2.1. Synthesis of coumarin derivatives II-IV$_{a-c}$.

Coumarin as all coloured compounds have a considerable interest to analytical chemists and forensic scientists, also to the physicians in diagnostic medicine, and to biologists involved in histological studies.

Owing to the importance of colour, dyes and pigments, a great interest has been focused on the relation between colour and molecular structure.

Thus, our interest is focused to synthesis some coumarin derivatives (II-IV$_{a-c}$) using 7-hydroxy coumarin I as a starting material.

Coumarin I was prepared according published procedure via cyclocondensation of resorcinol with malic acid in the presence of conc. H_2SO_4.

1- Preparation of 7. Hydroxycoumarin (Umbelliferone)$^{(1)}$:

Umbelliferone was prepared by cyclocondensation of resorcinol with malic acid. Thus 62.5ml of 4: 1 H_2SO_2 – HOAC was added to mixture of 15 gm of resorcinol and 12.3 gm of malic acid, the mixture was heated at 120^{o}C to give red solid of umbelliferone (m.p. = 226-228 ^{o}C). It's IR (KBr) show ν` 1700 (C=O), 1620 (C=C), 1226 (C-O-CO) and 3350 (C-OH) cm^{-1}, *c.f.* Chart 1.

2- Preparation of 7-allyloxycoumarin (II):

A mixture of 7-hydroxycoumarin (0.01 mole) and allyl bromide (0.1 mole) in dry acetone (140ml) in presence of anhydrous K_2CO_3 (0.01 mole) was refluxed for 15 hrs, the reaction mixture was filtered immediately while hot, and the solvent distilled off to give brown residue, crystallized from chloroform.

m.p. = 210-211 ^oC its IR (KBr) show $\bar{\nu}$ 1720 (C = 0), 1620 (C= C), 1226 (C-O-CO) cm^{-1} *c.f.* Chart 2, and PMR ($CDCl_3$) δ 4.6 ($-CH_2-O-$), δ 5.4 ($CH_2=$), δ 6 (= CH-), 6.2 – 7.6 ppm (aromatic), *c.f.* Chart 3.

3- Preparation of 7-propargyloxycoumarin III:

A mixture of 7-hydroxycoumarin (0.01 mole) and propargylbromide (0.1 mole) in dry acetone (140 mL) in presence of unhydrous K_2CO_3) (0.01 mole) was refluxed for 7 hrs. the reaction mixture was filtered immediately while hot, and the solvent distilled of to give 7-propargyloxycoumarin brown residue.

m.p = 205^oC its IR (KBr) show $\bar{\nu}$ 1705 (C = 0), 1620 (C = C), 1234 (C-O-C=O) cm^{-1} *c.f.* Chart 4, and PMR ($CDCl_3$) δ 2.5 ($CH\equiv$), δ 4.7 ($-CH_2-O$), δ 6.2 – 7.6 ppm (aromatic), *c.f.* Chart 5.

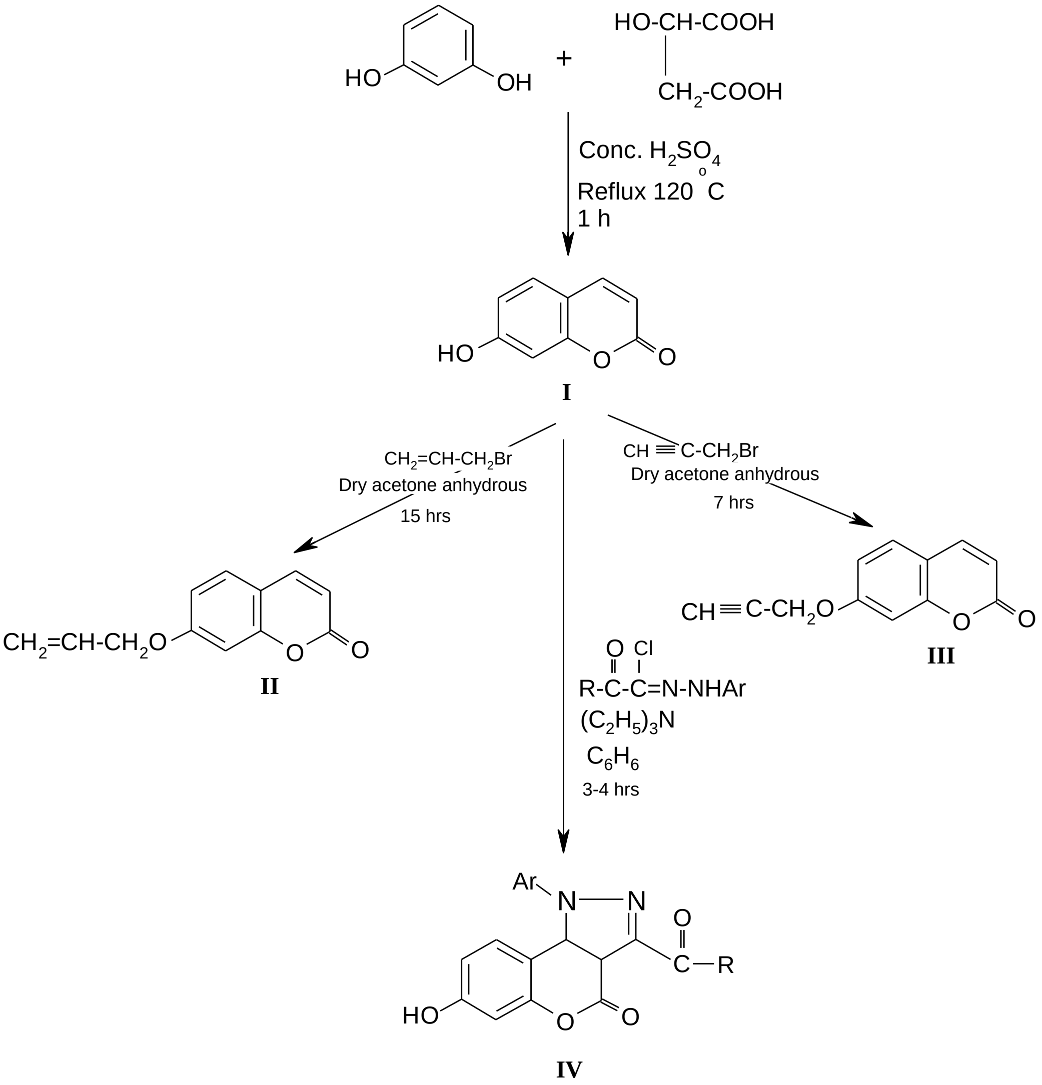
4- The cycloaddition of nitrilimine with 7-hydroxycoumarin:

To a solution of 7-hydroxycoumarin (0.05 mole) and nitrilimine derivatives (0.05 mole) in benzene (50 ml) was added triethylamine (0.7 ml) and the mixture was refluxed for 3-4 hrs and then cooled, the reaction mixture was filtered to remove the precipitated triethylamine hydrochloride. The solvent was then evaporated to give the crude products IV_{a-c}.

Dye IV_a had m.p. = 170- 172 ^oC (ethanol), IR (KBr) $\bar{\nu}$ 1700 (C = O), 1220 (C-O – C = O) cm^{-1}, PMR ($CDCl_3$) δ 2.52 (CH_3-C-), δ 3.06, 3.1 (-CH-CH-) δ 6.24 – 7.64 (aromatic) δ 8.65 (OH) ppm., *c.f.* Chart 6. The mass spectrum show m/z = 322, *c.f.* Chart 7.

Dye IV_b had m.p. = 180 – 182 ^oC (ethanol), IR (KBr) $\bar{\nu}$ 1700 (C= O), 1221 (C-O-CO) cm^{-1}, PMR ($CDCl_3$) δ 1.4 (CH_3-), δ 4.0 (-CH-H), δ 4.36 (-CH_2-O-), δ 8.35 (-O-H) ppm., *c.f.* Chart 8, the mass spectrum show m/z = 352, *c.f.* Chart 9.

Dye IV_c had m.p. 192 – 193 ^oC (ethanol) IR (KBr) $\bar{\nu}$ 1700 (C=O), 1220 (C-O-C=O) cm^{-1} PMR ($CDCl_3$) δ 1.35 (CH_3-), δ 3.9 (-CH_2-), δ 4.3, 4.35 (-CH-CH-), δ 6.32 – 8.39 (aromatic), δ 8.8 (-O-H) ppm., *c.f.* Chart 10, the mass spectrum show m/z = 397, *c.f.* Chart 11.



	Ar	**R**
a;	C_6H_5-	CH_3
b;	C_6H_5-	CH_3CH_2O-
c;	C_6H_5-NO_2(*p*-)	CH_3CH_2-O-

2.2 Effect of solvent on the absorption and fluorescence spectra of dye II-IV$_{a-c}$:

The previous literature survey illustrated the importance of 7-hydroxycoumarins as laser dyes, due to their broad tuning ranges, high photochemical stability and good lasing efficiency. It is also emphasized that lasing wavelength can be tuned within several tens of nanometers with the same lasing material by varying the solution parameters [pH, concentration, temperature, solvent] and characteristic of the apparatus used.

Absorption spectra were recorded with an unicam spectrophotometer, corrected fluorescence spectra were taken with a shimadzu 5301 PC spectrofluorometer in photoenergy center, Faculty of Science, Ain Shams University.

In this study, the absorption spectra of dyes II-IV$_{a-c}$ in methanol Figs. [1, 2] showed that, both of shape and position of the absorption bands are depends on the chemical structure.

The absorption and fluorescence spectra of dyes II-IV$_{a-c}$ are shown in Figs. [3-7]. It was observed that the change in photon energy causes a shift of the fluorescence spectrum to longer wave lengths, relative to the absorption spectra, which is noticed from the value of stokes shift, see Table [1].

Table [1]:

Dye number	**Absorption λmax. nm**	**Emission λmax. nm**	**Stockes shift [nm]**
II	290	385	95
	323	385	62
III	290	385	95
	323	385	62
IV_a	290	390	100
	344	390	46
IV_b	290	390	100
	327	390	63
IV_c	286	395	109
	362	455	93
	380	455	75

A- Effect of solvents on the absorption spectrum of dyes II-IV$_{a-c}$:

1- For dyes II:

The effects of solvents on the absorption spectra of 2 x 10^{-8} M dye II was shown in Figs. [8, 9] which show that, the absorption spectrum of dye II was changed in its nature and position of the bands by change the solvent. Also we notice that the highest intensity was observed for dye II in water [high probability of transition from ground state vibrational levels to the same excited state vibrational levels], but the lowest intensity was observed for dye II in glycerol [less symmetrical between ground state and excited state] i.e., low probability of transition.

The absorption spectral data of dye II in different solvents was listed in Table [2]. The Table showed that there is a relationship between molar absorptivity ε_{max}, oscillators strength [f] and half-band width $\Delta\bar{\nu}_{1/2}$ was increased as the solvents properties such as Z- value and E_T-value was increased and also as Z- value increased Figs. (10, 11) which reflect the dipole – dipole solute-solvent interaction and indicating that the dye II become less symmeterical in the high polar solvents such as water and alcohols. The same result was achieved when oscillator strength (f) was plotted against both of E_T- value and Z-value of the solvents. Figs. (12, 13). Moreover, the molar absorptivity ε_{max} of dye II in different solvents increased as the E_T-value of the solvent increased Fig. (14).

ii- For dye IV$_b$:

The effect of solvents on the absorption spectrum of 2 x 10^{-8} M dye IV$_b$ was showing Figs (15, 16) which illustrates that, the absorption spectra of dye IV$_b$ was affected by the solvent properties and the absorption spectrum of dye IV_b in glycerol has the lowest intensity (low probability of transition) and more stabilization of ground state by formation of dye – glyceral hydrogen bond in ground state. Also, the ε_{max}, $\Delta\bar{\nu}_{1/2}$ and oscillator strength (f) for dye IV_b in glyceral have the lowest values when compared by their values with other solvents which supports the above reason. Also, the absorption spectral data of dye IV_b in different solvents Table (3) show that, the λ_{max} of the absorption band of dye IV_b is slightly changed with solvent properties, but both of half-band width $\Delta\bar{\nu}_{1/2}$ and oscillator strength (f) were increased as both of E_T-value and Z-value of the solvent increase Figs. (17-20). The half-band width $\Delta\bar{\nu}_{1/2}$ and the oscillator strength (f) have the highest values in water.

iii- For dye IV_c:

The effect of solvents on the absorption spectrum of 2 x 10^{-8} M dye IV_c was shown in Figs. (21, 22) which shows that, the absorption spectrum of dye IV_c was affected by the solvent properties and its absorption spectrum in glycerol has the lowest intensity as mentioned above for dye II and dye IV_b also due to the same reason.

The absorption spectral data of dye IV_c was listed in Table (4) which show that λ_{max} of the absorption spectra were slightly or nearly unchanged as a function of solvent properties, but the half-band width $\Delta\bar{\nu}_{1/2}$was increase as both of E_T-value and Z-value of the solvent increased, also the highest $\Delta\bar{\nu}_{1/2}$ was observed for dye IV_c in DMF and its lowest value was observed for glycerol. The linear relationship between the $\Delta\bar{\nu}_{1/2}$and both of the E_T-value and Z-value of the solvent were illustrated in Figs. (23, 24), which showed a good correlations and reflect the dipole- dipole solute – solvent interactions, which become more in high polar solvent (water then alcohols). The same result was achieved when we study the relation between oscillator strength (f) and molar absorptivity ε_{max} with both of E_T-value and Z-value of the solvents Figs. (25-27).

Conclusions :

1- The λ_{max} of absorption spectra for dye II, IV_b and IV_c were slightly shifted with changed solvents properties.

2- The lowest intensity absorption spectrum for dyes II, IV_b and IV_c was observed in glycerol due to formation hydrogen band between solute and solvents in ground state.

3- Water has the good solvatochromism property for dye II and dye IV_b.

4- $\Delta\bar{\nu}_{1/2}$ for dyes II, IV_b and IV_c was increased as both of E_T- value and Z- value of the solvents increased.

5- $\Delta\bar{\nu}_{1/2}$ for dye IV_c has the highest value than that for dye IV_b for the same solvent. Which indicate that dye IV_c is the lowest symmetrical one.

