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THE ACTIVITY COEFFICIENTS OF THENOYLTRIFLUOROACETONE IN PENTAETHER

H. W. Crandall and D. L. Heisig

August 8, 1950

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THE ACTIVITY COEFFICIENTS OF THENOYLTRIFLUOROACETONE IN PENTAETHER

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August 8, 1950

ABSTRACT

The distribution coefficients of TTA in pentaether-water-nitric acid mixtures have been measured as a function of TTA and nitric acid concentrations.

The activity coefficients of TTA in pentaether containing 0.1M nitric acid and 2.7M water have been calculated.

The predominant form of TTA in wet pentaether has been shown to be the hydrate.

THE ACTIVITY COEFFICIENTS OF THENOYLTRIFLUOROACETONE IN PENTAETHER

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INTRODUCTION

In connection with a study of the extraction of uranium (VI) into pentaether by thenoyltrifluoroacetone,[1] abbreviated TTA, the distribution coefficients of TTA in pentaether-nitric acid mixtures have been measured as a function of TTA and nitric acid concentrations. From the distribution coefficients, activity coefficients have been calculated.

Consider the equilibrium:

$$(1)\quad TTA_W = TTA_{PE}$$

and its corresponding equilibrium constant

$$(2)\quad K_O = \frac{(TTA)_{PE}\ \gamma_{TTA_{PE}}}{(TTA)_W\ \gamma_{TTA_W}} = E\ \frac{\gamma_{TTA_{PE}}}{\gamma_{TTA_W}}$$

where $(TTA)_{PE}$ and $(TTA)_W$ represent the TTA concentrations in moles per liter in the pentaether and water phases, respectively, $\gamma_{TTA_{PE}}$ and γ_{TTA_W} are the corresponding activity coefficients, and

$$E = \frac{(TTA)_{PE}}{(TTA)_W}$$

is the distribution coefficient. Equation 2 assumes that the activities of the solvents are constant. At constant nitric acid concentration the activities of the solvents may vary slightly with a change in the concentration of TTA. However, this effect should be small, and in this report it is assumed that at

any fixed nitric acid concentration, the activities of the solvents are constant and that the change in the distribution coefficient of TTA accompanying an increase in TTA concentration is caused by a change in the activity of TTA.

Since the distribution coefficients of TTA in this system are large, the concentration of TTA in the aqueous phase is small, less than 0.02M when the initial TTA concentration is 1.50M and the initial aqueous nitric acid concentration is 0.5M. It is probable, therefore, that the TTA in the aqueous phase under these conditions obeys Henry's Law and that the activity coefficient of the TTA in the water phase is constant. The validity of this assumption has been discussed by King and Reas.[2]

If the standard state of TTA is taken as the infinitely dilute solution of TTA in pentaether which has been equilibrated with water containing a fixed concentration of nitric acid, then Equation 2 reduces to

$$(3)\quad \gamma_{TTA_{PE}} = \frac{E^{o}_{PE}}{E}$$

where E^{o}_{PE} is the distribution coefficient of TTA at infinite dilution in an equilibrium mixture of the pentaether, water, and nitric acid. When the nitric acid concentration is varied, Equation 3 does not hold as the system is complicated by the extraction of nitric acid into the pentaether phase[3] and the resulting changes in the activities of the solvents.

EXPERIMENTAL

E was determined experimentally by equilibrating TTA initially in pentaether with an equal volume of nitric acid for three hours at 25°C and then measuring the concentration of the TTA in the aqueous phase spectroscopically. The concentration of the TTA remaining in the pentaether was determined by the difference between the moles of TTA added and the moles found in the aqueous phase. Since

pentaether absorbs in the same region of the ultraviolet as does TTA in aqueous solution and since pentaether is somewhat soluble in water, the method used for the analysis of TTA in the aqueous phase was to equilibrate the aqueous phase with an equal volume of benzene for three hours at 25°C. The optical density, OD, of the TTA in the benzene was then measured at a convenient dilution with the Beckman Model DU spectrophotometer at 3500 Å, and from this value, using the extinction coefficient of 9910 as measured at 3500 Å in wet benzene by King and Reas,[2] the concentration of TTA in the aqueous phase was calculated. Blanks to correct for the absorption of pentaether were carried through the entire procedure. Corrections for the two or three percent of the TTA which remain in the aqueous phase after extraction by benzene[2] were not made since the accuracy of the measurements is not greater than five percent.

