.29	569.	1.62
545	20007.	0.28	40076.	0.30	316.	2.98
550	21047.	0.27	40646.	0.27	181.	0.96
555	21990.	0.24	41836.	0.30	101.	2.26
560	22774.	0.30	42659.	0.36	61.	3.86
565	23313.	0.31	41396.	0.44	41.	8.22
570	23307.	0.31	38120.	0.63		
575	22072.	0.31	30855.	0.72		
580	20412.	0.31	25889.	0.61		
585	17359.	0.30	19948.	0.86		
590	13771.	0.35	14802.	0.90		
595	11024.	0.59	11575.	1.17		
600	8470.	1.14	8719.	1.37		

! Defined as $s/\varepsilon \times 100$, where s is the standard deviation.

APPENDIX IX

Table 27

Spectrophotometric data for the equilibrium solutions of set A, used in the calculation of the function $K_1\varphi/r$ of equation (5.14) at each wavelength, at 25 ± 2°C.

The composition of each solution has been given in Table 13.

Sol. No.	Solvent; mol% methanol in benzene	Absorbance x 10^3					
		wavelength, nm.					
		540	555	560	565	570	580
1	8.38	178	195	207	211	209	177
2	"	202	222	237	240	239	204
3	"	242	264	281	286	284	240
4	"	259	285	304	309	309	258
5	"	304	335	356	362	359	303
6	"	356	394	420	428	426	360
7	"	375	415	442	449	446	377
8	"	396	438	468	477	475	406
9	"	425	470	502	510	507	433
10	"	465	515	550	560	558	473
11	"	478	528	564	575	571	482
12	"	494	548	585	596	593	508
13	"	519	575	613	625	620	529
!	"	574	636	678	690	686	583

Table 27 (continued)

Sol. No.	Solvent; mol% methanol in benzene	Absorbance x 10^3 wavelength, nm. 550	560	566	570
1	16.0	202	214	219	218
2	"	215	229	234	232
3	"	243	260	267	266
4	"	260	278	284	282
5	"	277	296	304	302
6	"	312	334	340	337
7	"	353	378	387	384
8	"	422	440	455	452
9	"	438	468	478	474
10	"	462	493	503	498
11	"	490	525	535	531
12	"	532	568	578	573
!	"	645	686	695	686

Sol. No.	Solvent; mol% methanol in benzene	540	550	560	565	570	580
1	23.0	168	183	195	198	195	163
2	"	203	220	234	237	234	193
3	"	228	248	264	268	266	220
4	"	265	289	308	312	307	255
5	"	327	358	383	388	385	320
6	"	346	382	406	412	407	337
7	"	372	410	437	445	438	365
8	"	402	442	472	478	472	391
9	"	445	491	525	533	526	437
10	"	460	509	543	551	545	452
11	"	480	530	568	577	570	475
12	"	510	563	602	609	602	502
!	"	577	638	679	689	678	568

Table 27 (continued)

Sol. No.	Solvent; mol% methanol in benzene	Absorbance x 10^3 wavelength, nm.			
		550	560	565	570
1	35.4	162	172	173	171
2	"	172	183	187	183
3	"	200	213	215	212
4	"	222	232	236	233
5	"	242	258	261	256
6	"	271	288	292	287
7	"	315	336	342	336
8	"	388	413	419	411
9	"	408	435	441	433
10	"	435	462	468	458
11	"	467	498	505	495
12	"	512	549	555	542
!	"	648	686	691	675

		550	560	570
1	35.4	177	187	187
2	"	220	234	234
3	"	261	278	279
4	"	299	320	321
5	"	367	390	392
6	"	419	448	451
7	"	504	538	542
8	"	590	632	638
9	"	608	652	655
10	"	640	682	682
11	"	685	732	733
12	"	710	758	758
!	"	768	814	814

Table 27 (continued)

Sol. No.	Solvent; mol% methanol in benzene	Absorbance x 10^3 wavelength, nm.					
		540	550	560	564	570	580
1	40.9	180	195	206	210	206	168
2	"	203	220	235	238	235	193
3	"	240	262	278	282	277	229
4	"	303	332	355	359	355	291
5	"	325	356	380	385	378	309
6	"	348	382	409	415	409	337
7	"	362	421	448	455	448	370
8	"	429	474	508	515	508	418
9	"	445	491	526	533	525	431
10	"	466	515	551	560	553	455
11	"	495	548	586	594	588	482
!	"	575	635	675	682	669	549

