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How to Estimate the Solubility of an Insoluble Compound - 1,3,5-Triamino-2,4,6-Trinitrobenzene (TATB)

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DISCLAIMER

HOW TO ESTIMATE THE SOLUBILITY OF AN INSOLUBLE COMPOUND - 1,3,5-TRIAMINO-2,4,6-TRINITROBENZENE (TATB)

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ABSTRACT

A simple method for estimating the solubility of TATB in various solvents is presented. We consider it unlikely that a solvent will be found in which TATB is more soluble than 0.1% (w/v). Exceptions are the so-called superacids in which the solubility of TATB exceeds 20% (w/v).

INTRODUCTION

The solubility characteristics of TATB are of interest to this Laboratory as well as to others in the ERDA complex. Cady and Larsson (1) determined the crystal structure of TATB. They stated that evidence for the strong intermolecular interaction in TATB (hydrogen-bonding) is indicated by the lack of an observable melting point and the low solubility in all solvents except concentrated sulfuric acid. Johnson (2) also stated that any likely solvent for TATB must be capable of hydrogen-bonding. We have previously reported the solubility of TATB in various sulfuric acid:water mixtures. (3)

We have now examined the solvent power of a wide variety of solvents for TATB. Because most solvents dissolve only a very small amount of TATB, conventional procedures for determining the solubility of TATB would involve careful weighing of microamounts of this material, after removal of the solvent. We have, therefore, developed a simple method for estimating the solubility of TATB in any solvent.

EXPERIMENTAL

Equipment and Materials. Beckman Model DK-2A Radio Recording Spectrophotometer; TATB, Lot B-377, manufactured by Cordova Chemical Co., Nimbus, CA. This is a representative production lot containing 0.43% total chloride and 0.36% ionic chloride; Solvents: highest purity available from commercial sources, used as received.

Procedure. Place several mg of TATB (no weighing is required) into a small volumetric flask (25 or 10-ml capacity). Add the solvent to be examined to the mark. Place the flask into an ultrasonic bath at ambient temperature (not to exceed 30°C) for about 5 min. Let the flask stand at ambient temperature until the undissolved TATB has settled out and the solution is transparent, for a minimum of 2 days. Measure the absorbance of the solution in a 1 cm cell vs a solvent blank. If the absorbance exceeds 1, dilute as required.

Calculations. The approximate solubility of TATB is given by

$$\text{solubility (ppm)} = A\,(10.33)(\text{dilution factor})$$

where A is the absorbance of the solution examined vs. the pure solvent, and the dilution factor is unity where no dilution is required.

RESULTS AND DISCUSSION

Our method for estimating the solubility of TATB in various solvents is based on the following assumptions:

(1) The molar absorbance, ε, of TATB in any solvent approximates its molar absorbance in concentrated sulfuric acid, approximately 25000 (4) near 330 nm.
(2) The density of the solvent is reasonably close to unity.
(3) The solution to be measures is saturated.

Calculations are based on $\varepsilon = A/C$, where A is the absorbance and C the concentration in moles/l for 1 cm path-length. By transposing

$$C(\text{moles/l}) = \frac{A}{\varepsilon} = \frac{A}{2.5 \times 10^{4}} = A(4 \times 10^{-5}), \text{ and}$$

$$C \text{ in g/l} = A(4 \times 10^{-5})(2.58 \times 10^{2})$$ where 2.58×10^{2} is the molecular weight of TATB, and finally

$$C \text{ in ppm} = A(4 \times 10^{-5})(2.58 \times 10^{2})(10^{3}) = A(10.33).$$

For solutions which have absorbances exceeding unity the proper dilutions must be made, and the proper dilution factor introduced in the above equation.

The absorption spectrum of TATB in DMSO is shown in Figure 1. This spectrum is very similar to that shown for TATB in sulfuric acid by Ungnade possessing two maxima, at 272 nm and at 324 nm. (4) Table I lists the estimated solubility of TATB in a variety of solvents, based on the absorbance maximum in the region of 320-355 nm. The spectra are quite similar to that in sulfuric acid. Solvents are listed in the order of decreasing solvent power for TATB.

Table II lists the absorbance maxima, λ_{max}, of TATB in various solvents. Some of the solvents absorb strongly near 280 nm and, therefore, the solutions have only one maximum, near 350 nm.

Of the solvents listed in Table II ethylenediamine, tetramethylguanidine, tetramethylglycinamide, and tetrabutylammonium hydroxide (Bu_4NOH) in methanol are strongly basic. In comparison to the other solutions, anomalous TATB spectra are observed in these basic solvents. The "normal" peaks occur near 270 nm and between 310 and 360 nm. It is possible that these solvents cause partial hydrolysis of the amino groups of TATB and/or attack on the nitro groups. The solubility of TATB in these bases is listed in Table III, with the assumption that no hydrolysis is taking place.