To make sure that three hours was sufficient time for TTA to reach equilibrium between the pentaether and nitric acid phases, a sample was equilibrated for five hours. The distribution of TTA in this experiment was the same as that in a corresponding sample which was equilibrated for three hours. Furthermore, it is evident from the data of King and Reas[2] that the hydrate-enol equilibria in benzene is reached within the three-hour equilibrium period used in equilibrating the aqueous phase with benzene and, therefore, that the concentration of the enol form of the TTA, which is the absorbing species at 3500 Å, is truly proportional to the concentration of the TTA present.

Noticeable volume changes occurred on mixing in both aqueous and pentaether phases when the initial concentration of the nitric acid was greater than 1.0M. The molarity of the nitric acid and of the TTA were corrected for the volume changes.

A few measurements of the TTA spectra in pentaether were made to determine whether the TTA existed mainly as the hydrate or enol in this solvent. These

measurements were made with a Cary Recording Spectraphotometer using 1 mm cells to reduce the absorption by the pentaether.

The pentaether used had been redistilled. That used in the experiments in Table I boiled at 210°C and 20 mm pressure, while that used in Table II boiled from 190°C and 9 mm pressure to 193°C and 11 mm pressure. The TTA was synthesized

Table I

The Distribution and Activity Coefficients of TTA in Pentaether Equilibrated with 0.5M Nitric Acid

Initial TTA Conc. in Pentaether M	Dilution	OD E=9910 at 3500 Å	Equilibrium Concentration TTA M in Pentaether	Equilibrium Concentration TTA M in H_2O	E	$\gamma_{TTA_{PE}}$
.00449	1	.145	.00448	.0146	307	
.00749	1	.252	.00746	.0254	294	
.0150	1	.506	.0149	.0511	291	
.0300	1	.995	.0299	.100	299	1.00
.0749	10	.263	.0746	.265	282	1.06
.150	10	.521	.149	.526	283	1.05
.150	10	.519	.149	.524	284	1.05
.300	20	.564	.299	1.14	262	1.14
.599	50	.553	.596	2.79	214	1.39
.899	100	.466	.894	4.70	190	1.57
1.20	100	.732	1.19	7.28	164	1.82
1.50	200	.523	1.49	10.6	141	2.11

Table II

The Variation of the Distribution Coefficient of TTA in Pentaether-Nitric Acid Mixtures with the Nitric Acid Concentration

Initial Conditions TTA = 0.0171M
Volume of the pentaether = 5 cc
Volume of H_2O = 5 cc

Ex. No.	Initial Conc. of HNO_3 M	Dilution	OD E=9910 at 3500 Å	Equilibrium Conditions H_2O HNO_3 M	H_2O TTA M x 10^5	Pentaether Vol. cc	Pentaether HNO_3 M	Pentaether TTA M	E
1	0	1	.585	0	5.9	5	0	.0170	288
3	.157	1	.560	.142	5.7	5	.015	.0170	298
4	.467	1	.620	.380	6.3	5	.087	.0170	270
5	1.58	2	.455	1.01	9.2	4.7	.57	.0181	197
6	2.74	2	.682	1.60	13.8	4.2	1.14	.0203	147

by M. W. Davis, Jr. and H. R. Lehman. The water analyses were made by C. N. Stover, Jr. using the Carl Fisher Method with the exception of the analysis of the TTA hydrate which was done by the University of California Analytical Laboratory.