Table (2): Absorption spectral data of dye (II) in different solvents:

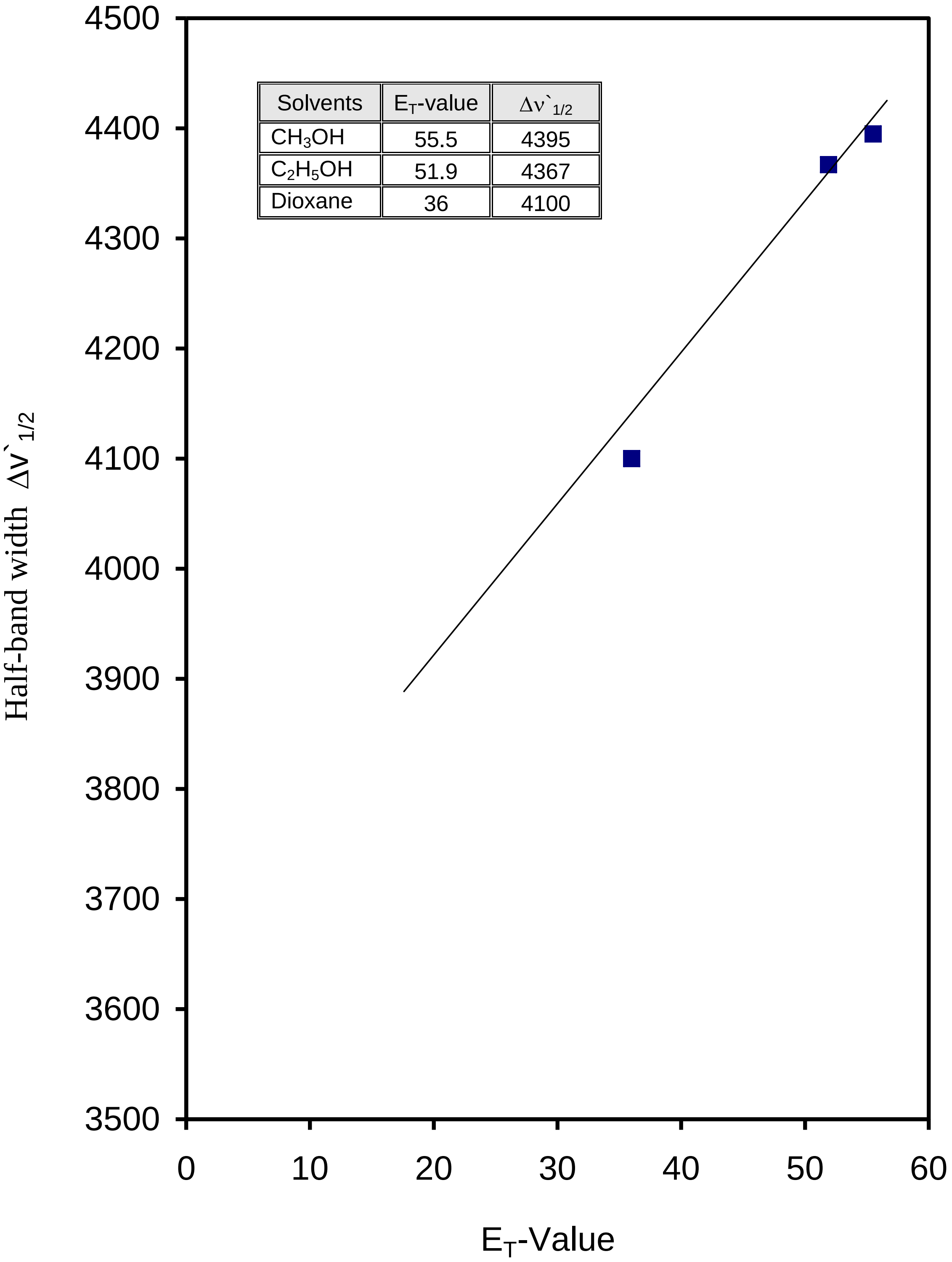
Solvent	Z	E_T	α	β	π	λ_{max}	ε_{max}	$\Delta\bar{\nu}_{1/2}$	f
H_2O	94.6	63.1	1.17	0.18	1.09	324	475	4797	98.43
CH_3OH	83.6	55.5	0.93	0.62	0.60	325	445	4395	84.49
C_2H_5OH	79.6	51.9	0.83	0.77	0.54	323	455	4367	85.84
CH_3CN	71.3	46.0	0.19	0.31	0.75	322	410	4183	74.09
DMF	68.5	43.8	0.00	0.69	0.88	331	350	3577	54.08
$CHCL_3$	63.2	39.1	-	-	-	327	430	4215	78.30
Dioxane	-	36.0	0.00	0.37	0.55	322	405	4100	71.73
Glycerol	-	-	-	-	-	331	200	3979	34.38
DCE	-	-	0.00	0.00	0.81	327	380	3847	63.15

ε = molar absorptivity 1. Mol^{-1}. Cm^{-1}

f = oscillator strength

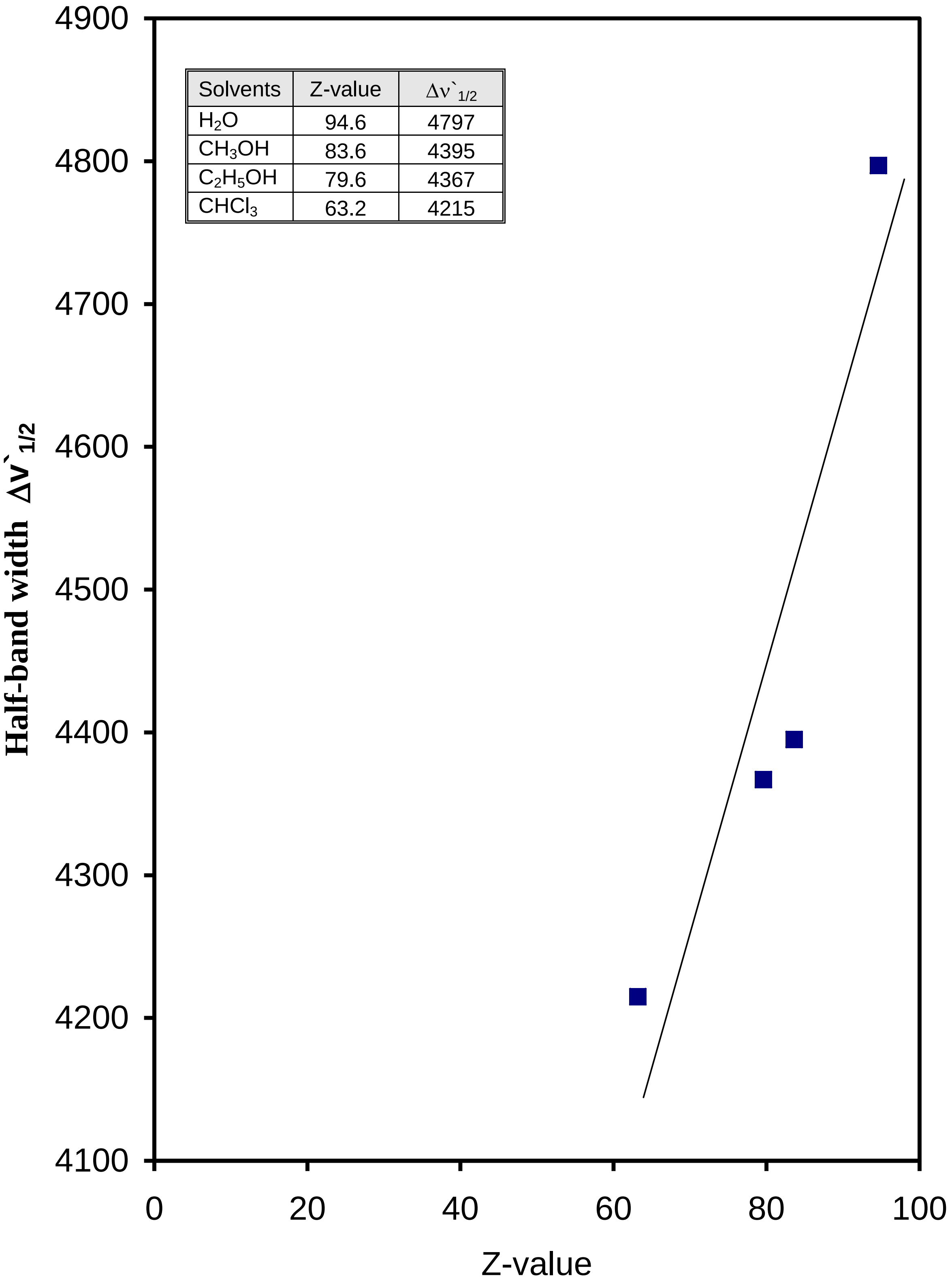
$f = 4.32 \text{ x } 10^{-9} \text{ x } \varepsilon_{max} \text{ x } \Delta\bar{\nu}_{1/2}$

DCE = Dichloroethane



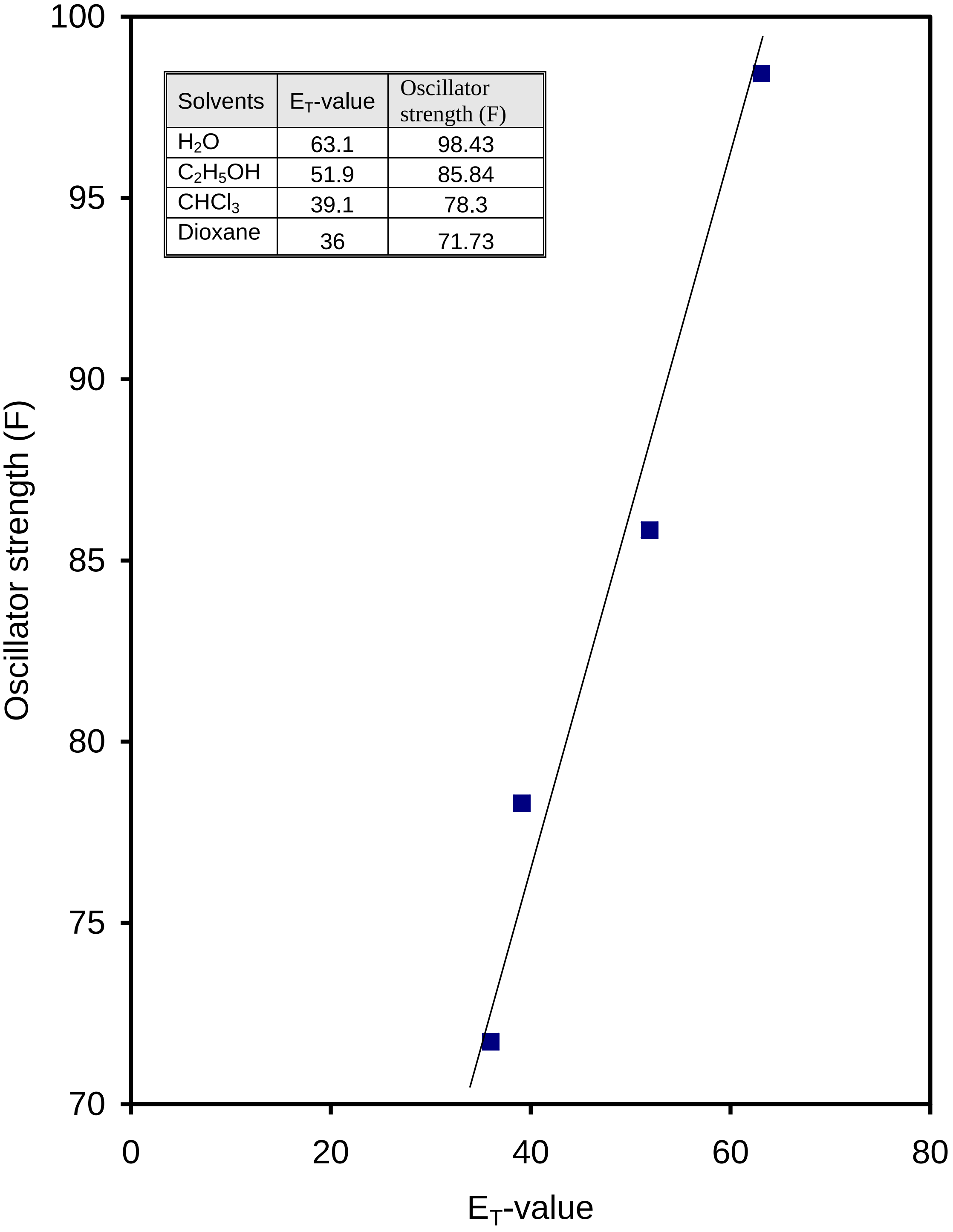
Solvents	E_T-value	$\Delta\nu`_{1/2}$
CH_3OH	55.5	4395
C_2H_5OH	51.9	4367
Dioxane	36	4100

Fig. (10): Relationship between $\Delta\nu_{1/2}$ and E_T-value of the solvents for dye II.



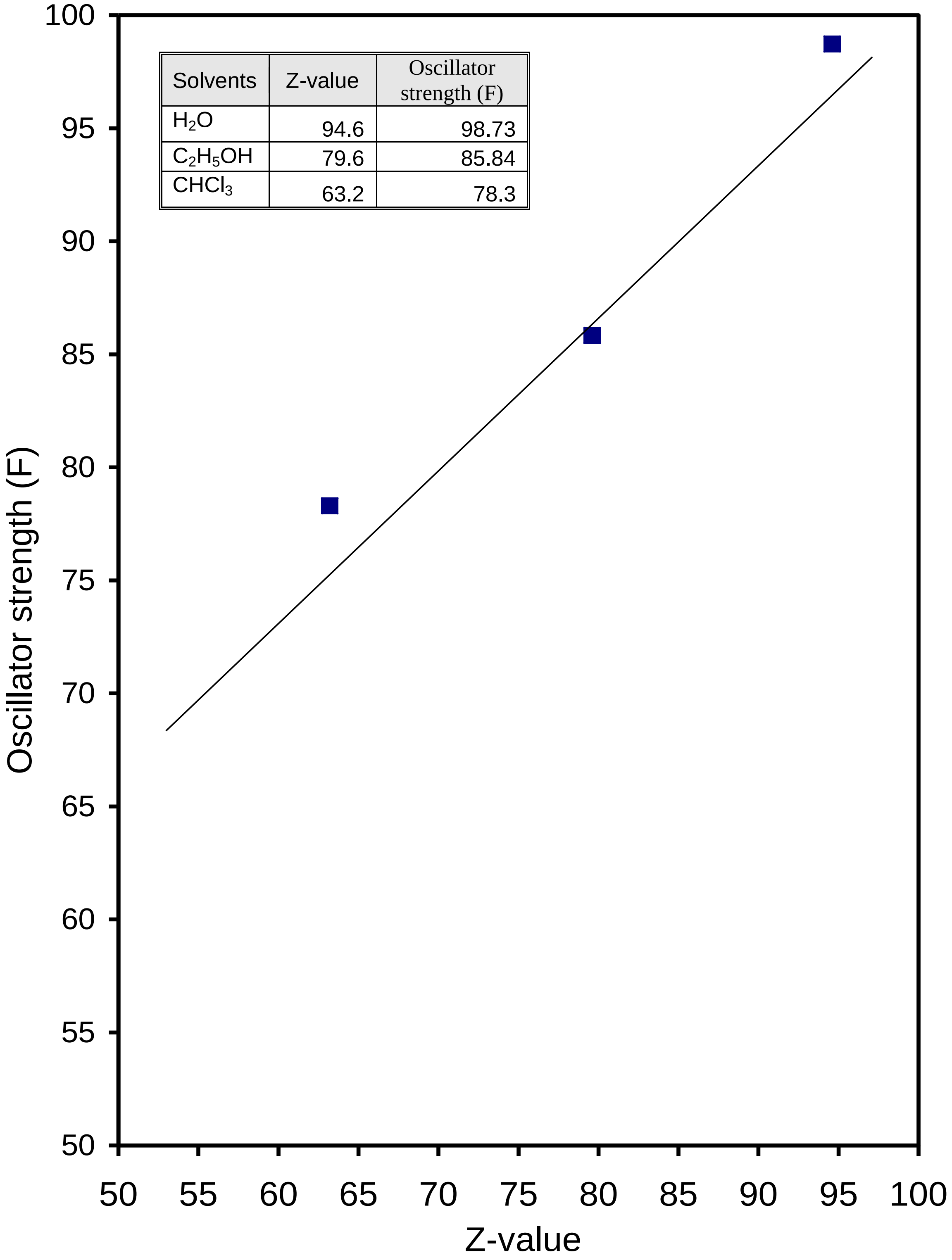
Solvents	Z-value	$\Delta\nu`_{1/2}$
H_2O	94.6	4797
CH_3OH	83.6	4395
C_2H_5OH	79.6	4367
$CHCl_3$	63.2	4215

Fig. (11): Relationship between $\Delta\nu_{1/2}$ and Z-value of the solvents for dye II.



