COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES DE L'UNIVERSITÉ D'ANKARA

Série B : Chimie

TOME 16 B ANNEE 1969

The Nature of Iodine in Various Solvents.

by

TURGUT GÜNDÜZ

2

Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

Communication de la Faculté des Sciences de l'Université d'Ankara

---

La Revue "Communications de la Faculté des Sciences de "Université d'Ankara" est un organe de publication englobant toutes les disciplines scientifiques représentées à la Faculté : Mathématiques pures et appliquées, Astronomie, Physique et Chimie théoriques, expérimentales et techniques, Géologie, Botanique et Zoologie.

La Revue, à l'exception des tomes I, II, III, comprend trois séries

Série A : Mathématiques, Physique et Astronomie.

Série B : Chimie.

Série C : Sciences naturelles.

En principe, la Revue est réservée aux mémoires originaux des membres de la Faculté. Elle accepte cependant, dans la mesure de la place disponible, les communications des auteurs étrangers. Les langues allemande, anglaise et française sont admises indifféremment. Les articles devront être accompagnés d'un bref sommaire en langue turque.

Adrese: Fen Fakültesi Tebliğler Dergisi, Fen Fakültesi, Ankara, Turquie

The Nature of Iodine in Various Solvents.

TURGUT GÜNDÜZ

Faculty of Tcience, Universıty of Ankara, Ankara, Turkey.*

(Recived February 21, 1969)

The color of iodine solutions changes with the nature of solvents. It is violet with the absorption band at about 520 mμ in solvents such as the alyphatic hydrocarbons, carbontetrochloride, chloroform, dichlorethane etc. In other solvents including benzene, ketones, alcohols, ethers etc is brown or brownish with the absorption band at about 450 mμ.

Although cryoscopic molecular weight determinations show that iodine is present in diatomic state in all solvents, the distribution behavior indicate that iodine in brown solutions is bound chemically to the solvents in equilibrium with the free iodine.

At present work behavior of iodine in various solvents including polar and nonpolar, has been investigated spectrophotometrically and has been found some interesting results such as iodine reacts with pure alcohols to give I_3^- complexe ion. This supports second view at least in the case of alcohols.

Though they somewhat change with the nature of solvent, this complex ion gives a pair of very strong and charateristic absorption bands with the peaks at about 292 mμ and 362 mμ.

If electron donating group is accepted to be D, the formation of I_3^- may occur either $DI^+ + I_3^-$ or $DH^+ + I_3^-$. Since polar solvents generally contain at least a free pair of electrons, favour the formation of I_3^-. Especially those solvents having the power of reducing (primary and secondary alcohols) bring about the reaction.

INTRODUCTION

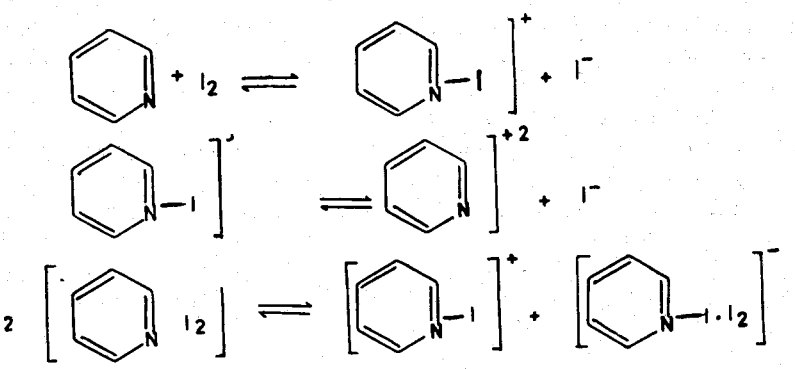
The color of iodine solutions varies with the nature of the solvents. It is violet in solvents such as the aliphatic hydrocarbons, carbontetrachloride, chloroform, dicloromethane, dichloroethane and carbondisulfide. In other solvents including benzene, toluene alcohols, ketones and ethers it is brown or brownish [1].

* Mailing address: Fen Fakültesi, Ankara, Turkey.

Brown solutions have tendeney to become violet when heated and revert to their original color on cooling [2]. Similar behavior is observed among the violet solutions too. For instance, when iodine solution in carbondisulfide, is cooled with dry-ice its color becomes brown.

The dissimilarities of colors of the solutions might come from the chemical reactions between iodine and solvents. To prove this a number of investigators have studied subject from the very different viewpoints.