RESULTS AND DISCUSSION

The distribution coefficients of TTA in an equilibrium mixture of pentaether and a 0.4M nitric acid phase are given in Table I along with the activity coefficients of TTA calculated from the distribution coefficients using Equation 3. It should be noted that at equilibrium under these conditions the composition of the pentaether phase is roughly 2.7M water, 2.9M pentaether, and 0.1M nitric acid while the aqueous phase contains 0.4M nitric acid and 0.17M pentaether.[3] In column 2 of Table I the Dilution is the factor that the benzene phase, which

had been equilibrated with an equal volume of TTA containing aqueous phase, was diluted before the optical density, OD, column 3, was measured. The distribution and activity coefficients are plotted in Fig. 1 which shows the variation of E with TTA concentration and in Fig. 2 which shows the corresponding variation of $\gamma_{TTA_{IE}}$.

The variation of the distribution coefficient of 0.017M TTA in mixtures of pentaether and nitric acid with the nitric acid concentration is shown in Table II and in Fig. 3. The values for the nitric acid distribution and volume changes shown in Table II have been obtained from the data of Stover and Crandall.[3] The concentration of the TTA in the pentaether phase shown in column 9, Table II, has been corrected for the volume changes in the system. The distribution coefficient of TTA when the initial nitric acid concentration is about 0.5M recorded in Table II is about eight percent lower than the corresponding value recorded in Table I. The over-all reproducibility of experiments using different stock solutions and run at different times appears to be about ten percent while those run as a series show a much higher reproducibility.

Unlike the activity coefficients of TTA in benzene which decrease with increasing TTA concentration,[2] presumably due to dimer formation, the activity coefficient of TTA in pentaether increases with TTA concentration. This must be due to the difference in the solvent-TTA interaction in the two cases.

In benzene-0.115M hydrochloric acid mixtures, the distribution coefficient of TTA at infinite dilution, E^{o}_{B}, has been reported by King and Reas[2] to be roughly 40. Furthermore, Connick and Reas[4] have found that the distribution coefficient of TTA at low concentrations in benzene-aqueous perchloric acid mixtures varies less than ten percent when the perchloric acid concentration varies from 0.01M to 1.0M. If it is assumed that in the region of 0.1 to 0.5M acid concentration the activity of TTA in the aqueous phase is roughly independent