In tetramethylglycinamide the peak at 345 nm decreases with time while a shoulder develops into a peak near 400 nm. This latter λ_{max} may be due to OH. Similarly, the peak at 408-410 nm in ethylenediamine and the peak near 427 nm in tetramethylguanidine may be caused by OH. In Bu_4NOH/methanol the initial broad maximum near 406-12 nm soon disappears, and the peak at 357 nm shifts to 365 nm with time. The absorbance in this latter region increases for about 16 days and then slowly decreases.

An attempt was made to dissolve TATB in dimethylsulfate. This material is a strong methylating agent, thus possibly attacking the amino groups of TATB. A saturated solution gradually turned darker, indicating a continuing reaction. No useful spectra were obtained.

Trifluroacetic acid was the only solvent in which λ_{max} at 287-9 was larger than the λ_{max} in the visible spectrum, at 352 nm.

Concentrated sulfuric acid dissolves >24% (w/v) of TATB at ambient temperature. The superacids listed in Table 4 also dissolve >20% (w/v) of TATB. We must stress that these acids are highly corrosive and hygroscopic, reacting violently with water. We used an ultrasonic bath to expedite the dissolution of TATB. The volumetric flasks containing TATB in these superacids should not be tightly stoppered because even at ambient temperature a slow reaction may occur generating sufficient pressure to shatter the flasks. These superacids have the formula XSO_3H where

$$X = OH, CF_3, F, \text{ or } Cl$$

which all are strongly electronegative groups. If $X = CH_3$ or C_2H_5 as in methane- and ethanesulfonic acids the solubility of TATB is considerably less as seen in Table I. TATB in the superacids and in other compounds containing the XSO_3H group has a λ_{max} between 315 and 335 nm. In all other solvents this λ_{max} occurs near 350 nm.

The precursor of TATB, 1,3,5-trichloro-2,4,6-trinitrobenzene, and the possible impurities arising in TATB manufacture, 1,3,5-trichloro-2,4-dinitrobenzene (T-3) and 1,3,5,6-tetrachloro-2,4-dinitrobenzene (T-4) do not have absorption maxima in the region of 320-360 nm in DMSO.

We do not believe that any solvents will be found to bridge the tremendous gap between ∿820 ppm (for methanesulfonic acid) and ⩾200,000 ppm (for the superacids). However, we hope that this paper will stimulate some thought and evoke ideas on possible additional solvents. The procedure outlined above will facilitate a quick estimate of the solubility of TATB in such "new" solvents.

REFERENCES

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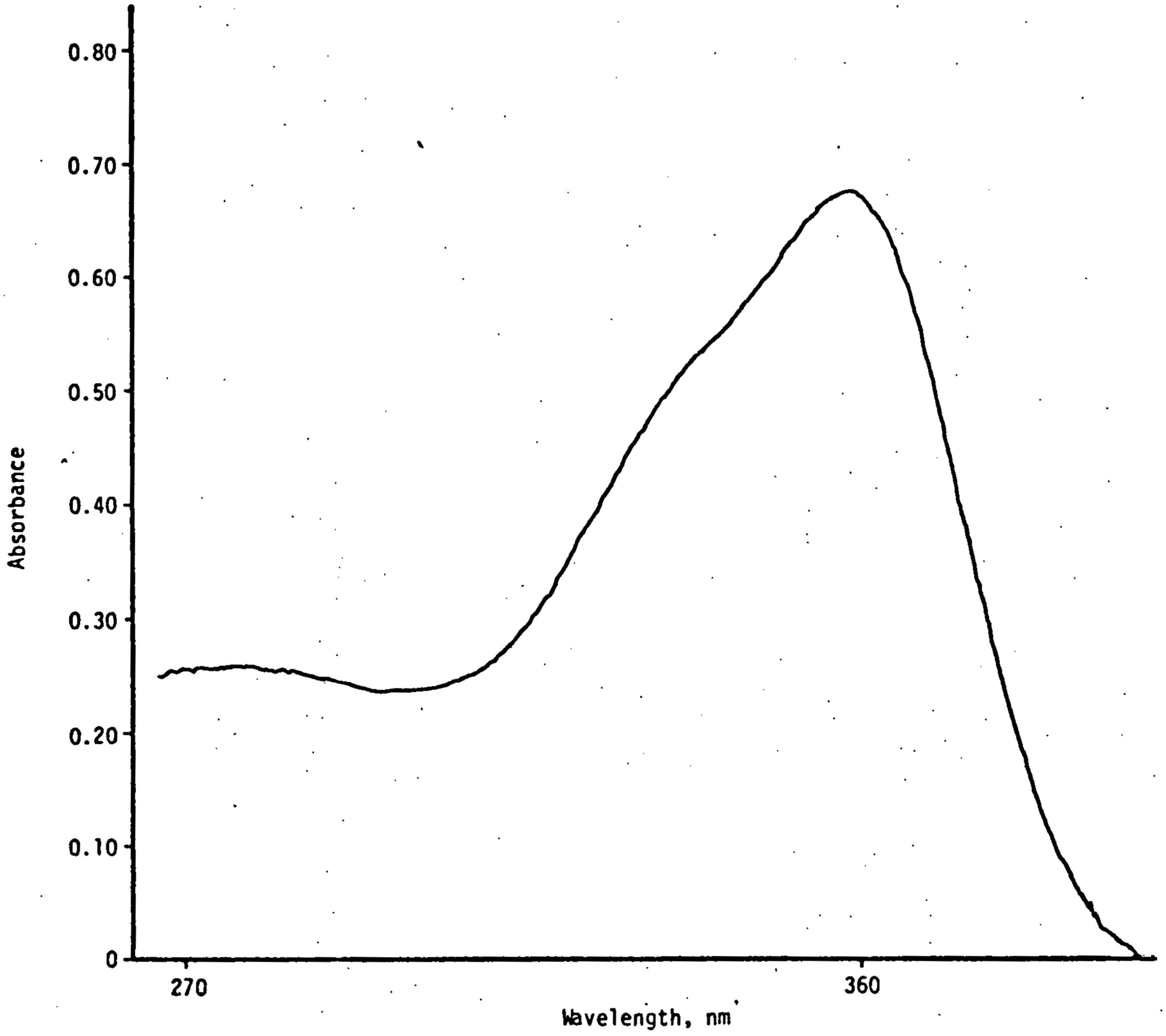