Precise molecular weight determinations made by Beckman have proved that iodine is present in the diatomic state in all solvents [3]. This result indicates that there is no chemical reaction between iodine and any kind of solvent. On the other hand Audrieth and Birr have found that pyridine solution of iodine conducts electricity and the value of this is about 130 units per molecule at infinite dilute solutions, [4]. They explained this result by the gradual dissociation of iodine.

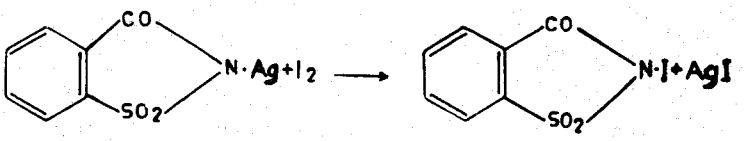


Subsequent studies of several reserach workers have supported this amphoteric behavior of iodine in the presence of pyridine [5], [6]. They have also found that brown solutions of iodine have shown fairly big dipole moments in comparison to the violet solutions. This also indicates that brown solutions contain polarized molecules of iodine,

$$D\ I^{+}\text{——}I^{-}$$

Positive part of the iodine molecule is stablized by the unshared electron pair of solvents (D represents a donor).

It has also been shown that brown solutions of iodine are much more reactive on unsaturated fats than the violet solutions are [7]. Further more brown solutions in polar solvents such as dioxane, alcohols, ethers react with the silver salt of saccharine to yield the theroritical amounts of silver iodide. Whereas the others, only yield very slight quantity of silver iodide.



The marked dissimilarities in properties of brown and violet solutions are observed in the spectra of the solutions. Getman and Weyl have studied the spectra of solutions and have come to the conclusion that brown solutions give absorption bans at about 450 mμ and violet solutions 520 mμ [8], [9], [10]. The over-all spectra of the violet solutions are very similar to that of iodine in vapor state.

Among the solvents benzene and toluene also give a red-brown solutions in spite of not having contained a free pair of electrons like polar solvents. Even carefully purified and dried benzene gives the same color [11].

EXPERIMENTAL

In this present work, the nature of iodine in various solvents (polar and nonpolar) has been investigated spectrophotometrically and found some interesting results.

Absorption bands of violet solutions have been found to be the same as recorded in literature, with the characteristic peaks at about 520 mμ, Fig-1 and 2. Molar extinction coefficients of the solutions have also been calculated and found to be 900–1000, Fig–3 and 4. Whereas the absorption bands of the brown solutions have been found entirely different. The solutions of

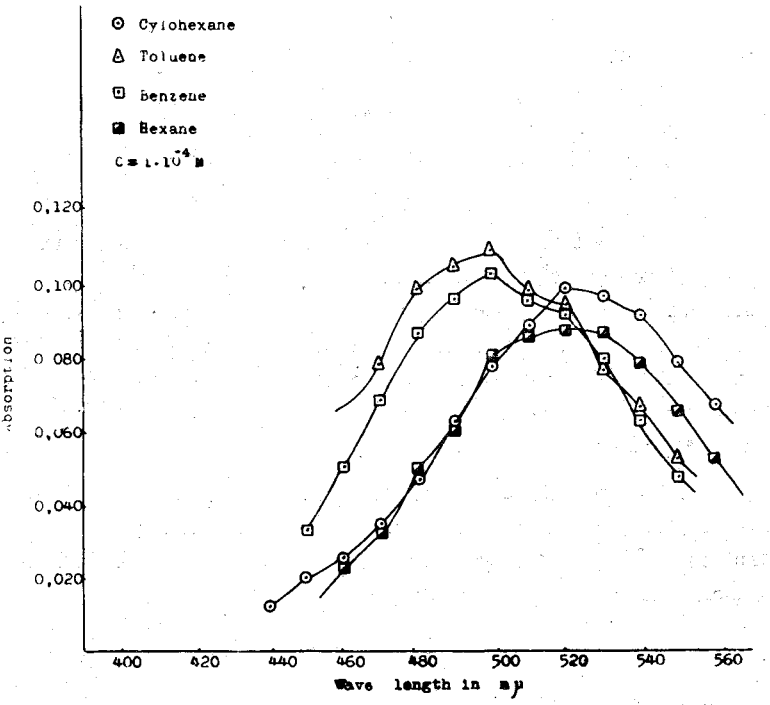

Cyclohexane
Toluene
Benzene
Hexane
C = 1.10⁻⁴ M
0,120
0,100
0 080
0,060
0,040
0,020
absorption
400
420
440
460
480
500
520
540
560
Wave length in mμ