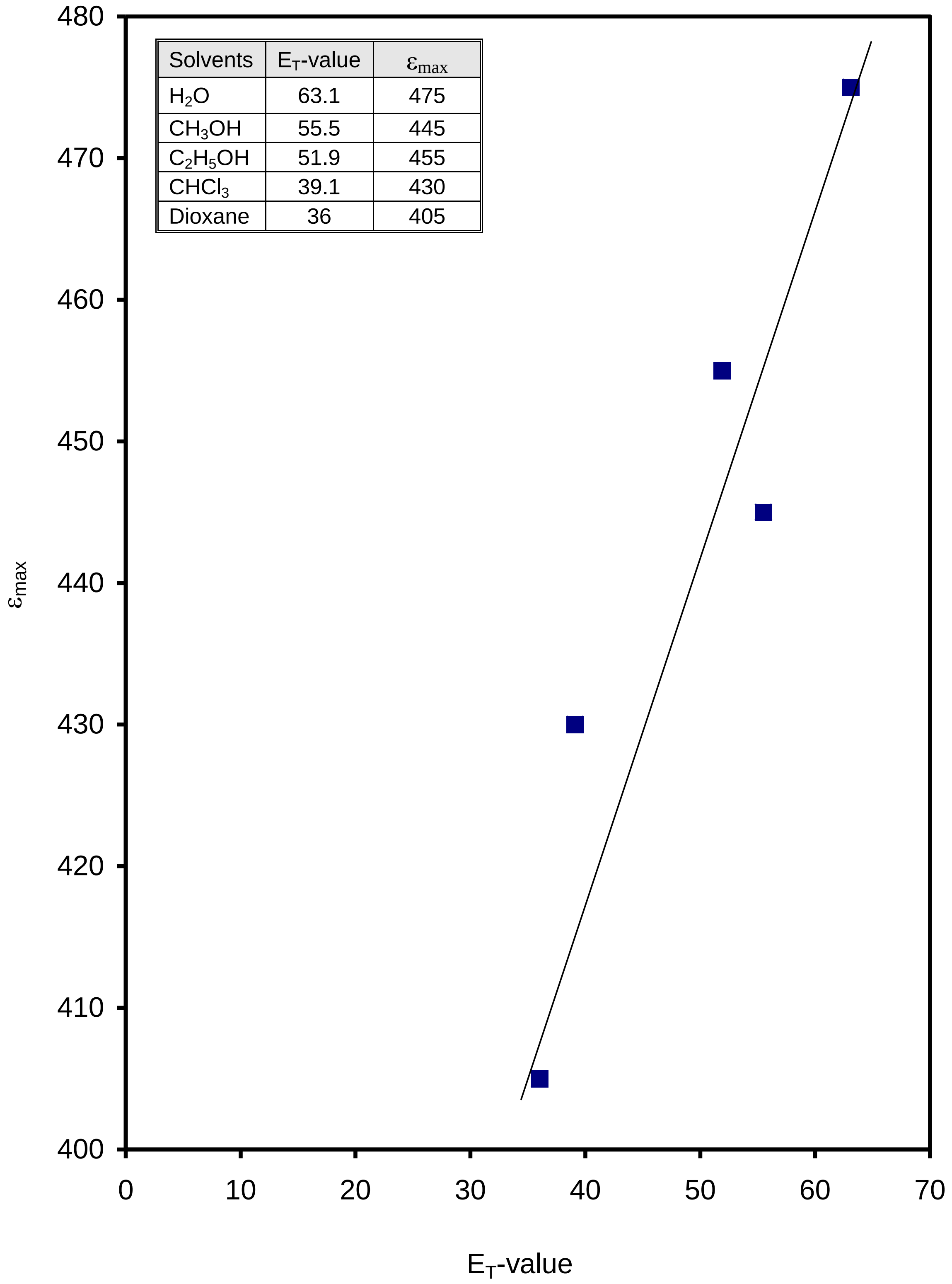
Solvents	E_T-value	Oscillator strength (F)
H_2O	63.1	98.43
C_2H_5OH	51.9	85.84
$CHCl_3$	39.1	78.3
Dioxane	36	71.73

Fig. (12): Relationship between oscillator strength (f) and E_T-value of the solvents for dye II.



Solvents	Z-value	Oscillator strength (F)
H_2O	94.6	98.73
C_2H_5OH	79.6	85.84
$CHCl_3$	63.2	78.3

Fig. (13): Relationship between oscillator strength (f) and Z-value of the solvents for dye II.



Solvents	E_T-value	ε_{max}
H_2O	63.1	475
CH_3OH	55.5	445
C_2H_5OH	51.9	455
$CHCl_3$	39.1	430
Dioxane	36	405

Fig. (14): Relationship between molar absorptivity ε_{max} and E_T-value of the solvents for dye II.

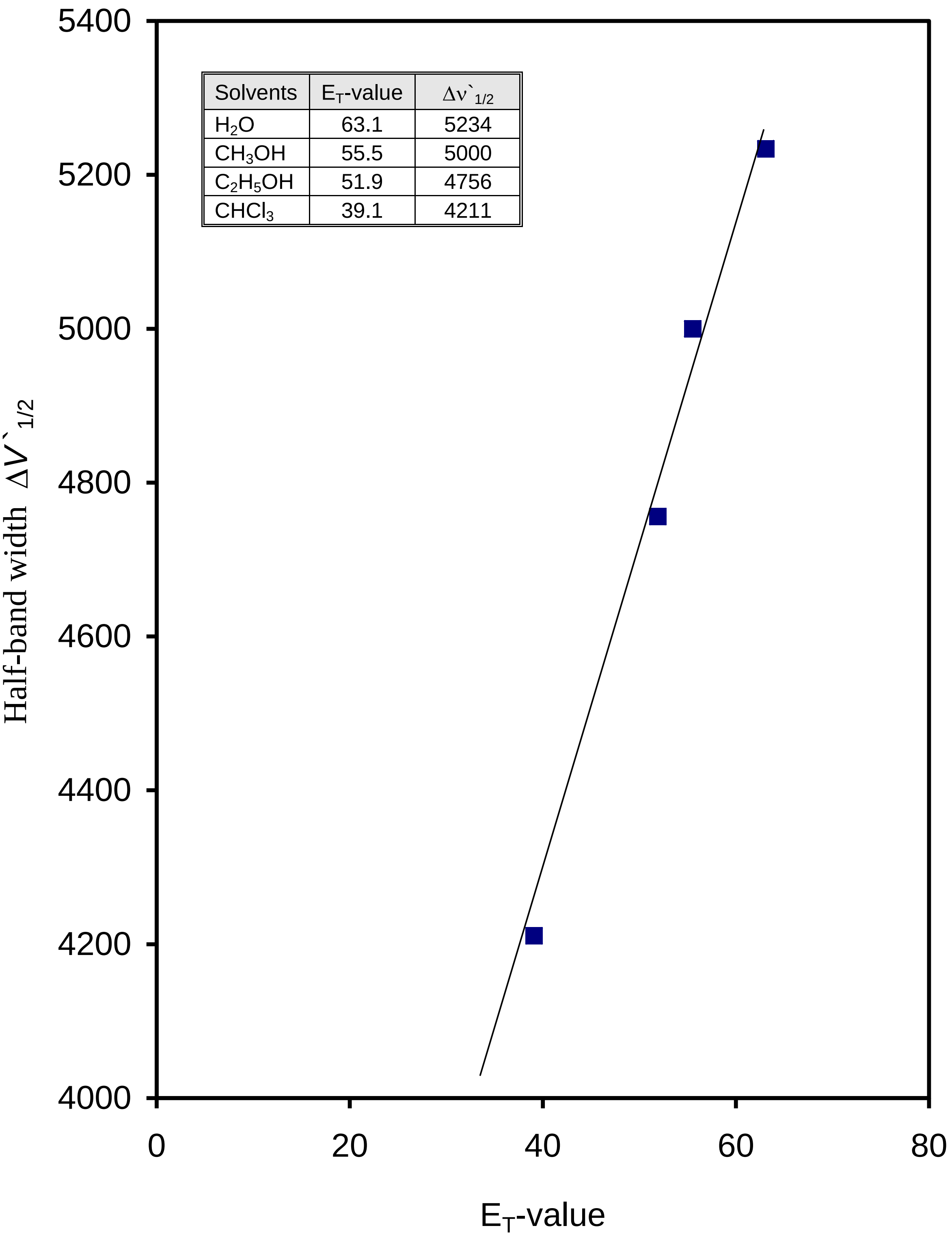
Table (3): Absorption spectral data of dye (IV_b) in different solvents:

Solvent	Z	E_T	α	β	π	λ_{max}	ε_{max}	$\Delta\bar{\nu}_{1/2}$	f
H_2O	94.6	63.1	1.17	0.18	1.09	327	1095	5234	247.59
CH_3OH	83.6	55.5	0.93	0.62	0.60	325	1100	5000	237.60
C_2H_5OH	79.6	51.9	0.83	0.77	0.54	327	1125	4756	231.14
CH_3CN	71.3	46.0	0.19	0.31	0.75	325	925	4925	196.80
DMF	68.5	43.8	0.00	0.69	0.88	326	915	3920	154.95
$CHCL_3$	63.2	39.1	-	-	-	326	1015	4211	184.64
Dioxane	-	36.0	0.00	0.37	0.55	323	995	5080	218.36
Glycerol	-	-	-	-	-	335	260	4138	46.48
DCE	-	-	0.00	0.00	0.81	324	1105	7481	228.23

