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Spectrophotometric Determination of Trace Amounts of Iodine in Nonpolar Solvents

by

TURGUT GÜNDÜZ

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Spectrophotometric Determination of Trace Amounts of Iodine in Nonpolar Solvents

TURGUT GÜNDÜZ*

Section of Analytical Chemistry, Faculty of Science
University of Ankara, Ankara, Turkey

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A new spectrophotometric method for determining trace amounts of iodine in nonpolar solvents, such as the aliphatic hydrocarbons, carbontetrachloride, benzene, etc, has been developed. By this method it is possible to determine $1 . 10^{-6}$ m/l of iodine, with the accuracy of spectrophotometric determinations, by using a dilute solution of hexamethylmelaminium iodide in chloroform. This compound is easily obtainable in pure and solid state (Prepared by us).

Since iodine dissolves and sublimes easily it is very difficult to determine it by extracting it without loss from nonpolar solvents to polar solvents or water. So the proposed new method enables one to determine iodine easily without extracting it into polar media.

INTRODUCTION

Recently, there have been tousands of publications on the determinations of trace amounts of substances in various media [1, 2, 3, 4, 5].

In the present study a new spectrophotometric method is described for determining trace amounts of iodine in nonpolar solvents by using a dilute solution of hexamethylmelaminium iodide in chloroform.

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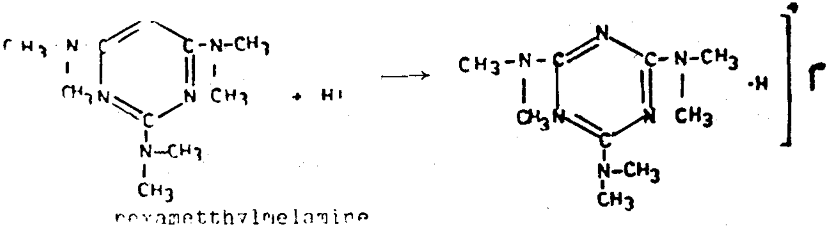
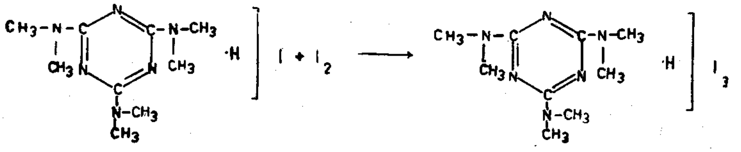
* Mailing Address: Fen Fakültesi, Ankara, Turkey.



This method is based on the strong absorption bands of I_3^- complex ion with the peaks at about 292 mμ and 362 mμ

Although they vary more or less, with the nature of solvents, the molar extinction coefficients of these peaks are about 36000 for the first (292 mμ) and 25000 for the second (362 mμ) [6], [7]. So the first peak is much more suitable for determinations and is used.

Hexametylemelaminium iodide readily dissolves in polar solvents including chlorofrom but does not dissolve in nonpolar solvents such as hexane, cyclohexane, carbontetrachloride, and even in benzene. When a nonpolar solvent containing iodine is treated with a solution of hexamethylmelaminium iodide in chloroform, it gives polyiodides depending on the ratios of iodine to iodide.



If there is more iodine, then hepta or nona iodides are produced (not penta iodide) [6], [8]. In order to shift equilibrium to the right and favor the formation of hexamethylmelaminium triiodide, an excess of hexamethyleaminium iodide is added into the medium.