Fig-1

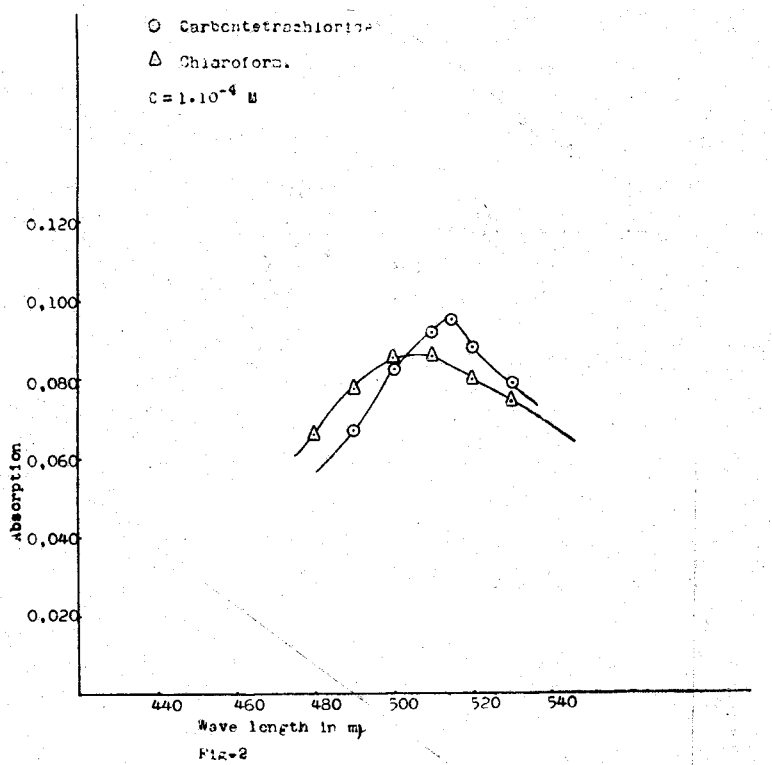

Carbontetrachloride
Chloroform.
C = 1.10⁻⁴ M
0.120
0,100
0,080
0,060
0,040
0,020
Absorption
440
460
480
500
520
540
Wave length in mμ

Fig-2

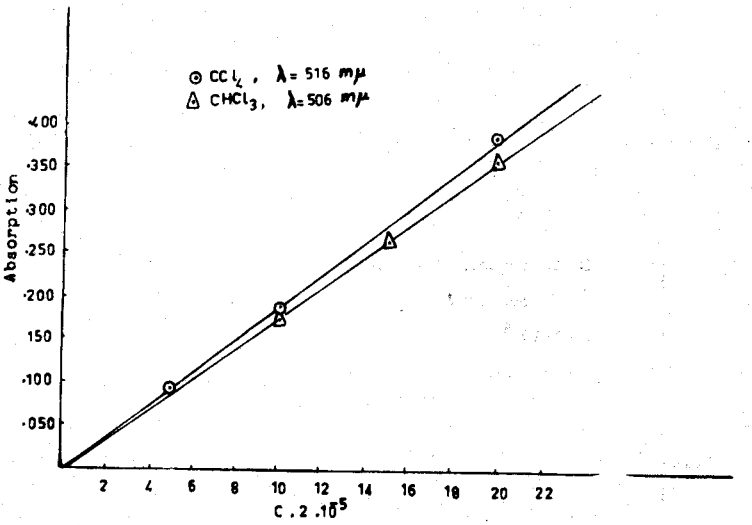

⊙ CCl_4, λ= 516 mμ
△ $CHCl_3$, λ=506 mμ
Absorption
·400
·350
·300
·250
·200
150
·100
·050
2 4 6 8 10 12 14 16 18 20 22
C . 2 .10^{-5}