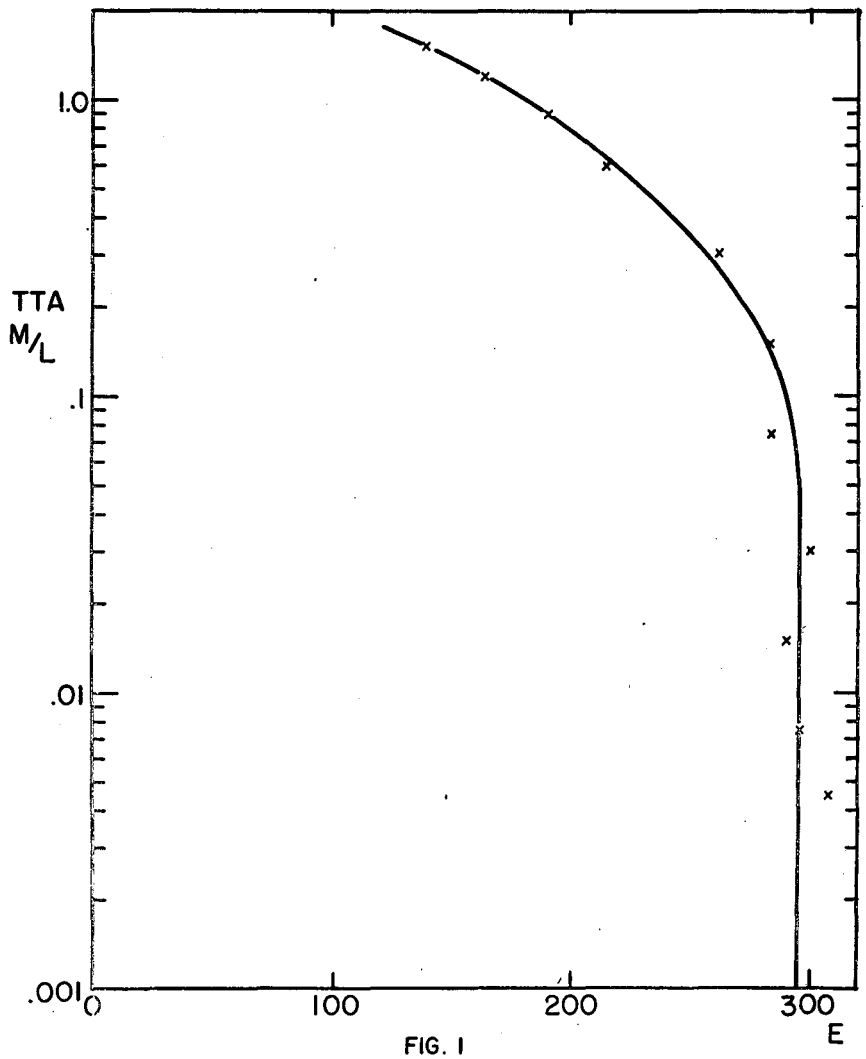

FIG. I

THE DISTRIBUTION COEFFICIENT OF TTA IN PENTAETHER - 0.5 M NITRIC ACID MIXTURES AS A FUNCTION OF THE TTA CONCENTRATION. MU 700

(FROM THE DATA IN TABLE I)

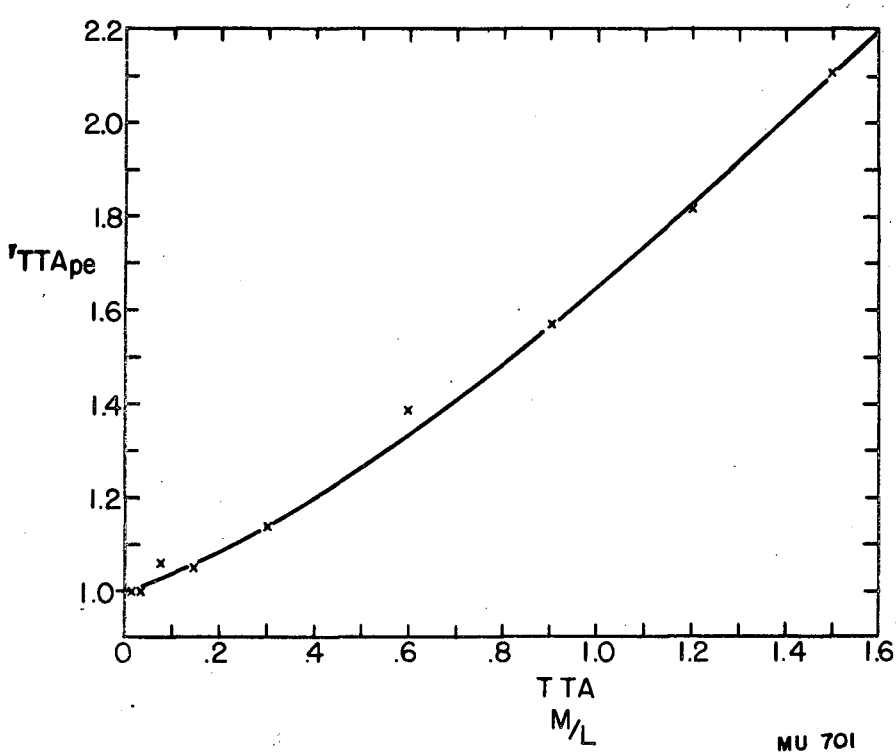

FIG. 2

(FROM THE DATA IN TABLE I)

THE ACTIVITY COEFFICIENTS OF TTA IN PENTAETHER EQUILIBRATED WITH 0.5 M NITRIC ACID.