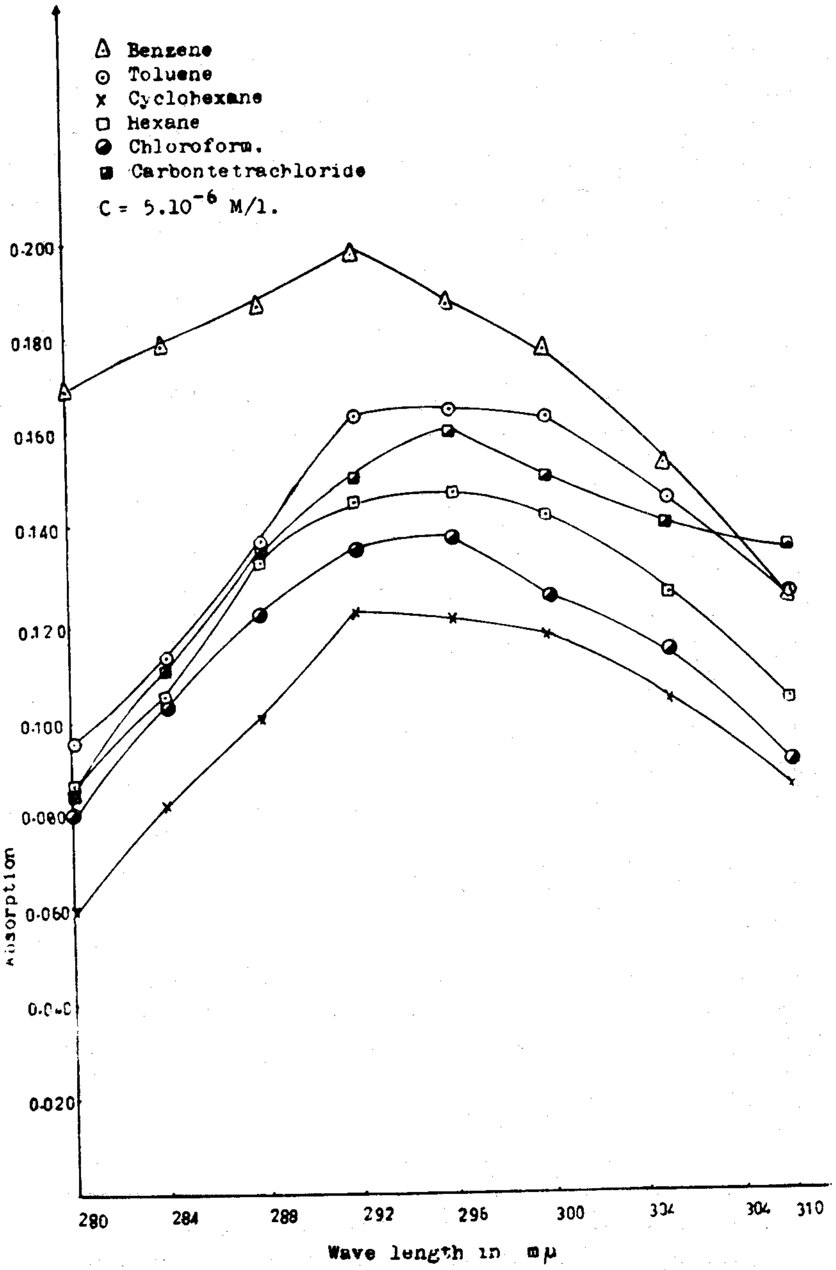

Δ Benzene
⊙ Toluene
x Cyclohexane
□ Hexane
◐ Chloroform.
■ Carbontetrachloride
C = 5.10^{-6} M/l.
0.200
0.180
0.160
0.140
0.120
0.100
0.080
0.060
0.040
0.020
Absorption
280
284
288
292
296
300
304
304
310
Wave length in mμ

Fig-1

Though the peak in some solvents shifts to the higher wavelengths (up to 296 mμ) this does not make much difference in the absorption, in comparison to the absorption at 292 mμ. Because absorption bands make generally a broad shoulder in this region, Fig-1. So in any solvent it is possible to make measurements at 292 mμ.

TABLE - 1.

Solvent	Required (m/1)	Found (m/1)
Cyclohexane	$2,00.10^{-6}$ $1,00.10^{-6}$ $4,00.10^{-6}$	$1,98.10^{-6}$ $1,05.10^{-6}$ $4,04.10^{-6}$
Hexane	$3,70.10^{-6}$ $1,85.10^{-6}$	$3,65.10^{-6}$ $1,65.10^{-6}$
Carbontetrachloride	$2,46.10^{-6}$ $1,23.10^{-6}$	$2,25.10^{-6}$ $1,26.10^{-6}$
Benzene	$2,00.10^{-6}$ $1,00.10^{-6}$ $5,00.10^{-7}$	$1,90.10^{-6}$ $1,00.10^{-6}$ $5,00.10^{-7}$
Toluene	$2,00.10^{-6}$ $5,00.10^{-7}$	$1,90.10^{-6}$ $6,00.10^{-7}$

EXPERIMENTAL

Hexamethylmelaminium iodide, a white crystalline compound, is prepared by passing dry hydrogen iodide through the solution of hexamethylmelamine in dry ether, and is recrystallized from dry methanol or acetone. 10^{-2} molar solution of the compound in chloroform is used as a reagent [8.mg of hexamethylmelaminium iodide is dissolved in 250 ml of pure chloroform).