Fig-3

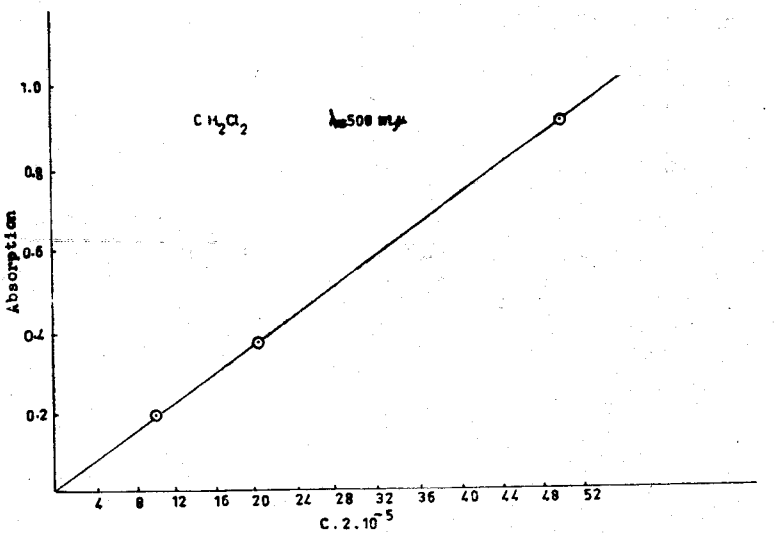

CH_2Cl_2
λ=508 mμ
Absorption
1.0
0.8
0.6
0.4
0.2
4 8 12 16 20 24 28 32 36 40 44 48 52
C . 2 .10^{-5}

Fig-4

methylalcohol, ethylalcohol, isopropylalcohol ethylmethylketon and dioxane have been studied. In the case of alcohols have been observed two conspicuous absorption bands with the peaks (they somewhat difer from solvent to solvent) at about 292 mμ and 362 mμ Fig–5, insread one peak, at about 450 mμ as indicated in literature [1], [12], [13]. Iodine in acetone and ethylmethylketone has shown only one absorption band with a peak at about 365 mμ Fig–6. Whereas the iodine in dioxane, has shown fairly broad absorption band at about 450 mμ but is entirely black below 330 mμ Fig–6. [1], [13].

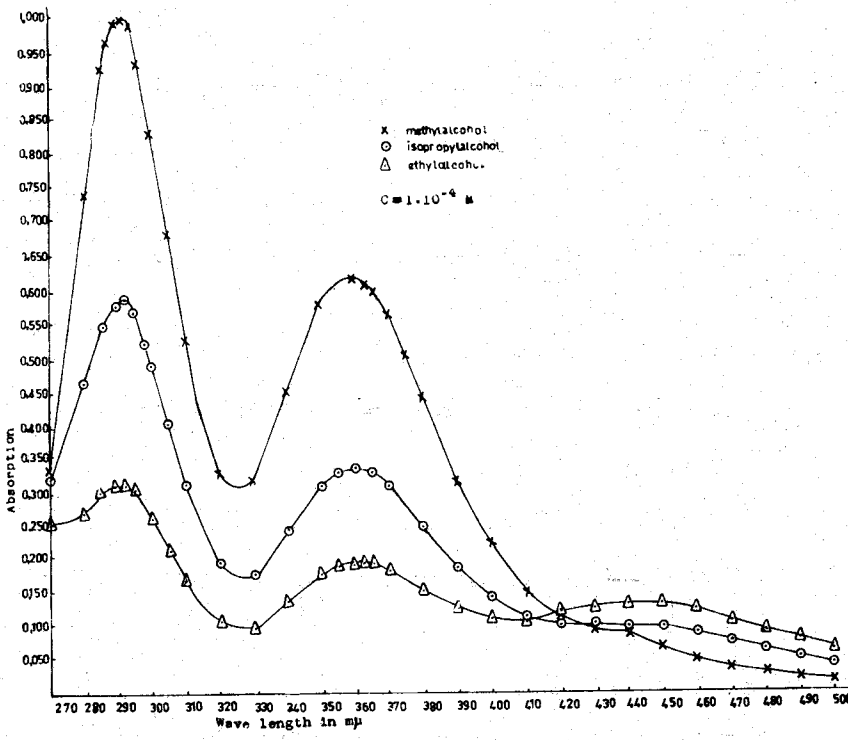
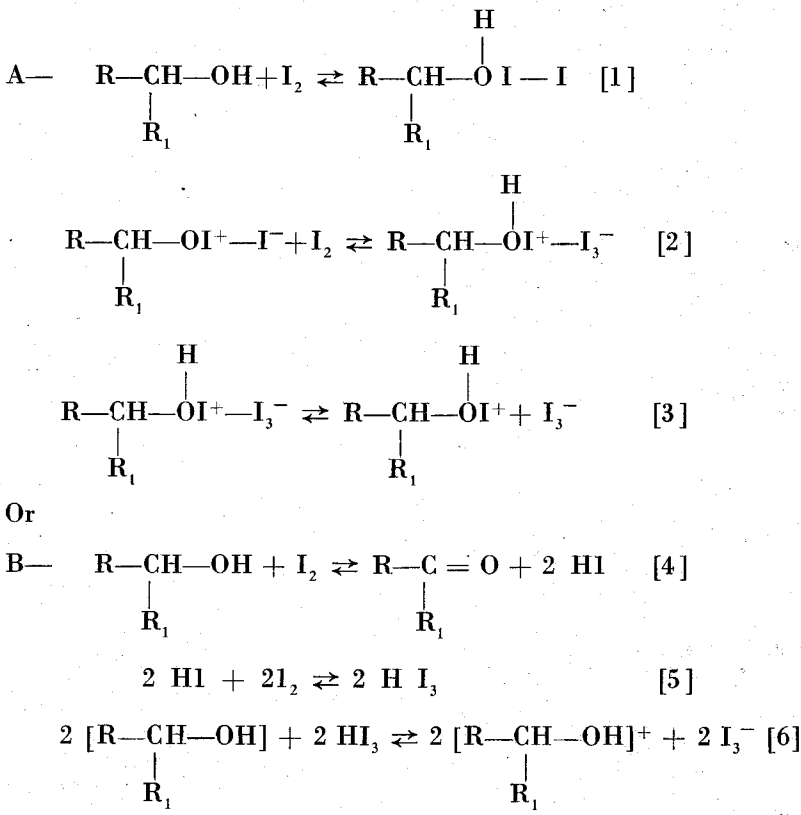