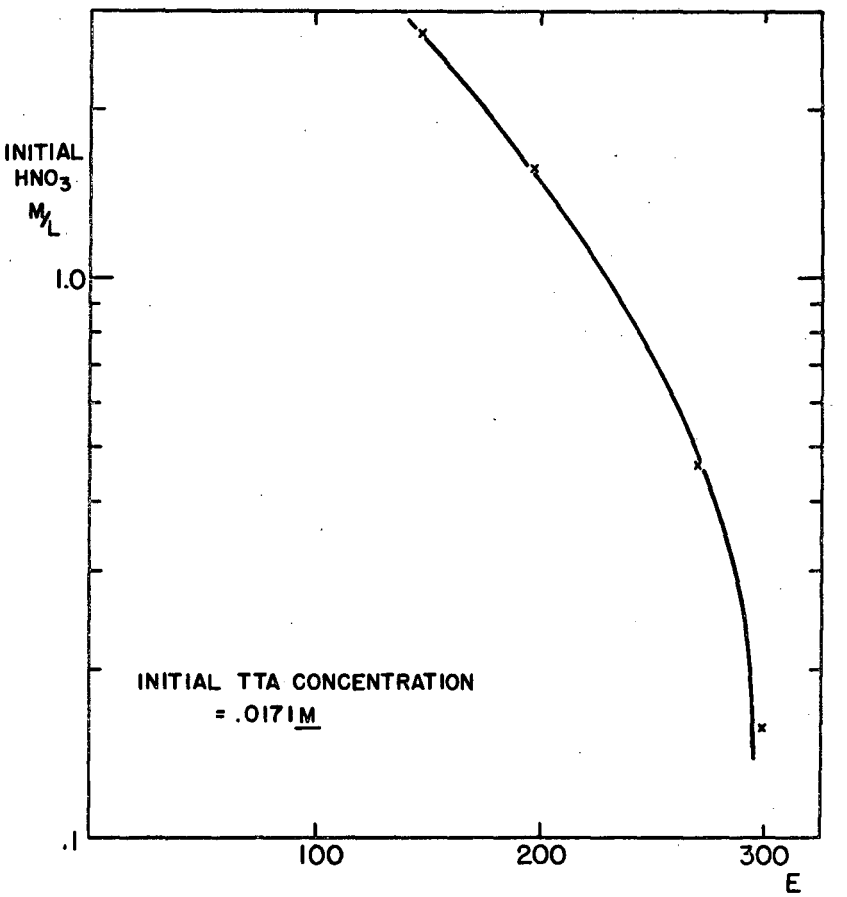

FIG. 3
(FROM THE DATA IN TABLE 2)

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THE DISTRIBUTION COEFFICIENT OF TTA IN PENTAETHER – NITRIC ACID MIXTURES AS A FUNCTION OF THE NITRIC ACID CONCENTRATION.

of the acid concentration and, moreover, independent of the particular acid used, then the distribution coefficient of TTA measured in benzene-0.115M hydrochloric acid mixtures, $E^{o}_{B} = 40$, may be compared with that measured in pentaether-0.5M nitric acid systems, $E^{o}_{PE} = 300$, and the ratio of their values taken as a measure of the TTA-solvent interaction for the two solvents. Since the distribution coefficient of TTA is greater by a factor of seven or eight in pentaether than in benzene, it can be concluded that the solvent-TTA interaction is much stronger in pentaether than in benzene.

On the basis that TTA in its infinitely dilute solution in pentaether is strongly associated with the solvent, the increase in the activity coefficient of TTA with an increase in the TTA concentration may be interpreted as a decrease in the TTA-pentaether interaction. However, this is necessarily a highly simplified picture of the changes taking place.

Stover and Crandall[3] have concluded that competition exists between water and nitric acid for positions in the pentaether in the system H_2O-HNO_3-pentaether. Table III indicates that this is also true of TTA. However, since TTA is a

Table III

The System Pentaether-Nitric Acid-TTA

Initial Concentrations		Equilibrium Concentration			
Pentaether	H_2O	Pentaether			
TTA M	HNO_3 M	HNO_3 M	H_2O M	Pent. M	H_2O-(TTA)(.8) M
0	.504	.090	2.7	2.9	2.7
1.13	.504	.085	4.0	---	3.1
1.51	.504	.080	4.1	---	2.9
1.63	.504	.077	4.1	---	2.8

large molecule, one would not expect it to replace nitric acid or water readily unless the pentaether-TTA attraction was considerably greater than that between pentaether and water or nitric acid. The data in column 3 of Table III show that the addition of TTA to a pentaether-nitric acid mixture reduces the nitric acid concentration in the pentaether layer slightly. In column 6 of Table III the total amount of water found in the pentaether has been corrected for the amount bound to the TTA (80% hydrate) to give the free water in the system. The data are insufficiently accurate to determine whether water has been driven from the pentaether by the addition of TTA.