ε = molar absorptivity 1. Mol^{-1}. Cm^{-1}

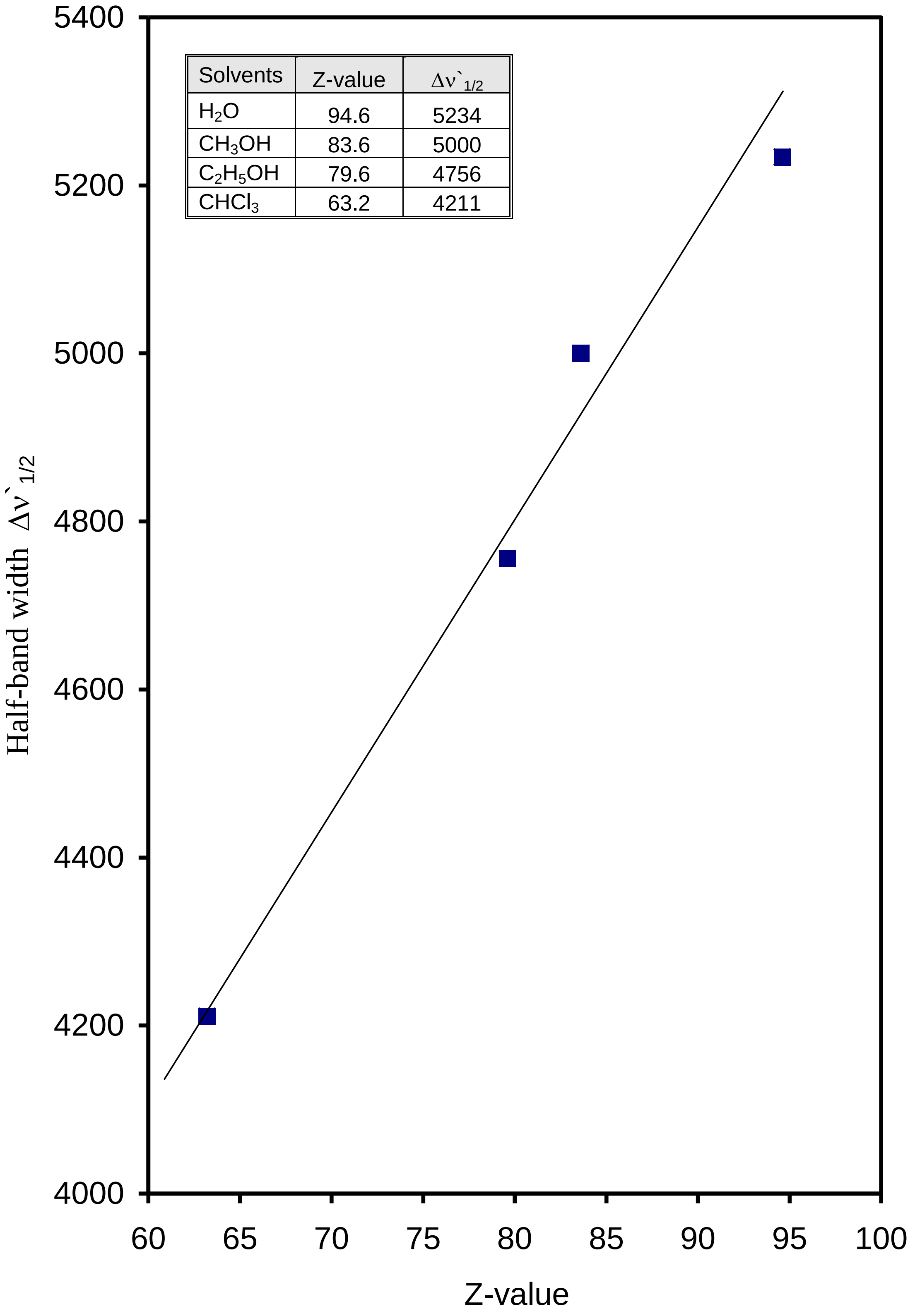
f = oscillators strength

$f = 4.32 \times 10^{-9} \times \varepsilon_{max} \times \Delta\bar{\nu}_{1/2}$



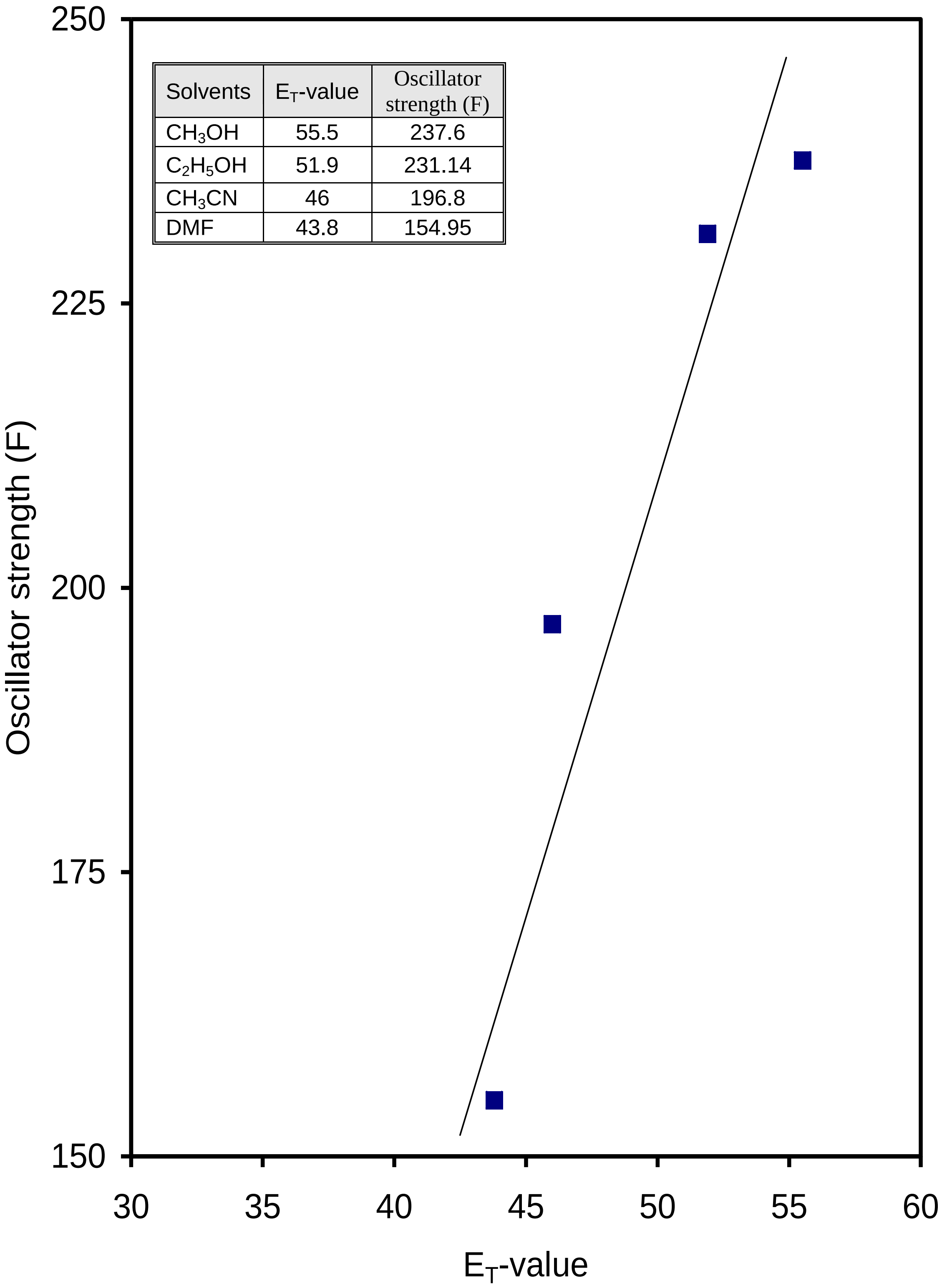
Solvents	E_T-value	$\Delta \nu`_{1/2}$
H_2O	63.1	5234
CH_3OH	55.5	5000
C_2H_5OH	51.9	4756
$CHCl_3$	39.1	4211

Fig. (17): Relationship between half-band width $\Delta \nu`_{1/2}$ and E_T-value of the solvents for dye IV_b.



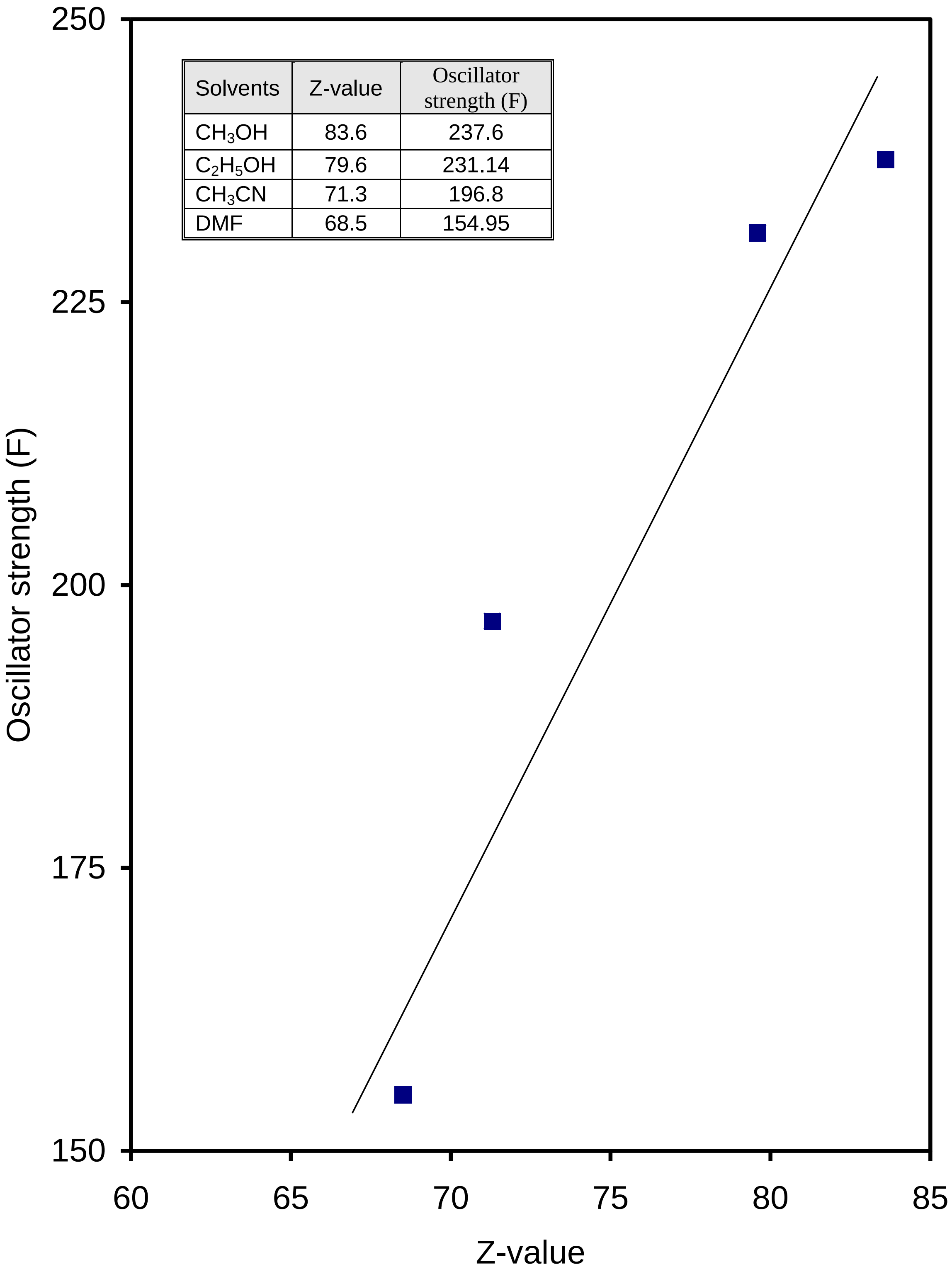
Solvents	Z-value	$\Delta\nu`_{1/2}$
H_2O	94.6	5234
CH_3OH	83.6	5000
C_2H_5OH	79.6	4756
$CHCl_3$	63.2	4211

Fig. (18): Relationship between half-band width $\Delta\nu`_{1/2}$ and Z-value of the solvents for dye IV_b.



Solvents	E_T-value	Oscillator strength (F)
CH_3OH	55.5	237.6
C_2H_5OH	51.9	231.14
CH_3CN	46	196.8
DMF	43.8	154.95

Fig. (19): Relationship between oscillator strength (f) and E_T-value of the solvents for dye IV_b.



Solvents	Z-value	Oscillator strength (F)
CH_3OH	83.6	237.6
C_2H_5OH	79.6	231.14
CH_3CN	71.3	196.8
DMF	68.5	154.95

Fig. (20): Relationship between oscillator strength (f) and Z-value of the solvents for dye IV_b.

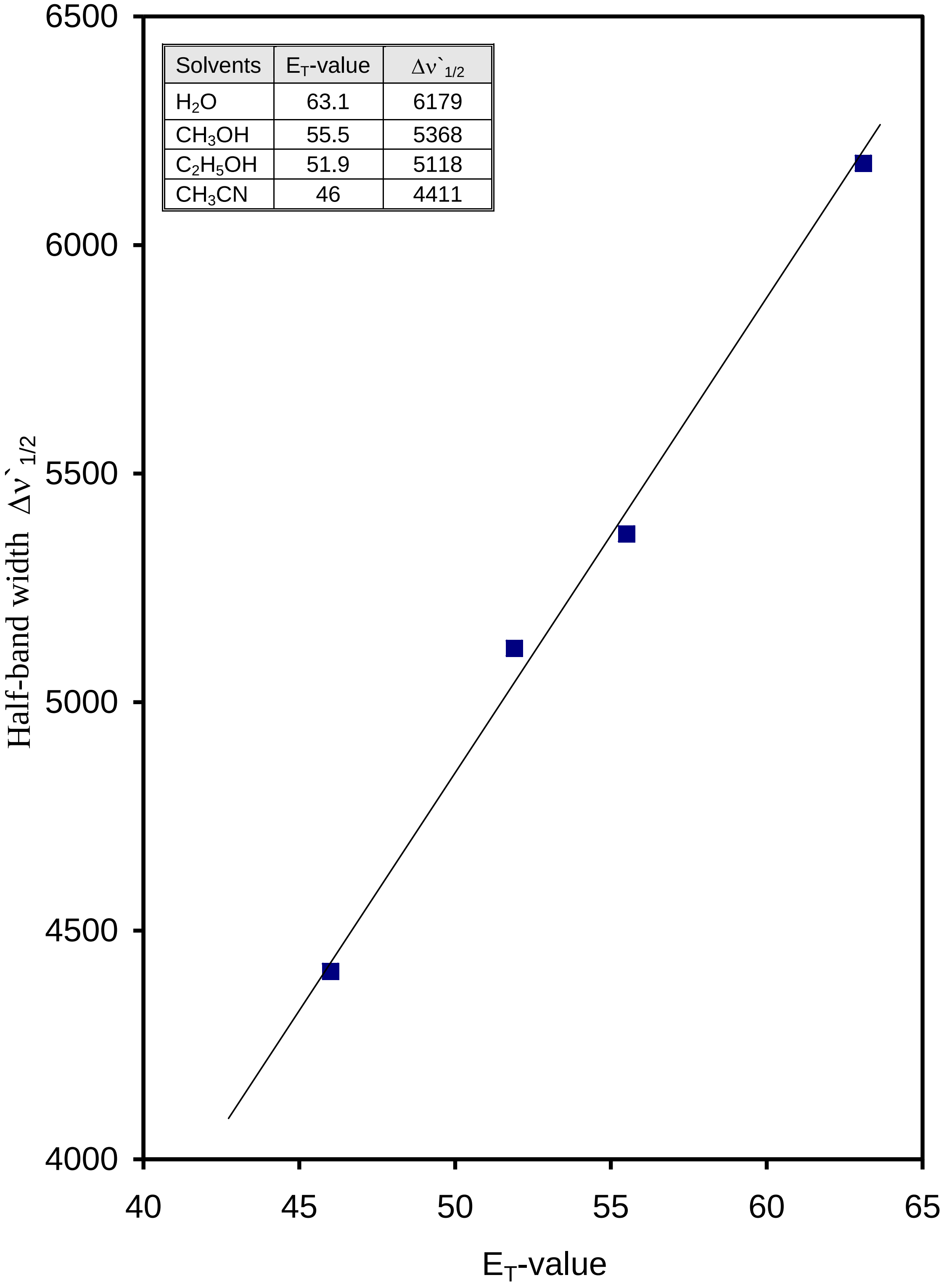
Table (4): Absorption spectral data of dye (IV_c) in different solvents:

Solvent	Z	E_T	α	β	π	λ_{max}	ε_{max}	$\Delta\bar{\nu}_{1/2}$	f
H_2O	94.6	63.1	1.17	0.18	1.09	369	1000	6179	266.93
CH_3OH	83.6	55.5	0.93	0.62	0.60	367	1380	5368	320.01
C_2H_5OH	79.6	51.9	0.83	0.77	0.54	367	1300	5118	287.43
CH_3CN	71.3	46.0	0.19	0.31	0.75	367	1280	4411	243.91
DMF	68.5	43.8	0.00	0.69	0.88	369	955	6475	267.13
$CHCL_3$	63.2	39.1	-	-	-	365	1230	5785	307.39
Dioxane	-	36.0	0.00	0.37	0.55	366	1290	4323	240.91
Glycerol	-	-	-	-	-	372	640	4104	113.47
DCE	-	-	0.00	0.00	0.81	366	1230	5740	305.00