		540	550	560	570	580
1	55.2	160	172	183	177	137
2	"	185	199	212	204	158
3	"	220	238	254	245	190
4	"	248	269	285	275	214
5	"	287	312	332	322	250
6	"	309	336	357	344	268
7	"	338	369	392	380	295
8	"	351	382	407	394	305
9	"	370	404	430	415	320
10	"	422	462	492	478	372
11	"	442	482	513	498	392
12	"	468	512	546	532	416
13	"	479	527	560	545	426
14	"	498	546	584	568	445
!	"	578	634	670	652	522

Table 27 (continued)

Sol. No.	Solvent; mol% methanol in benzene	Absorbance x 10^3 wavelength, nm.				
		570	550	560		
1	59.4	236	219	236		
2	"	252	232	247		
3	"	266	240	258		
4	"	287	265	282		
5	"	308	283	302		
6	"	331	309	331		
7	"	366	337	362		
8	"	380	358	379		
9	"	405	372	398		
10	"	460	425	452		
11	"	542	505	539		
12	"	598	572	609		
!	"	813	761	813		
		540	550	560	570	580
1	76.7	142	152	158	147	107
2	"	162	173	183	171	128
3	"	198	214	225	209	153
4	"	261	283	298	280	206
5	"	285	309	325	307	222
6	"	310	338	358	335	248
7	"	355	386	406	380	284
8	"	410	448	476	447	332
9	"	429	468	496	464	343
10	"	452	496	525	493	362
11	"	490	537	568	530	391
!	"	586	639	670	622	460

! The absorbance values for this solution are A_o values.

APPENDIX X

Table 28

Spectrophotometric data for the equilibrium solutions of set A, used in the calculation of the function $K_2\varphi/p$ of equation (5.23) at each wavelength, at $25 \pm 2^{\circ}C$.

The composition of each solution has been given in Table 15.

Sol. No.	Solvent; mol% methanol in benzene	Absorbance x 10^3		
		wavelength, nm.		
		550	560	566
1	16.0	728	764	748
2	"	711	746	731
3	"	692	726	717
4	"	704	737	724
5	"	668	708	704
6	"	677	715	709
7	"	659	696	692
8	"	651	687	686
9	"	643	679	678
10	"	616	652	652
11	"	616	654	654
12	"	583	620	625
!	"	539	576	586

Table 28 (continued)

Sol. No.	Solvent; mol% methanol in benzene	Absorbance x 10^3 wavelength, nm.
		550
1	35.4	559
2	"	553
3	"	547
4	"	540
5	"	531
6	"	528
7	"	521
8	"	512
9	"	502
10	"	489
11	"	475
12	"	460
!	"	385

		540	550	560
1	35.4	734	759	788
2	"	715	742	770
3	"	700	729	762
4	"	676	712	745
5	"	662	700	728
6	"	655	692	722
7	"	638	678	710
8	"	623	665	698
9	"	605	652	684
10	"	587	632	665
11	"	555	603	638
!	"	489	540	574

Table 28 (continued)

Sol. No.	Solvent; mol% methanol in benzene	Absorbance x 10^3 wavelength, nm.		
		540	550	560
1	41.0	844	875	894
2	"	830	870	890
3	"	823	860	885
4	"	808	650	872
5	"	795	844	867
6	"	778	825	855
7	"	767	811	845
8	"	755	804	832
9	"	735	764	815
10	"	685	736	772
11	"	650	704	741
12	"	633	688	725
!	"	571	627	665

		540	550	560
1	50.9	864	892	918
2	"	855	890	915
3	"	836	872	896
4	"	825	865	892
5	"	815	856	872
6	"	792	845	862
7	"	786	829	854
8	"	762	810	835
9	"	740	792	820
10	"	691	746	772
11	"	637	688	725
!	"	569	622	659

Table 28 (continued)

Sol. No.	Solvent; mol% methanol in benzene	Absorbance x 10^3 wavelength, nm.			
		540	550	554	560
1	76.7	678	698	709	698
2	"	661	685	695	687
3	"	647	672	680	676
4	"	636	663	675	667
5	"	626	657	664	656
6	"	612	643	656	646
7	"	598	627	638	630
8	"	573	606	618	610
9	"	568	602	613	610
10	"	534	568	584	579
11	"	495	532	542	542
!	"	403	438	451	458
		540	550	554	560
1	89.8	948	990	992	952
2	"	930	978	994	950
3	"	915	962	975	935
4	"	915	962	972	935
5	"	885	936	948	915
6	"	880	930	938	908
7	"	855	905	918	894
8	"	838	888	892	872
9	"	810	868	875	860
10	"	738	792	810	796
11	"	681	745	754	747
12	"	661	715	731	730
!	"	580	651	659	659

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