From the above discussion it can be seen that in the TTA-nitric acid-water-pentaether system, changes in the concentration of one component cause changes in the distribution of the others. For this reason care should be used in applying the activity coefficients of TTA measured in pentaether-0.5M nitric acid mixtures to pentaether systems containing different amounts of nitric acid or to systems containing additional components such as uranyl nitrate.

In order to determine whether the predominant form of TTA in wet pentaether is the hydrate or the enol form found on wet benzene by King and Reas,[2] the spectra of TTA in pentaether was measured under various conditions. Solutions of 0.000754M (Solution I) and 0.00113M (Solution II) TTA in pentaether were prepared and their spectra recorded. Solutions I and II were then equilibrated with equal volumes of water for six hours at 31.5°C, after which the pentaether phases were removed and placed in a water bath at 25°C for twenty-four hours before their spectra were measured. The solutions were equilibrated at 31.5°C to prevent a water phase from appearing when the solutions were irradiated by the spectrophotometer light beam since the solubility of water in pentaether decreases with increasing temperature.

An attempt was made to prepare the pure hydrate by equilibrating TTA with a 0.1M hydrochloric acid solution. A water analysis showed that the sample prepared contained 6.1 ± .1 percent water or eighty-one percent hydrate. A portion of this sample was dissolved in pentaether (Solution III) and its spectra measured. Molar extinction coefficients for all the solutions whose spectra were measured are given in Table IV. The absorption curves for 0.000754M TTA

Table IV

Molar Extinction Coefficients of TTA in Pentaether

λ Å	E .000754M TTA Dry	E .000754M TTA Wet	E .00113M TTA Dry	E .00113M TTA Wet	E .00148M TTA 81% Hydrate by Water Analysis	E TTA in Dry Benzene
2600	3450	7690	3450	7700	7560	
2700	4910	7690	4960	7520	7560	
2800	5840	6760	5750	6730	6820	
2900	6630	7160	6550	7170	7230	
2950	7030	6760	6900	6810	7030	7730
3000	7690	6100	7430	7170	6340	
3100	9150	3830	8760	3890	3980	10400
3200	10610	2650	9820	2740	2370	12300
3300	11080	2260	10000	2300	1760	12450
3400	10480	2120	9560	2120	1490	
3500	9880	1860	9200	1950	1350	10950
3600	9420	1720	8940	1770	1280	10450
3730	7030	1320	6810	1330	878	
3860	3050	530	2920	443	270	
3980	0	0	0	0	0	
4100						

both wet and dry as well as the eighty-one percent hydrate sample are shown in Fig. 4.

The molar extinction coefficients of TTA in pentaether, Table IV, columns 2 and 4, are ten to twenty percent lower than those obtained in dry benzene by King and Reas,[2] Table IV, column 7, although the shape of the curves and the position of the peaks is the same within 25 Å. It is not known whether the lower molar extinction coefficients are due to the presence of some hydrate in the system, to the change in solvents, or to experimental error. The use of 1-mm cells could introduce some error since any slight variation in the angle that the cell makes with the light path will change the length of the solution through which the light passes. However, the extinction coefficients calculated from different solutions agree to about five percent so that it is unlikely that the use of 1-mm cells can explain the lowered molar extinction coefficients.

King and Reas found that the molar extinction coefficient of TTA at 2950 Å was essentially the same for both the hydrate and the enol forms, and this was found to be true in pentaether also, Table IV. The fact that the molar extinction coefficient in pentaether at 2950 Å is 6910 as compared to 7730 in benzene indicates that the low extinction coefficients are not due to the presence of TTA hydrate in the pentaether solution. Thus the most likely explanation for the lower molar extinction coefficients in benzene as compared to pentaether seems to be the effect of the change in solvents.