ε = molar absorptivity 1. Mol^{-1}. Cm^{-1}

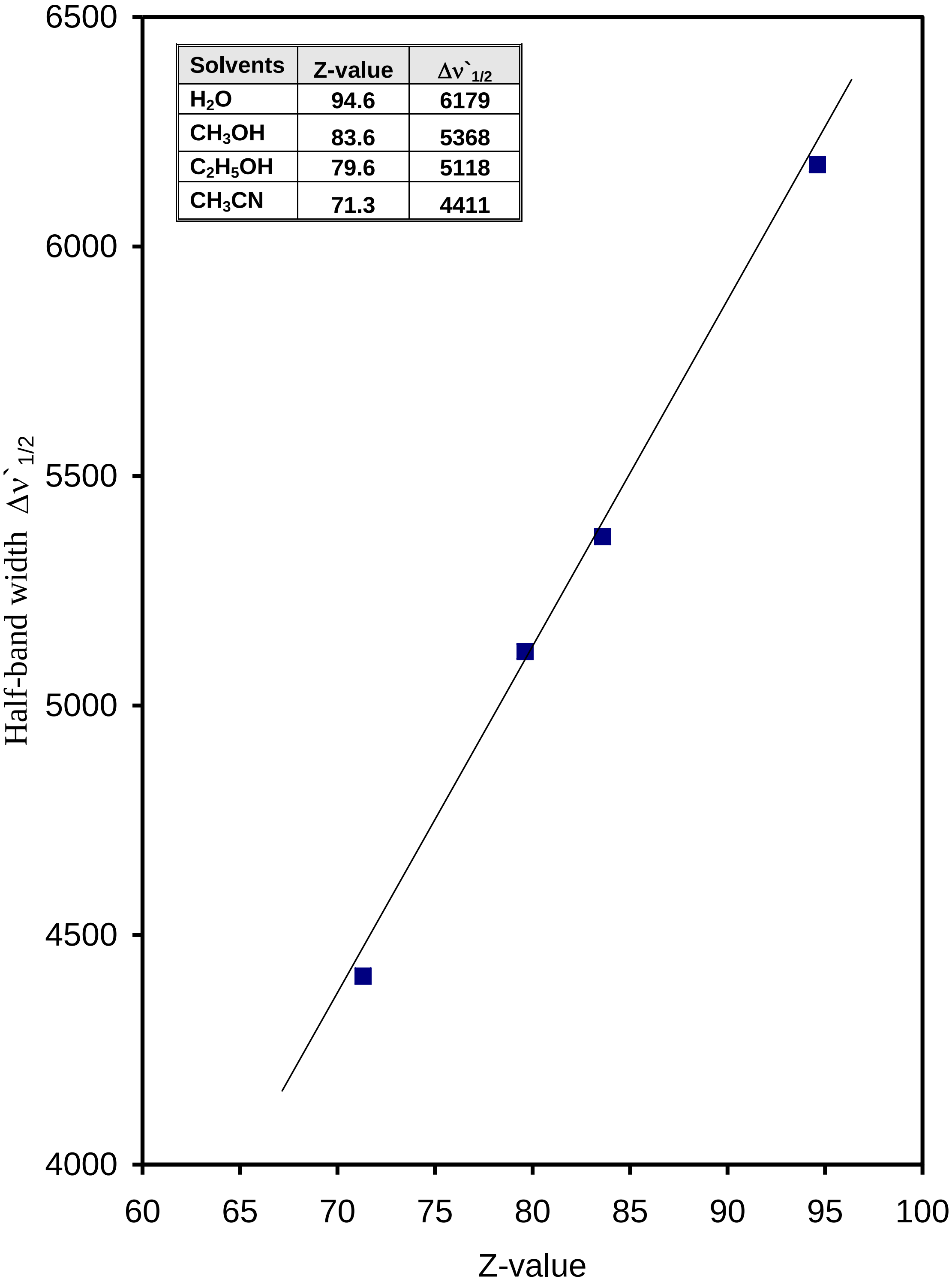
f = oscillator strength

$f = 4.32 \times 10^{-9} \times \varepsilon_{max} \times \Delta\bar{\nu}_{1/2}$



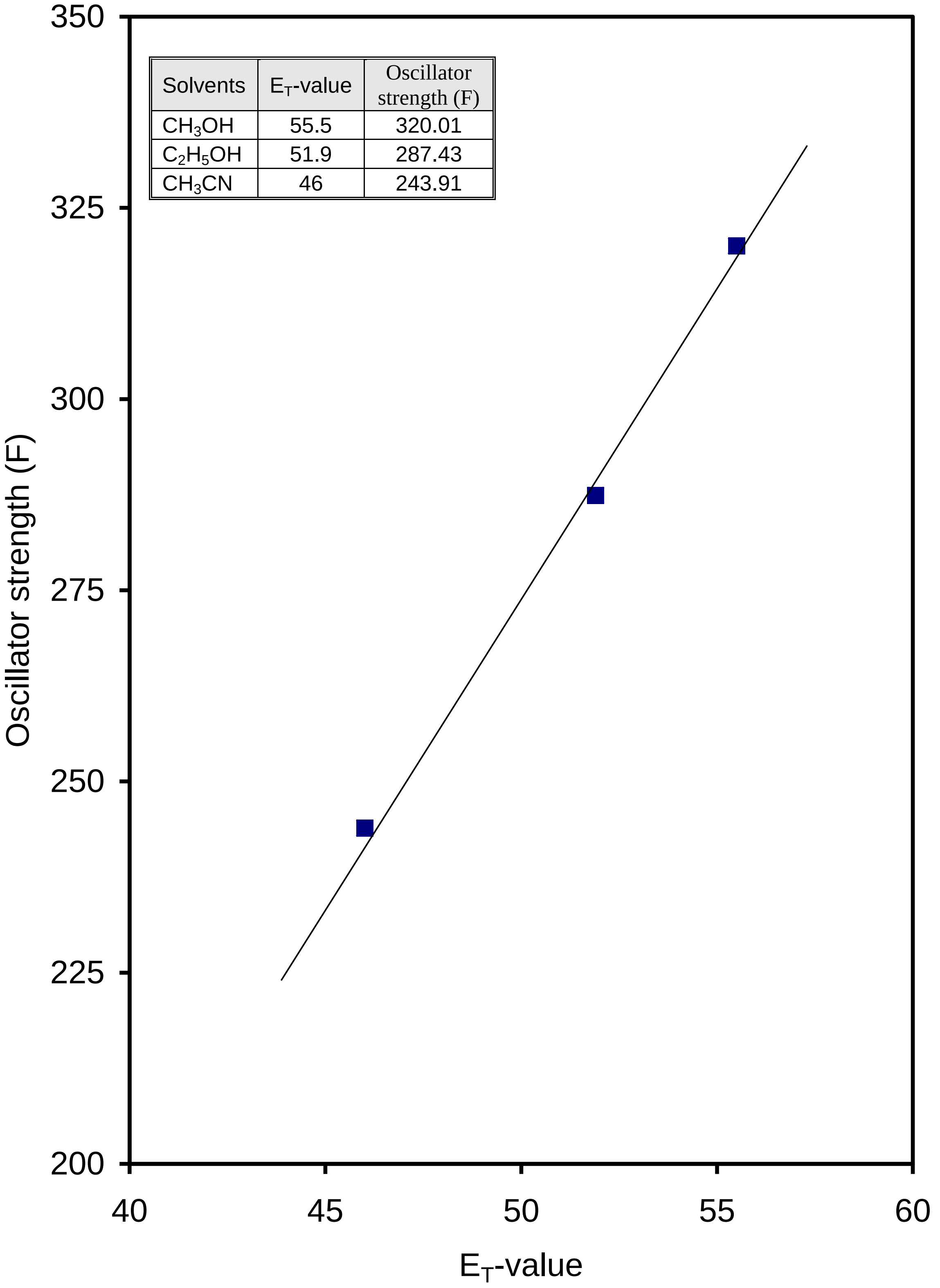
Solvents	E_T-value	$\Delta\nu`_{1/2}$
H_2O	63.1	6179
CH_3OH	55.5	5368
C_2H_5OH	51.9	5118
CH_3CN	46	4411

Fig. (23): Relationship between half-band width $\Delta\nu`_{1/2}$ and E_T-value of the solvents for dye IV_C.



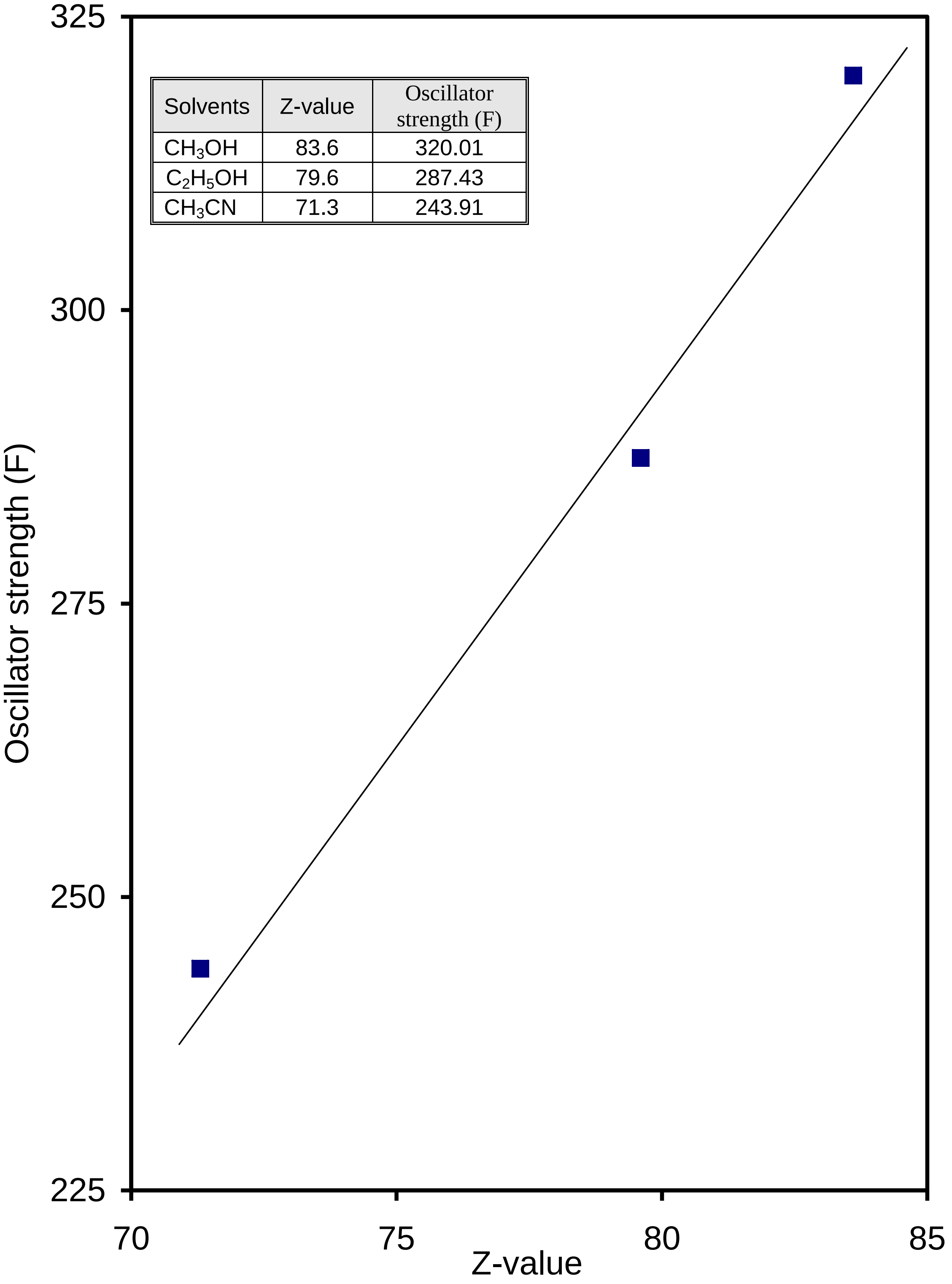
Solvents	Z-value	$\Delta\nu`_{1/2}$
H_2O	94.6	6179
CH_3OH	83.6	5368
C_2H_5OH	79.6	5118
CH_3CN	71.3	4411

Fig. (24): Relationship between half-band width $\Delta\nu`_{1/2}$ and Z-value of the solvents for dye IV_C.



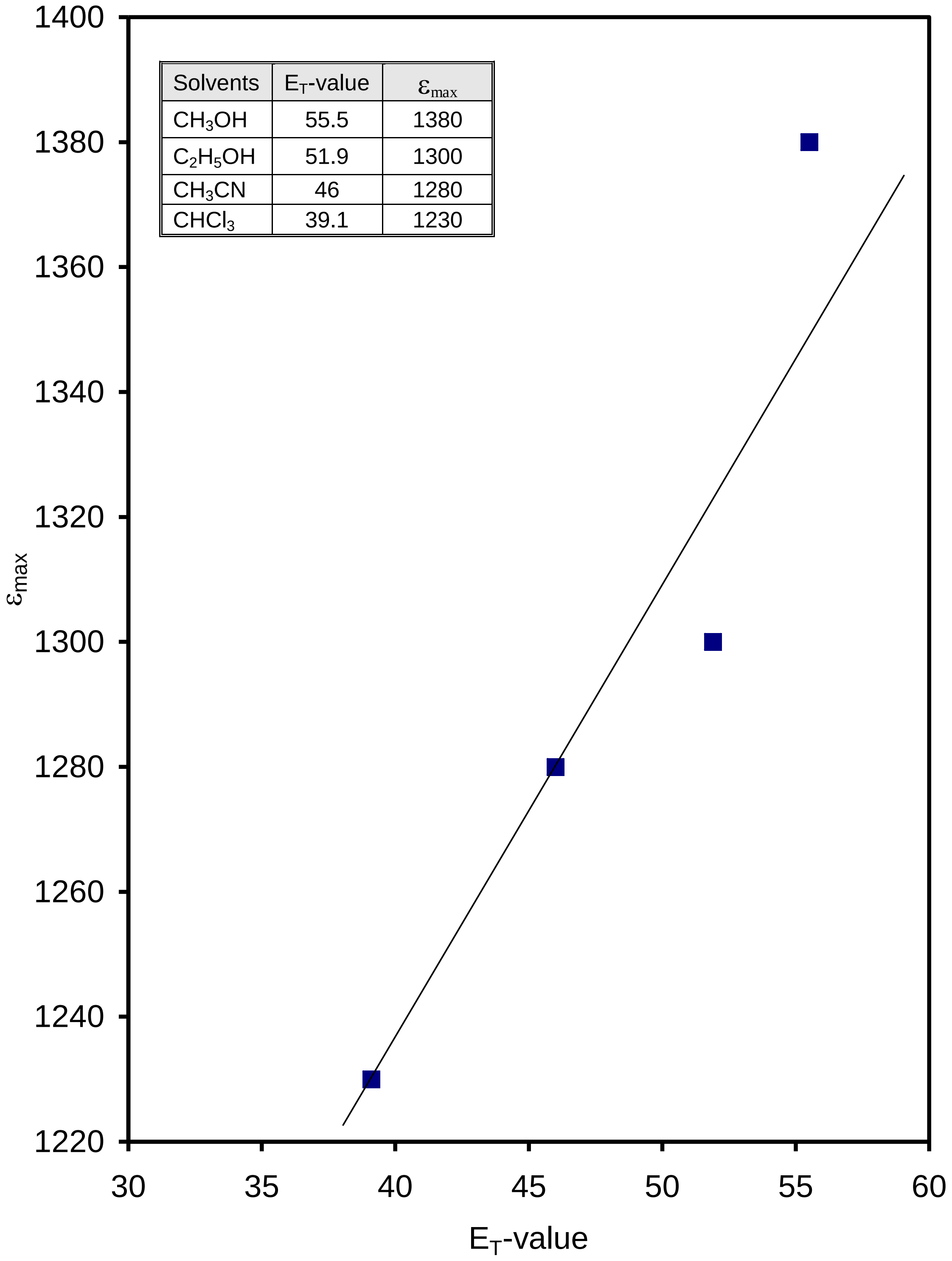
Solvents	E_T-value	Oscillator strength (F)
CH_3OH	55.5	320.01
C_2H_5OH	51.9	287.43
CH_3CN	46	243.91

Fig. (25): Relationship between oscillator strength (f) and E_T-value of the solvents for dye IV_C.