Figure 1. Absorption spectrum of TATB in DMSO (saturated solution)

Table I. Estimated Solubility of TATB in Various Solvents

Solvent	Solubility, ppm
Methanesulfonic acid	820
Hexamethylphosphortriamide	150
Ethanesulfonic acid	120
DMSO	70
Hexafluoroacetone sesquihydrate	68
N-methyl-2-pyrrolidinone	58
N,N-dimethylacetamide	33
DMF	27
Tetramethylurea	26
Dimethyl methylphosphonate	22
N,N-dimethylpropionamide	16
γ-butyrolacetone, bis(dimethylamino)phosphochloridate, conc. nitric acid	14
3-methylsulfolane	13
Pyridine	12
Trimethylphosphate	11
Dimethylcyanamide, vinyl sulfone	8
Methyl dichlorophosphate	7
N-methylformamide, tetrahydrofuran (uninhibited)	6
Methyl methanesulfonate	5
Trimethylphosphite	4
Acetone, dimethyl carbamoyl chloride	3
Acetonitrile, acetic anhydride, trifluoroacetic acid	2
Acetic acid	1
Hexamethyldisilazane, trifluoroacetic anhydride, hexafluorobenzene, pentafluoropyridine, perfluoro-2-butyltetrahydrofuran, water, methanol	< 1

Table II. Absorbance Maxima for TATB in Various Solvents

Solvent	λ_{max} UV	λ_{max} near-UV
conc. sulfuric acid	272	324
chlorosulfonic acid		335
ethylenediamine		408-10
methanesulfonic acid		315-7
tetramethylguanidine		356, 427
Bu_4NOH, 25% in methanol		357, 406-12
hexamethylphosphortriamide	270-2	350
ethanesulfonic acid		320
DMSO	272-4	356
hexafluoroacetone sesquihydrate	266-8	353
N,N,N',N'-tetramethylglycinamide		345
N-methyl-2-pyrrolidinone	266-8	355
N,N-dimethylacetamide		353
DMF	268-70	353-4
tetramethylurea	269-70	353
dimethyl methylphosphonate	268-70	352-3
N,N-dimethylpropionamide		353
γ-butyrolacetone	268-70	353
bis(dimethylamino)phosphochloridate	269-70	352
conc. nitric acid		360-3
3-methylsulfolane		354
pyridine		356
trimethylphosphate	268-70	352-3
dimethylcyanamide		353
vinyl sulfone		355
methyl dichlorophosphate		322
N-methylformamide		353
tetrahydrofuran	264-7	344
methyl methanesulfonate	266-8	353
trimethyl phosphite	270	348
acetone		348-50
dimethyl carbamoyl chloride		352
acetonitrile	268-70	352
acetic anhydride		351-2
trifluoroacetic acid	287-9	352
acetic acid	$\sim$260	349-51

Table III. Apparent Solubility of TATB in Basic Solvents

Solvent	Solubility, ppm
ethylenediamine	2195
tetramethylguanidine	485
Bu_4NOH, 25% in methanol	390
N,N,N',N'-tetramethylglycinamide	67

Table IV. Super Solvents for TATB
(solubility >20% (w/v)

concentrated sulfuric acid
chlorosulfonic acid
fluorosulfonic acid
trifluoromethanesulfonic acid

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