King and Reas also found that the hydrate of TTA does not absorb appreciably at 3500 Å in benzene.[2] Assuming this to be true in pentaether as well as benzene and using the molar extinction coefficient for the enol obtained for TTA in pentaether at 3500 Å, E = 9540, and the data in column 6 of Table IV, the percent enol in Solution III was calculated and found to be fourteen percent in fair agreement with the value of nineteen percent calculated from water analysis.

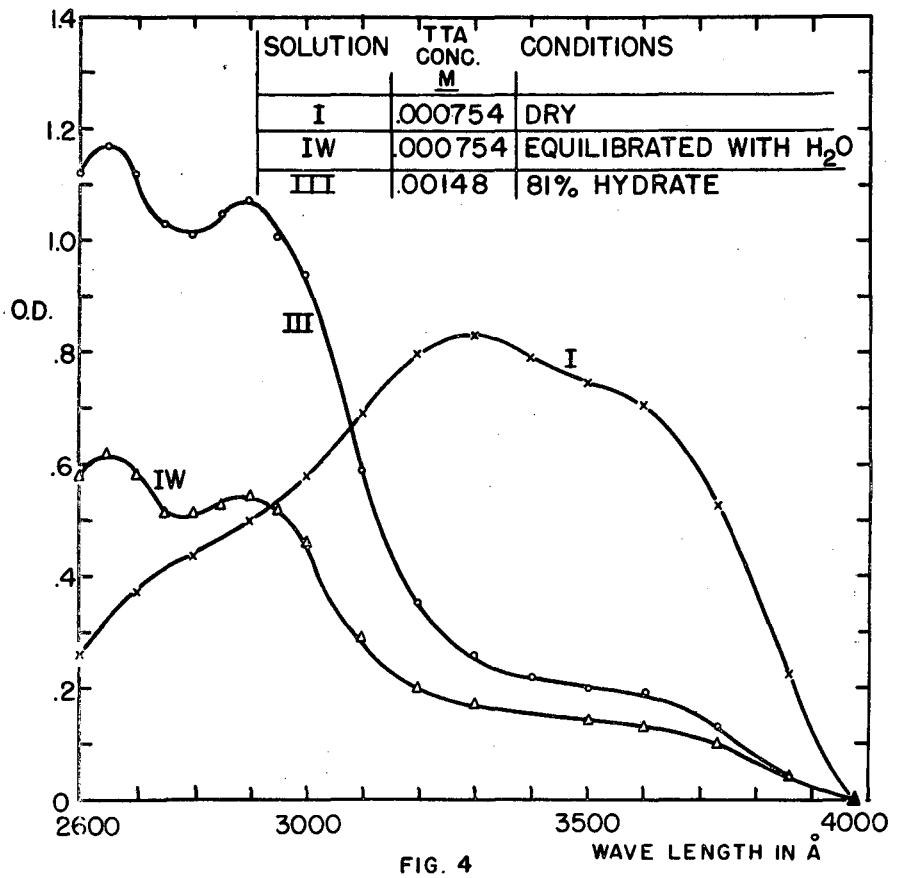

FIG. 4
(FROM THE DATA IN TABLE 4)

ABSORPTION SPECTRA OF TTA IN PENTAETHER

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163431

It was felt that this agreement was evidence that the absorption in the region of 3500 Å by Solution III was due to the presence of the enol and not to a difference in the spectra of the hydrate in pentaether as compared to benzene.

It was then assumed that the absorption at 3500 Å by the wet TTA solutions, i.e., those solutions of TTA in pentaether which had been equilibrated with water, was due to the presence of some of the enol form of the TTA. Using the molar extinction coefficient of the TTA enol in pentaether and the data for wet TTA solutions recorded in columns 3 and 5 of Table IV, the percent enol present in these solutions was found to be twenty percent. It was concluded that the major species of TTA in wet pentaether solutions is the hydrate which composes about eighty percent of the TTA in the pentaether.

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