Since, even 50 % chloroform (by volume) in any nonpolar solvent is a good solvent for either hexamethylmelaminium iodide or hexamethylmelaminium triiodide is used as solvent in experiments. In order to get this mixture, the solution of hexamethylmelaminium iodide is added to the solution of iodine in nonpolar solvent in equal volume.

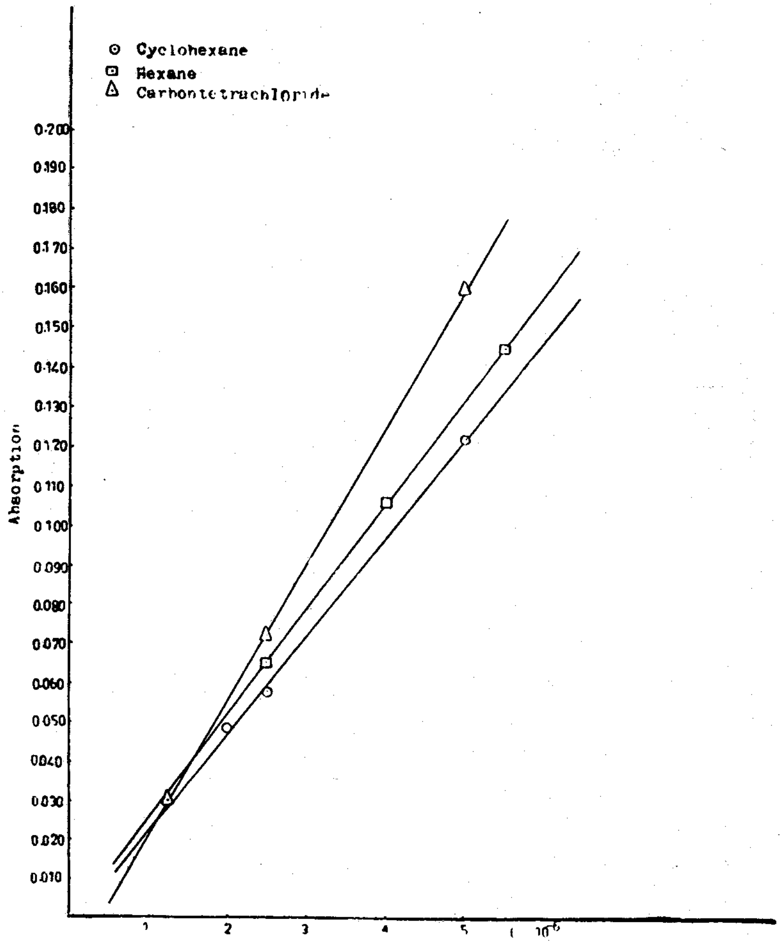


Fig -2

The solution of hexamethylmelaminium iodide must be prepared immediately before use and must be kept in the dark in colored ground glass stoppered bottles.

Measurements must be made within 10 minutes after reagent has been added to the solution containing trace amounts of iodine.

General procedure determination of trace amounts of iodine is as follows:

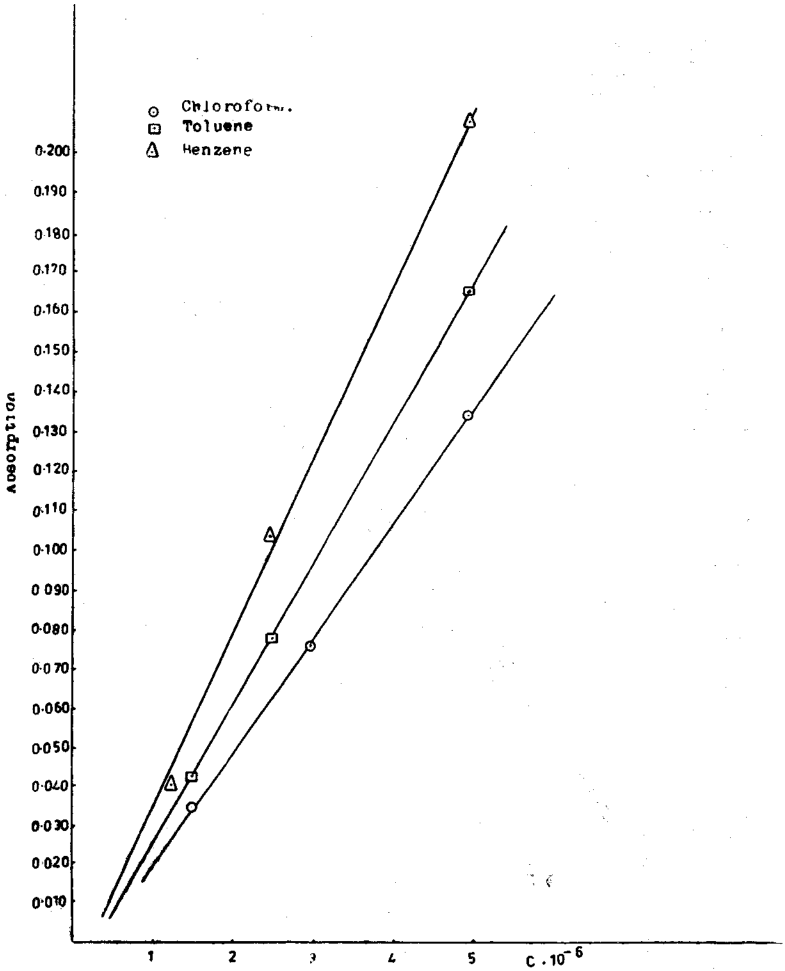


Fig-3

2 ml of solution containing trace amounts of iodine is put in a one-cm-thick silica cell and then onto it 2 ml of freshly prepared hexamethylmelaminium iodide is added. Stoppered cell is shaken properly and absorbance of it at 292 $m\mu$ is measured, against a blank which is a mixture of 2 ml of solvent and 2 ml of reagent (10^{-4}M bexamethylmelaminium iodide in $CHCI_3$). As it is seen from Fig–2–3 absorbance in benzene is the highest

among the other solvents. So this means that if iodine from any medium is extracted to a solvent, this solvent must be preferably benzene. By using the curves in Fig–2 and 3 it is easily possible to determine the amounts of iodine.

A number of samples containing iodine have been analyzed and the results have been found, in good agreement with the reguired ones, Table – 1.

RESULTS AND DISCUSSION

By this new method it is possible to determine trace amounts of iodine ($1{,}0.10^{-6}$m/l) in nonpolar solvents using working curves as in Fig–2 and 3. The examination of curves shows that Lambert-Bouger - Beer law is obeyed fairly well even in lower concentrations.

$$\mathrm{Log}\,\frac{I_0}{It} = Elc$$

Concentrations exceeding 10^{-4}m/l for hexamrethylmelaminium iodide are not useful (too much absorbence).

Examinations of Fig -1 and 2 and 3 give also some additional good information:

a – A reaction is a function of the reactants and the solvent being used as medium.

b – The broadness of an absorption band and the wave length of the peak depends upon the solvent. For instance in the case of benzene the peak is sharp and at 292 mμ. But in the case of toluene the peak is not sharp and round about 294 mμ.

Apparatus and Materials.

Measurements have been made on a Beckman DU Spectrophotometer, equipped with a Beckman DU Power Supply, by using a pair of matched one-cm-thick silica cells.

Solvents supplied from the Reidel-De Haen A. G. (Pure) and E. Merck (pure). Before use all chemicals are redistilled and collected constant boiling fractions.

Iodine supplied from E. Merck (pure) and resublimed before use.

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ÖZET

Alifatik hidrokarbonlar, karbontetraklorür, benzene gibi polar olmıyan çözücüler içinde bulunan eser halde iyodu tayin etmek için yeni bir metod bulunmuştur. Bu metodda hekzametilmelaminium iyodürün kloroform içindeki seyreltik çözeltisi kullanılmakta ve litrede 1,3.10^{-6}m iyot spektrofotometrik olarak kolayca tayin edilebilmektedir. Bu maksatla kullanılan ayıraç (hekzametilmelaminium iyodür) katı halde saf olarak elde edilebilmektedir (tarafımızdan yapılmıştır).

Kolaylıkla çözündüğü ve süblimleştiği için iyodu polar olmıyan bir çözücüden kayıpsız olarak polar olan bir çözücüye veya sulu ortama almak çok güçtür. Yeni verilen metod sayesinde böyle bir işleme lüzum kalmadan iyot polar olmıyan çözücülerde dahi kolaylıkla tayin edilebilmektedir.

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