Fig- 5

RESULTS AND DISCUSSION

The peaks observed at about 292 mμ and 362 mμ are characteristic of I_3^- complexe ion. This has been shown on solid I_3^- and I_7^- containing hexamethylmelaminium polyiodide complexes by us (study is being published in the Journal of the Chemical Society) and by others on other complexes [14], [15].

The formation of this complexe ion in alcoholic media can be explained either,



(R and R_1 represent H or alkyl).

Experiments have been done either by taking strict precautions to exclude moisture or without taking any percautions and have been observed no change at-all in the over-all spectra.

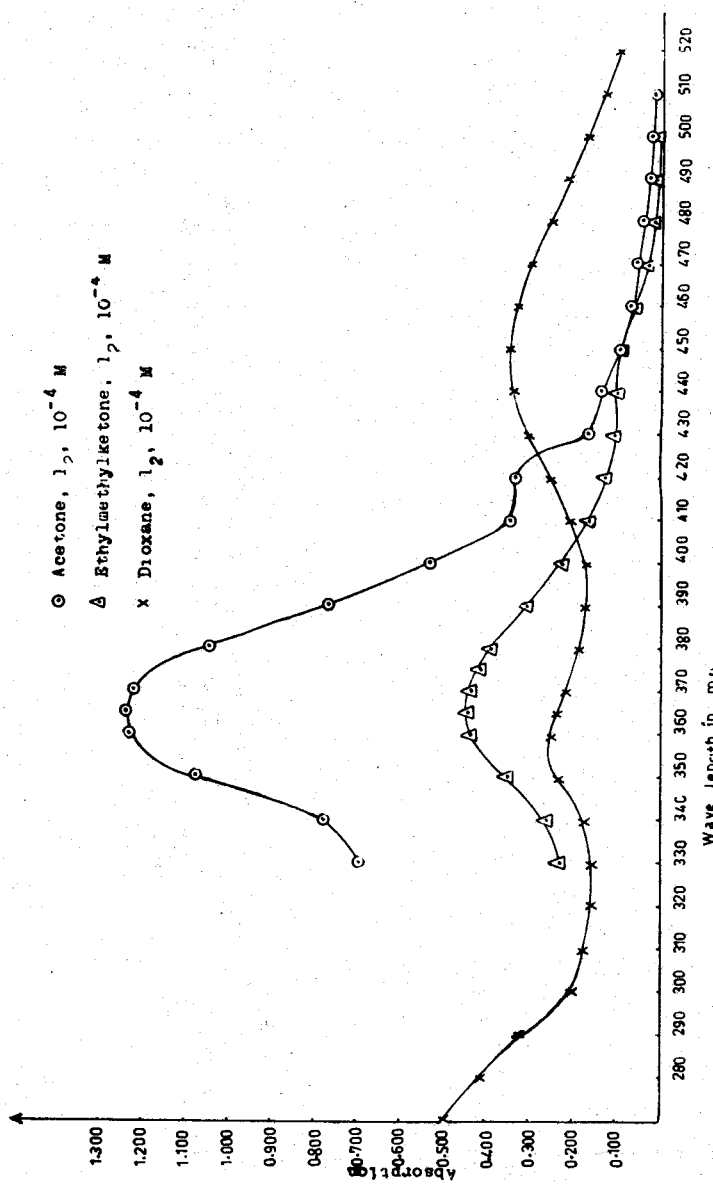
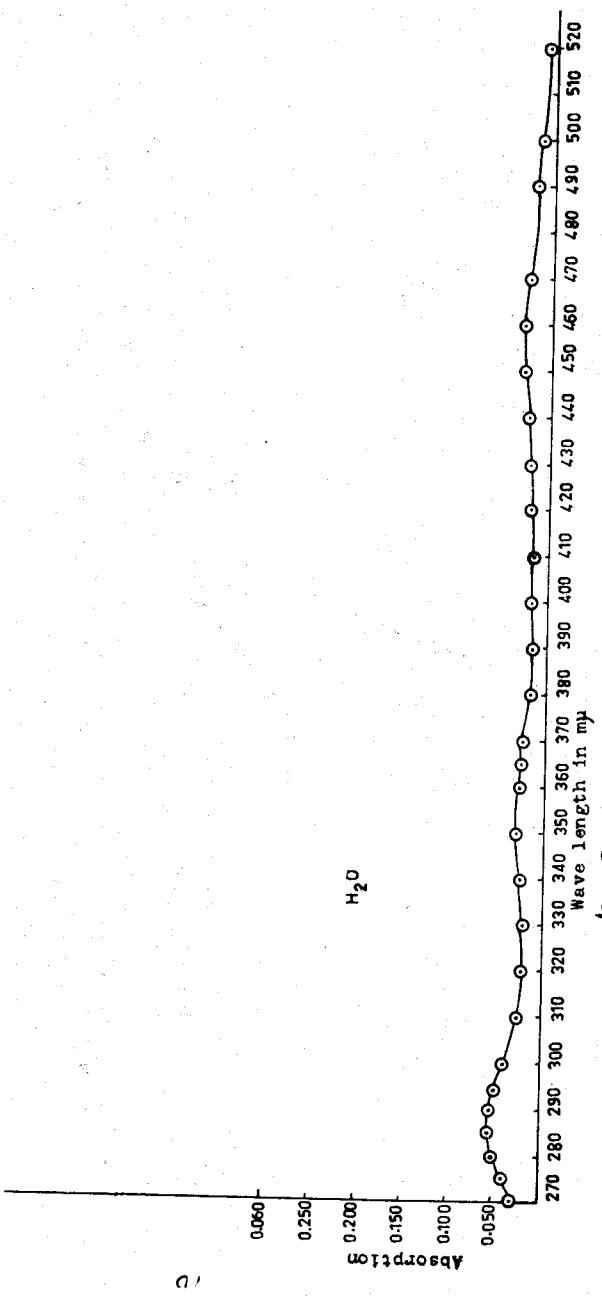

⊙ Acetone, I_2, 10^{-4} M
Δ Ethylmethylketone, I_2, 10^{-4} M
× Dioxane, I_2, 10^{-4} M
Absorption
1·300
1·200
1·100
1·000
0·900
0·800
0·700
0·600
0·500
0·400
0·300
0·200
0·100
280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450 460 470 480 490 500 510 520
Wave length in mμ

Fig-6


Absorption
0.050
0.100
0.150
0.200
0.250
0.060
270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450 460 470 480 490 500 510 520
Wave length in mμ
H_2O

So this means that moisture is not harmful. In addition to this, when iodine is treated with distilled water at room temperature no peaks are observed. But, when iodine is boiled with distilled water and then is cooled as quickly as possible, characteristic peaks at about 292 mμ and 362 mμ are observed, but very faintly, Fig–7. After some time, absorption decreases and peaks disappear.

Molar extinction coefficient of I_3^- complex is about 36000 at 292 mμ [15], [16]. This varies somewhat with the nature of solvent [17]. In the experiments observed molar extinction coefficients in methylalcohol is 9950 an hour after preparation. This value decreases very slowly by the time. This is probably due to advancing of reaction (B). The solution of HI does not give any absorption band in this range.

In the other two solvents calculated molar extinction coefficients, are 3050 for ethylalcohal and 5780 for isopropylalcohol, an hour later.

Although the peak of I_3^- complex at about 362 mμ is observed in the case of ethylmethylketone and dioxane the peak at about 292 mμ is not observed. This is probably due to blackness of the solutions in this range.

APPARATUS AND MATERIALS

Measurements have been made on a Beckman DU Spectrophotometer equipped with a Beckman DU Power Supply.

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

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

REFERENCES

[1] F. H. Getman; J. Am Chem. Soc. (1928), **50,** 2883.

[2] Lachman: J. Am. Chem. Soc. (1903), **25,** 50.

[3] Beckman. Z; Physik. Chem. (1907), **58,** 543

[4] Audrieth and Birr; J. Am. Chem. Soc (1933), **55,** 668.

[5] Fairbrother; Nature, (1947), **160,** 87.

[6] C. Reid and R. S. Mulliken; J. Am. Chem. Soc. (1954), **76,** 3869

[7] Margosches and Hinner; Chem. Zentr. (1924), **95,** 2648.

[8] Weyl; Angew. Chem. (1939), **48,** 573.

[9] W. B. Person, R. E. Humphrey and A. I. Popov; J. Am. Chem. Soc. (1959), **81,** 273.

[10] W. B. Person, W. C. Golton and A. I. Popov; J. Am. Chem. Soc. (1963), **85,** 891.

[11] Hildebrand and Jenks; J. Am. Chem. Soc. (1920), **42,** 2180.

[12] C. Reid and R. S. Mulliken; J. Am. Chem. Soc. (1954), **76,** 3869.

[13] I. Kleinberg and A. W. Davidson; Chem. Rev. (1948), **42,** 601

[14] A. I. Popov and R. F. Swensen; J. Am. Chem. Soc. (1955), **77,** 3724.

[15] A. J. Hamilton and L. E. Sutton; Chem. Com. (1968), 460.

[16] Autrey. A. D. and Connick. R; J. Am. Chem. Soc. (1951), **73,** 1842.

[17] Katzin, L. I; J. Chem. Phys. (1952), **20,** 1165.

ÖZET

Iyot çözücülerde çeşitli renklerle çözünür. Alifatik hidrokarbonlar, karbontetlorür, kloroform, dikloroetan gibi çözücülerde viyole renkte çözünür ve 520 mμ civarında bir absorpsiyon maksimumu meydana getirir. Benzen de dahil olmak üzere, alkoller, eterler ve ketonlarda kahverengi veya kırmızı - kahverengi çözeltiler verir ve 450 mμ civarında bir absorpsiyon maksimumu meydana getirir.

Kriyoskopik molekül ağırlıkları tayini iyodun bütün çözücülerde iki atomlu olarak çözündüğünü göstermesine rağmen, dağılma neticeleri çözücüye kimyasal olarak bağlı olduğunu göstermektedir.

Bu çalışmada iyodun polar ve polar olmıyan çeşitli çözücülerdeki durumu spektrofotometrik olarak incelendi ve alkoller içinde I_3^- kompleks iyonunu meydana getirdiği tesbit edildi. Bu da iyodun hiç değilse alkollerde kimyasal olarak bağlı olduğu fikrini açıkça sağlamaktadır.

Çözücüye göre az çok değişmesine rağmen bu kompleks iyon 292 ve 362 mμ dalga boylarında karakteristik bir çift absorpsiyon maksimumu meydana getirir.

Elektron veren grup D olarak kabul edilirse I_3^- ün teşekkülü ya $DI^+ + I_3^-$ veya $DH^+ + I_3^-$ şeklinde kabul edilebilir. Polar çözücüler en aşağı bir ortaklanmamış elektron çiftine sahip olduklarından I_3^- kompleks iyonunun teşekkülünü kolaylaştırırlar.

Prix de l'abonnement annuel

Turquie : 15 TL ; Etranger : 30 TL.
Prix de ce numéro : 5 TL (pour la vente en Turquie).
Prière de s'adresser pour l'abonnement à : Fen Fakültesi Dekanlığı
Ankara Turquie.

Ankara Üniversitesi Basımevi - 1969