Solvents	Z-value	Oscillator strength (F)
CH_3OH	83.6	320.01
C_2H_5OH	79.6	287.43
CH_3CN	71.3	243.91

Fig. (26): Relationship between oscillator strength (f) and Z-value of the solvents for dye IV_C.



Solvents	E_T-value	ε_{max}
CH_3OH	55.5	1380
C_2H_5OH	51.9	1300
CH_3CN	46	1280
$CHCl_3$	39.1	1230

Fig. (27): Relationship between the molar absorptivity ε_{max} and E_T-value of the solvents for dye IV_C.

2.3 Effect of solvent on the fluorescence spectra of dyes II, IV$_b$ and V$_c$:

i- For dye II:

The effect of solvent on the fluorescence spectra of 2 x 10^{-8} M of dye II λ_{ex}= 323 nm was shown in figs. (28, 29) which show that, the fluorescence spectrum of dye II in water has the most intensity which indicate that dye II in water become more solvated by water molecules which surrounded dye II more than the other solvents. Also, it was observed that the quantum yield ϕ_f (the ratio between molecules that emit radiation relative to the total molecules in the excited state) has the higher value related to ϕ_f in the other solvents, this due to water make dye II emit radiation through fluorescence and decrease the other radiation less Figs. (31, 32).

The fluorescence spectrum data of dye II are listed in Tables (5, 6). Blue shift in fluorescence wave length was observered in polar solvent such as alcohols Fig. (30). On the other hand, emission maxima of dye II in water is longer wave length than in the other polar aprotic solvents (such as alcohols) which indicate that the hydrogen bonding character of water contributes to a greater extent to the stability of excited sate which increased the quantum yield ϕ_f and decreased the other radiationless. Furthermore, the relation between band width $\Delta\nu$` for dye II and E_T-value are shown in Fig. (33).

ii- for dye IV$_b$:

The effect of solvents on the fluorescence spectra of 2 x 10^{-8} M of dye IV$_b$ λex = 327 nm was shown in Figs (34, 35). The good solvatochromism of water make the fluorescence spectrum of dye IV$_b$

in water is the highest intensity for all the other organic solvents see Fig. (34) and also see table (7, 8). Also red shift of the fluoresence wavelength in water was observed rather than in the other polar aprotic solvents which indicates that the hydrogen bonding interaction between the day and water which contributes to a great extent to the stability of the excited state and decrease the radiationless. Tables (7, 8) illustrate that the value of ϕ_f in glycerol is the highest one followed by water, methanol and ethanol which indicate that the value of ϕ_f increase by increase rigidity (vicousity) and hydrogen bonding between solute – solvent.

Figs. (36-38) give good correlation between fluorescence intensity, quantum yield ϕ_f and $\Delta\bar{v}$ of dye IV_b, as a function of E_T-value of the solvent which general increases as E_T-value of the solvent increases.

iii- For dye IV_c:

The effect of solvents on the fluorescence spectrum of 2×10^{-8} M of dye IV_c $\lambda ex= 263$ nm was shown in Fig. (39) as mentioned above that water play an important role in solvatochromism of dye IV_c in the excited state, and both of fluorescence intensity, quantum yield ϕ_f are enhanced in water rather than other aprotic solvent (alcohols), also emission maxima of dye IV_c in water at longer wavelength than in other aprotic solvents (alcohols) which indicated that the hydrogen bonding character of water contributes to a great extent to the stability of the excited state Fig. (40) also Figs. (41, 42) give good correlation between fluorescence intensity, quantum yield ϕ_f and $\Delta\nu$` of dye IV_c as a function of E_T value of the solvents which general they are increased as E_T- value of the solvent increased.

Conclusions:

1- The quantum yield ϕ_f of dyes II, IV_b, V_c are very small when compared with that of 7-hydroxycoumarin this due to

a- for dye II the rotational of allyloxy group around the σ-bond make the dye II out- of the plane and make the dye lose its energy as thermal energy or other forms of radiationless process.

b- For dye IV_b the rotational of ester groups and phenyl group around σ-bond make the dye more and more out of plane and lose its energy as thermal energy or other forms of radiationless decayed, but for dye IV_c there is an extra- p-NO_2 which increase the above reason so ϕ_f of dye IV_c is less than that of dye IV_b in the same solvent.

2- Water in both of dyes II, IV_b and VI_c play an important role in solvatochromism and formation of hydrogen bond with the dyes in excited state which lead to red shift of wavelength, increase in fluorescence intensity and high value of quantum yield ϕf.

3- The E_T-value of the solvents give good correlation with both of λ_{max} , ϕ_f, $\Delta\nu$`, and fluorescence intensity for dyes II, IV_b, and IV_c.

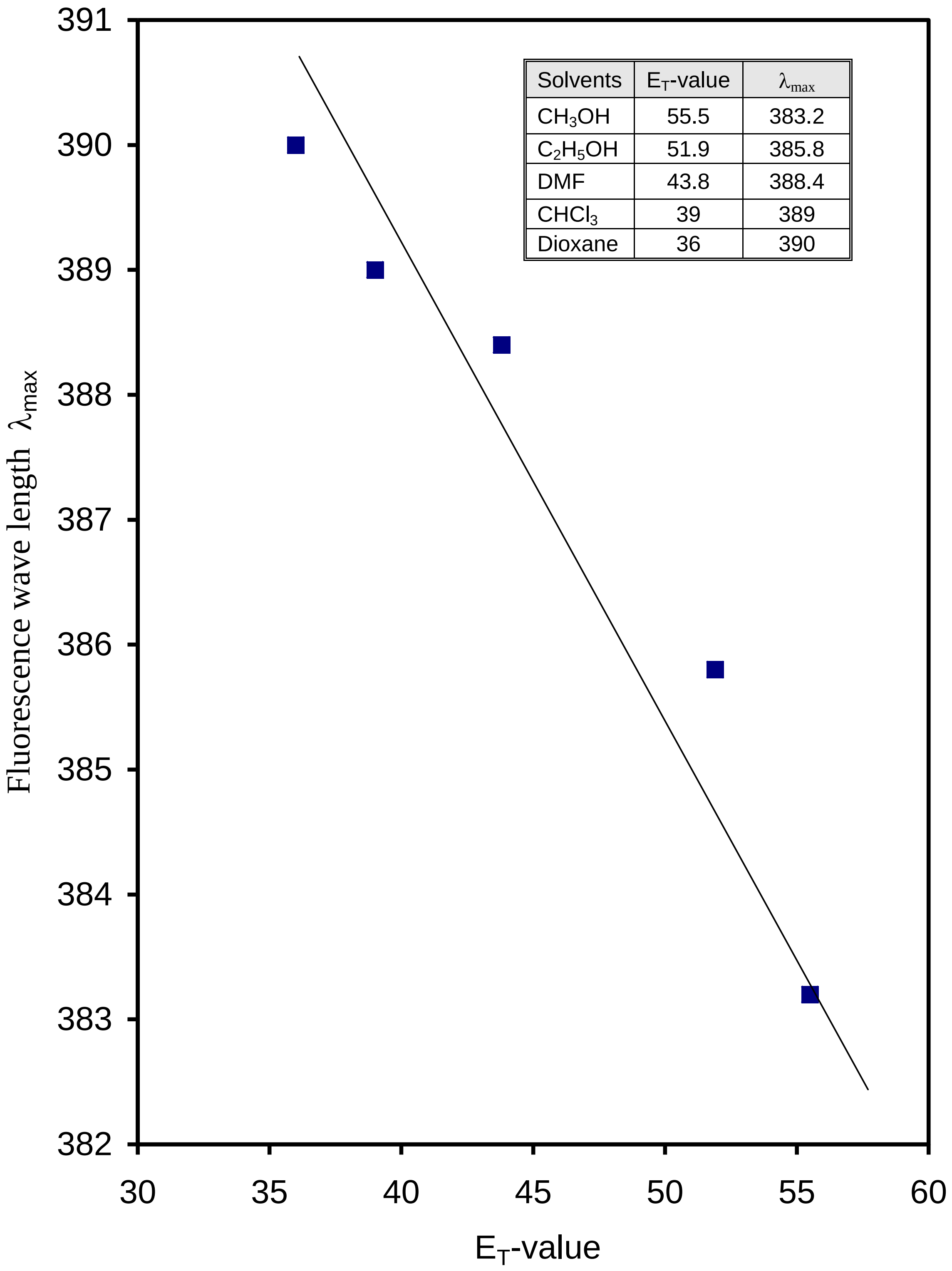
Table (5): Absorption and fluorescence spectra data of dye II :

Solvent	λ_{amax}	λ_{Fmax}	α	β	π	A_{max}	Peak area	ϕ_F
H_2O	324	390.2	1.17	0.18	1.09	0.095	490907.0	0.151
Methanol	325	383.2	0.93	0.62	0.60	0.089	199140.4	0.065
Glycerol	331	385.8	-	-	-	0.040	203253.2	0.148
Ethanol	323	385.8	0.83	0.77	0.54	0.091	164907.9	0.052
Chloroform	327	389.0	-	-	-	0.086	172714.6	0.058
Acetonitril	322	380.6	0.19	0.31	0.75	0.082	174624.5	0.062
DCE	327	384.6	0.00	0.00	0.81	0.076	138485.2	0.053
Dioxane	322	390.0	0.00	0.37	0.55	0.081	141513.3	0.051
DMF	331	388.4	0.00	0.69	0.88	0.070	121314.6	0.050

Anthracene in ethanol has been taken as a fluorescence standard. The quantum yield = 0.27 ± 0.036. absorbance of anthracene at 323 nm = 0.036 and peak area = 332353.5.

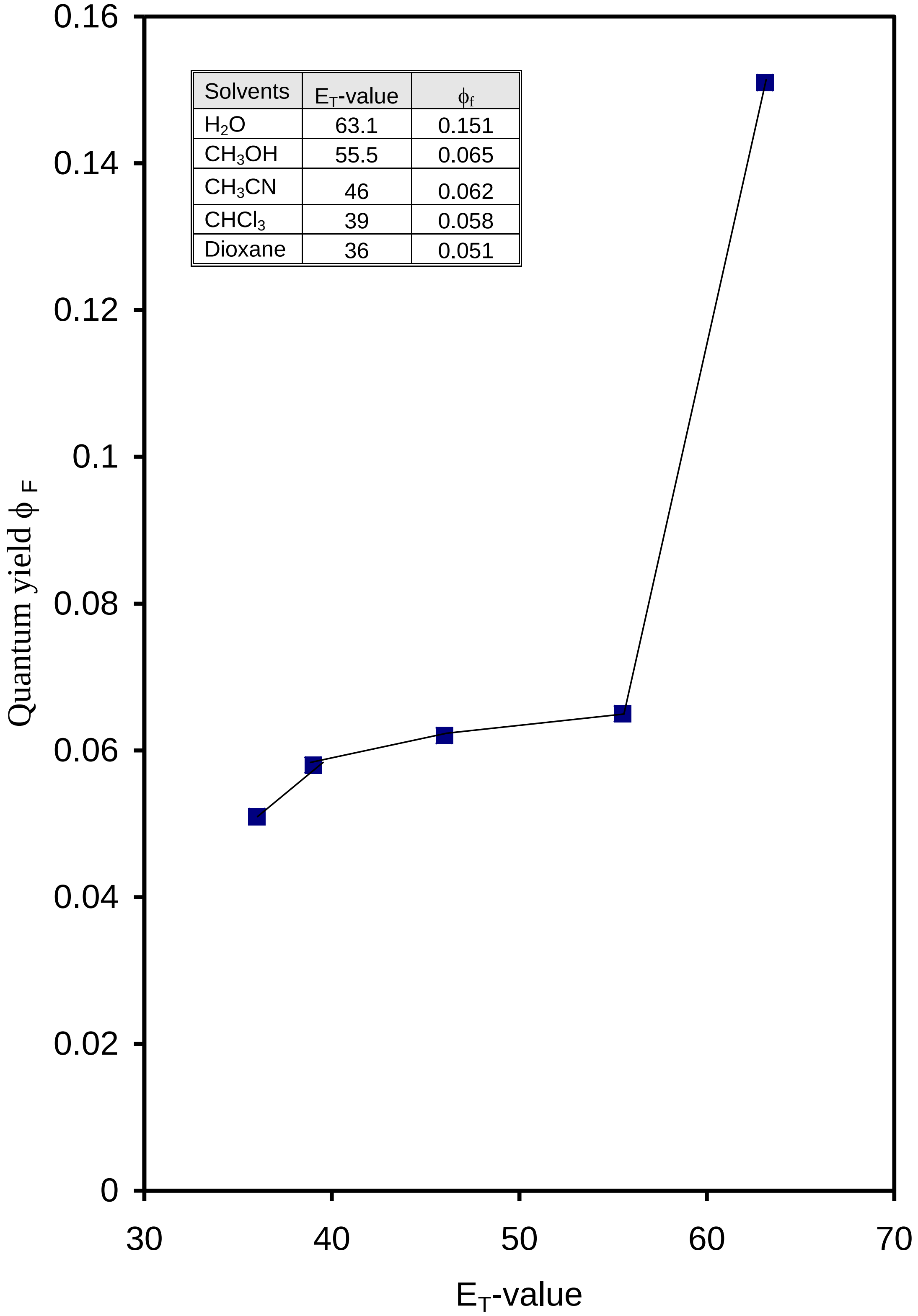
Table (6): Spectral data of dye II in different solvents:

Solvent	α	β	π	E_T	$\lambda_{a\ max}$	$\lambda_{f\ max}$	$\bar{\nu}_A$	$\bar{\nu}_F$	$\Delta\bar{\nu} = \bar{\nu}_A - \bar{\nu}_F$	$\varepsilon \times 10^4$
H_2O	1.17	0.18	1.09	63.1	324	390.2	30864	25627	5237	475
MeOH	0.93	0.62	0.60	55.5	325	383.2	30769	26096	4673	445
EtOH	0.83	0.77	0.54	51.9	323	385.8	30959	25920	5039	455
Glycerol	-	-	-	-	331	385.8	30211	25920	4291	200
MeCN	0.19	0.31	0.75	46	322	380.6	31055	26274	4781	410
DMF	0.00	0.69	0.88	43.8	331	388.4	30211	25746	4465	350
$CHCl_3$	-	-	-	39	327	389	30581	25706	4875	430
Dioxane	0.00	0.37	0.55	36	322	390.0	31055	25641	5414	405
DCE	0.00	0.00	0.81		327	384.6	30581	26001	4580	380



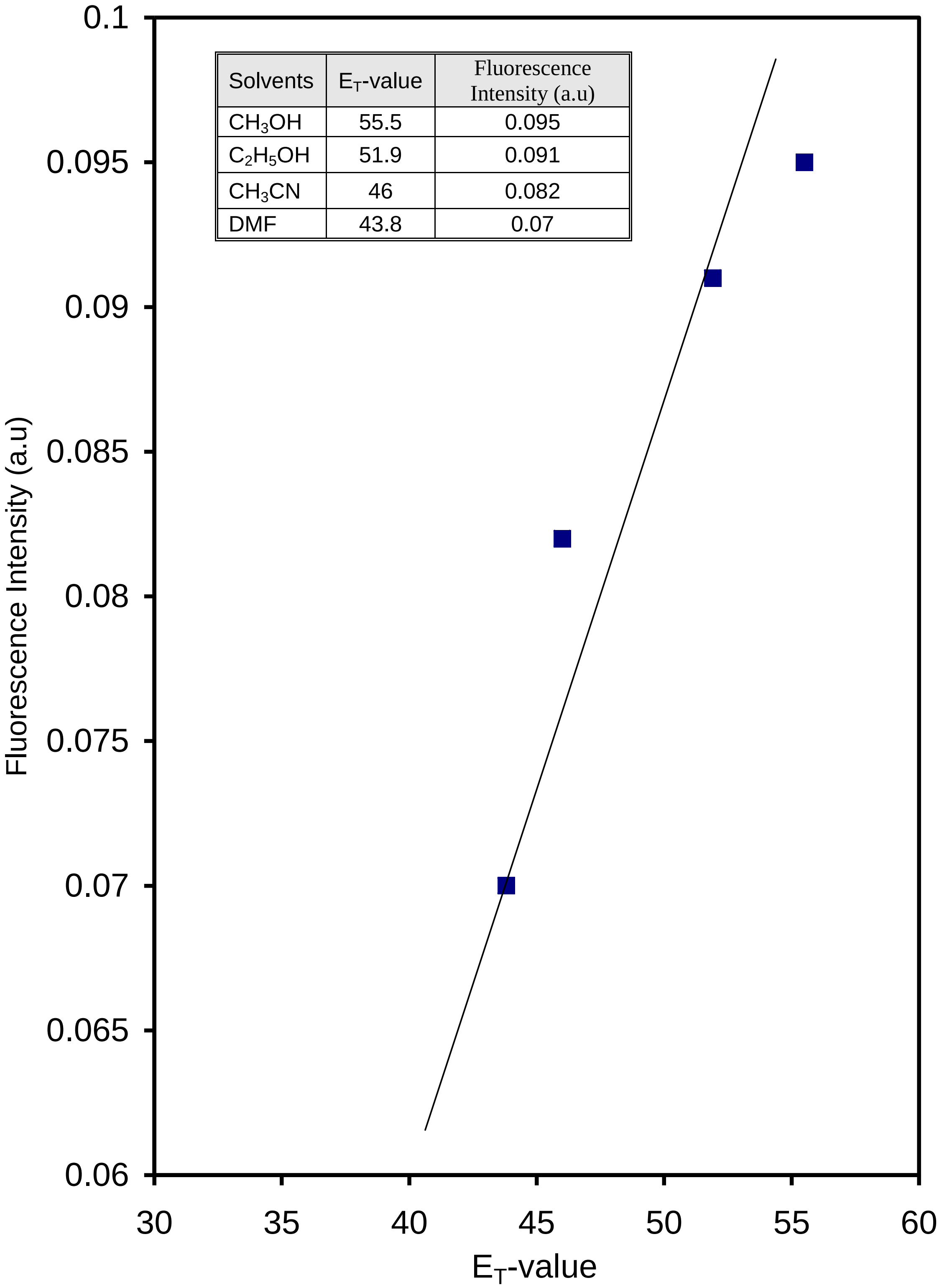
Solvents	E_T-value	λ_{max}
CH_3OH	55.5	383.2
C_2H_5OH	51.9	385.8
DMF	43.8	388.4
$CHCl_3$	39	389
Dioxane	36	390

Fig. (30): Relationship between fluorescence wavelength λ_f and E_T-value of the solvents for dye II.



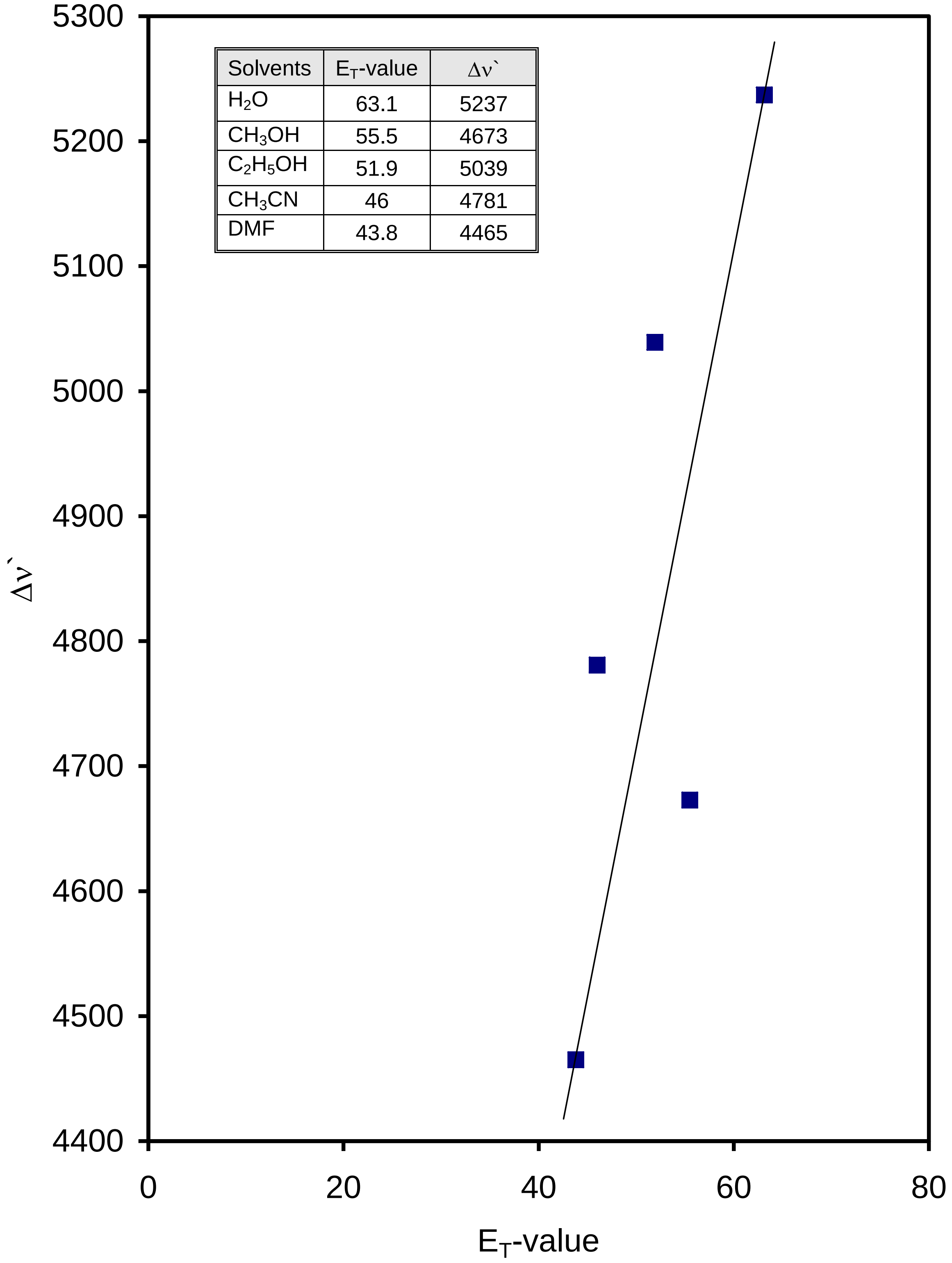
Solvents	E_T-value	ϕ_f
H_2O	63.1	0.151
CH_3OH	55.5	0.065
CH_3CN	46	0.062
$CHCl_3$	39	0.058
Dioxane	36	0.051

Fig. (31): Relationship between quantum yield ϕ_f and E_T-value of the solvents for dye II.



Solvents	E_T-value	Fluorescence Intensity (a.u)
CH_3OH	55.5	0.095
C_2H_5OH	51.9	0.091
CH_3CN	46	0.082
DMF	43.8	0.07

Fig. (32): Relationship between fluorescence intensity and E_T-value of the solvents for dye II.



Solvents	E_T-value	Δν`
H_2O	63.1	5237
CH_3OH	55.5	4673
C_2H_5OH	51.9	5039
CH_3CN	46	4781
DMF	43.8	4465

Fig. (33): Relationship between band width Δν` and E_T-value of the solvents for dye II.

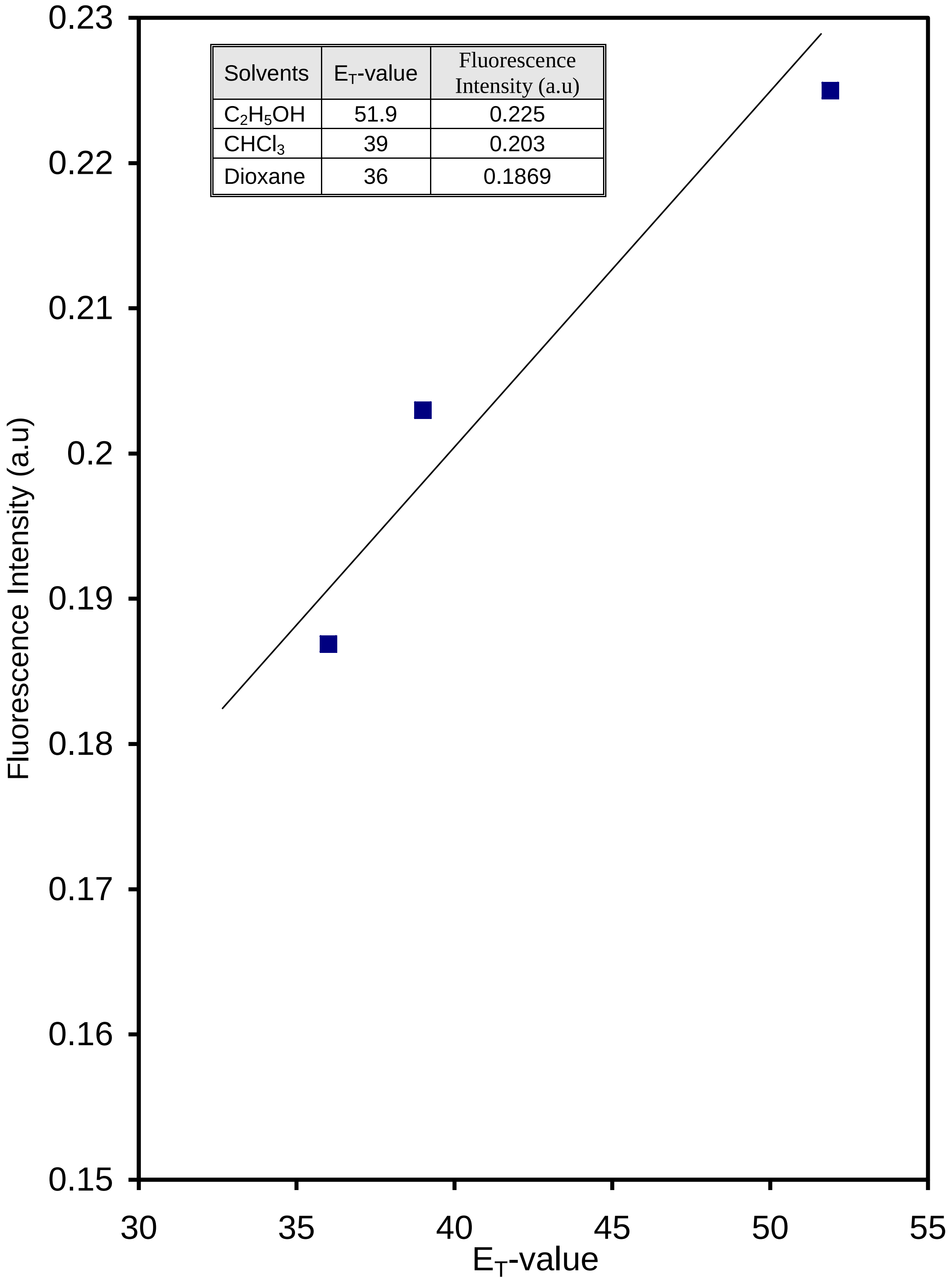
Table (7): Absorption and fluorescence spectral data for dye IV_b:

Solvent	$\lambda_{a\ max}$	$\lambda_{F\ max}$	α	β	π	A_{max}	Peak area	ϕ_F
H_2O	327	454.0	1.17	0.18	1.09	0.219	14765.05	0.088
Methanol	325	388.4	0.93	0.62	0.60	0.220	6395.06	0.038
Ethanol	327	390.0	0.83	0.77	0.54	0.225	5888.65	0.034
DMF	326	445.6	0.00	0.69	0.88	0.183	5399.86	0.038
Glycerol	335	396.0	-	-	-	0.052	3563.23	0.090
DCE	324	386.4	0.00	0.00	0.81	0.221	3734.73	0.022
Acetonitril	325	463.2	0.19	0.31	0.75	0.185	4160.12	0.029
Cholorform	326	386.2	-	-	-	0.202	4205.17	0.027
Dioxane	323	436.0	0.00	0.37	0.55	0.192	3479.92	0.022

Anthracene in ethanol has been taken as a fluorescence standard. The quantum yield = 0.27 ± 0.03 absorbance at 327 nm = 0.031 and peak area= 6368.56

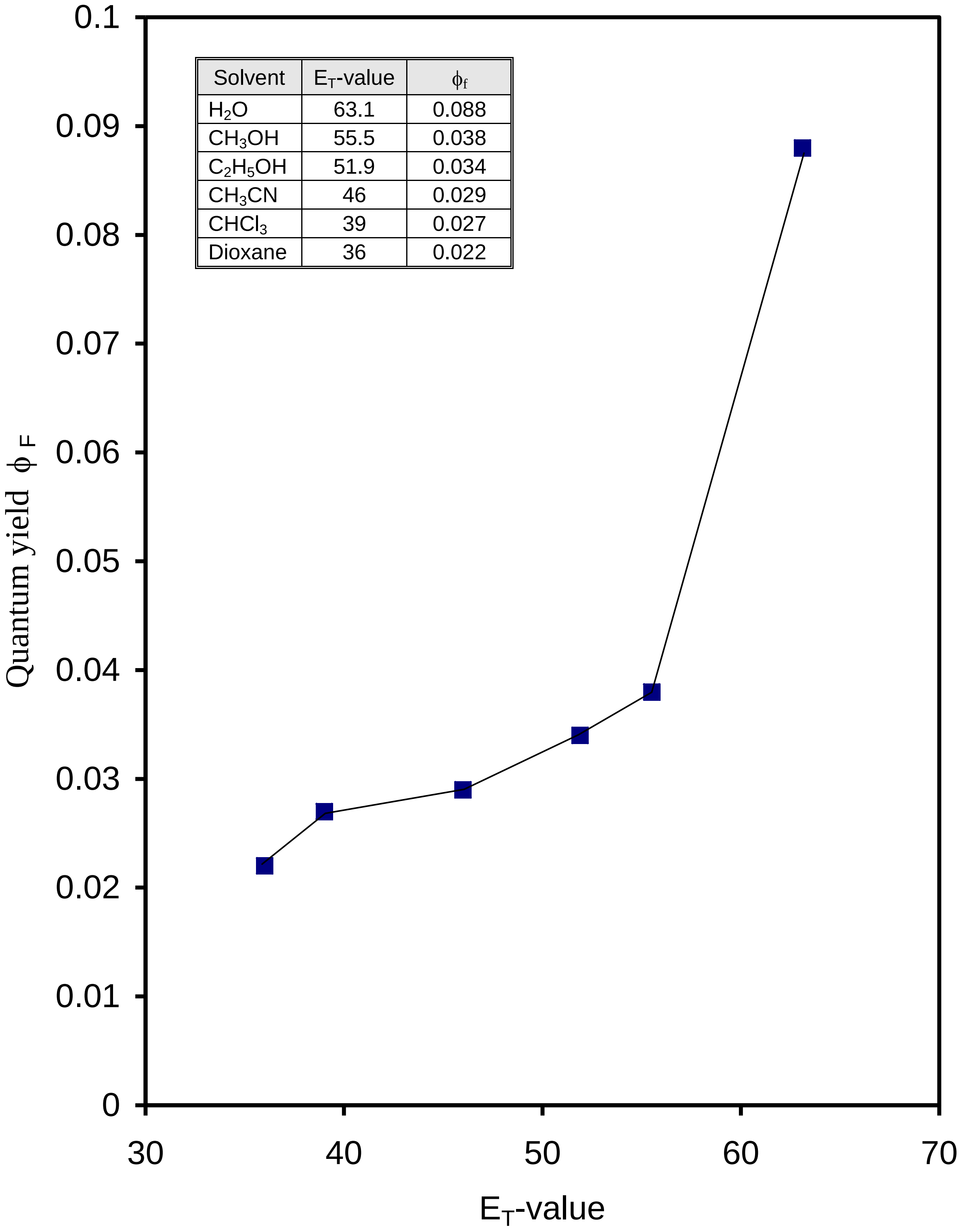
(Table 8): Spectral data of dye IV_b in different solvents:

Solvent	α	β	π	E_T	$\lambda_{a\ max}$	$\lambda_{f\ max}$	$\bar{\nu}_A$	$\bar{\nu}_F$	$\Delta\bar{\nu} = \bar{\nu}_A - \bar{\nu}_F$	$\varepsilon \times 10^4$
H_2O	1.17	0.18	1.09	63.1	327	454	30581	22026	8555	1095
MeOH	0.93	0.62	0.60	55.5	325	388.4	30769	25746	5023	1100
EtOH	0.83	0.77	0.54	51.9	327	390	30581	25641	4940	1125
Glycerol	-	-	-	-	335	396	29850	25252	4598	260
MeCN	0.19	0.31	0.75	46	325	463.2	30769	21588	9181	925
DMF	0.00	0.69	0.88	43.8	326	445.6	30674	22441	8233	915
CHCl3	-	-	-	39	326	386.2	30674	25893	4781	1015
Dioxane	0.00	0.37	0.55	36	323	436	30959	22935	8024	995
DCE	0.00	0.00	0.81	-	324	386.4	30864	25879	4985	1105



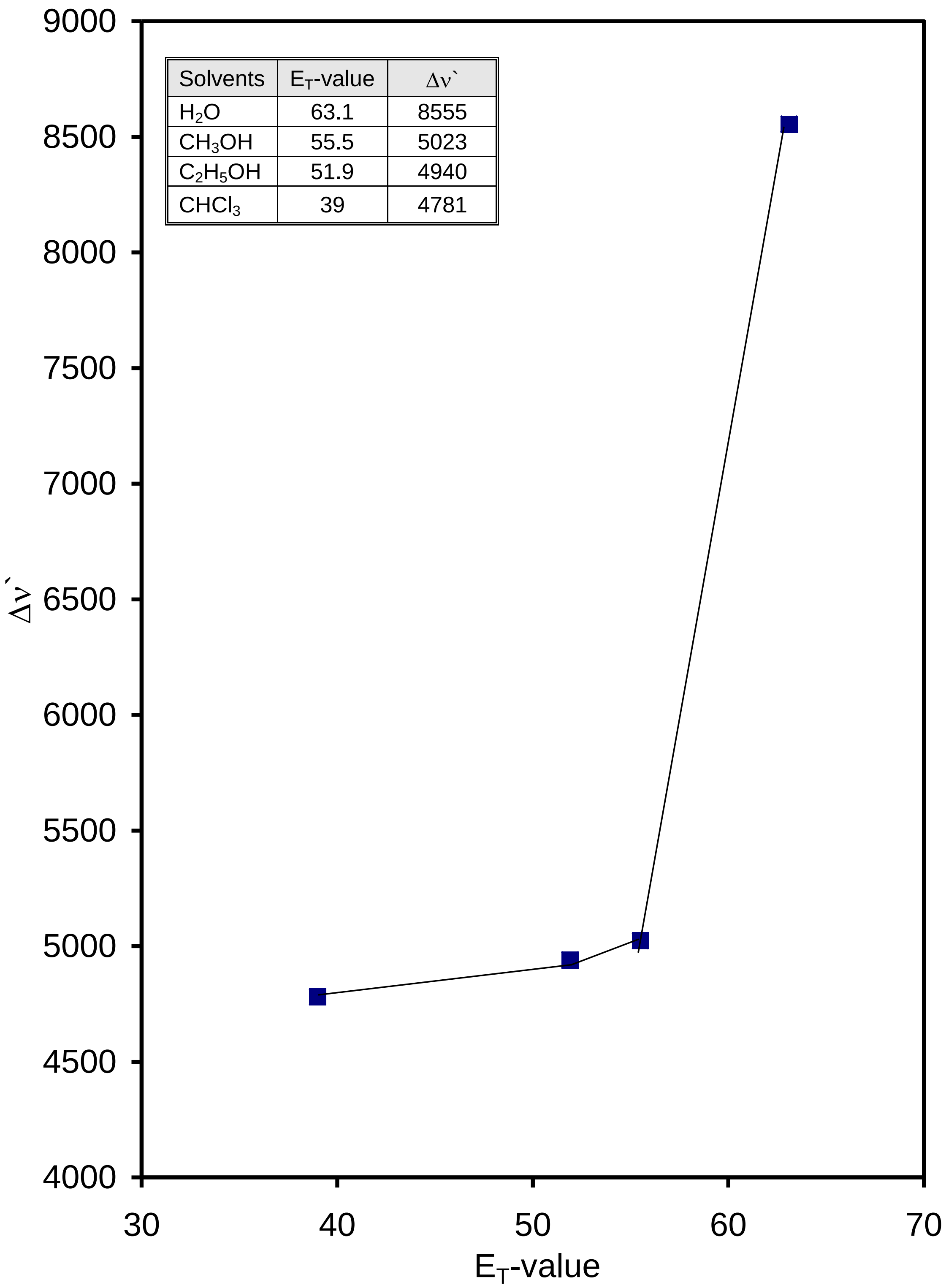
Solvents	E_T-value	Fluorescence Intensity (a.u)
C_2H_5OH	51.9	0.225
$CHCl_3$	39	0.203
Dioxane	36	0.1869

Fig. (36): Relationship between fluorescence intensity (a.u) and E_T-value of the solvents for dye IV_b.



Solvent	E_T-value	ϕ_f
H_2O	63.1	0.088
CH_3OH	55.5	0.038
C_2H_5OH	51.9	0.034
CH_3CN	46	0.029
$CHCl_3$	39	0.027
Dioxane	36	0.022

Fig. (37): Relationship between fluorescence quantum yield ϕ_f and E_T-value of the solvents for dye IV_b.



Solvents	E_T-value	Δν\`
H_2O	63.1	8555
CH_3OH	55.5	5023
C_2H_5OH	51.9	4940
$CHCl_3$	39	4781

Fig. (38): Relationship between Δν\` and E_T-value of the solvents for dye IV_b.

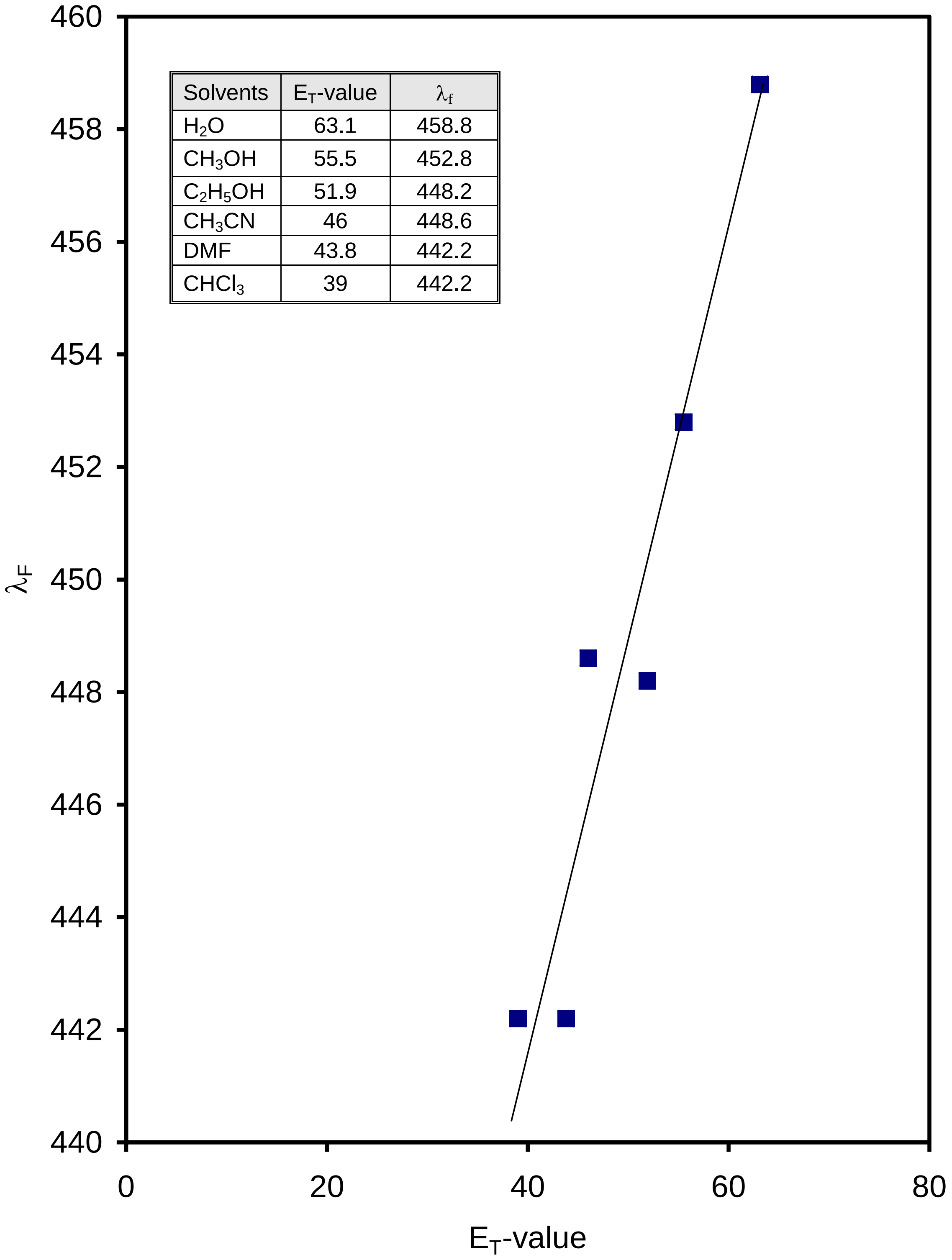
Table (9): Absorption and fluorescence spectral data for dye IV_c:

Solvent	$\lambda_{a\ max}$	$\lambda_{F\ max}$	α	β	π	A_{max}	Peak area	ϕ_F
H_2O	369	458.8	1.17	0.18	1.09	0.200	97613.26	0.012
Glycerol	372	448.0	-	-	-	0.128	99184.76	0.019
Methanol	367	452.8	0.93	0.62	0.60	0.276	91995.85	0.008
Acetonitril	367	448.6	0.19	0.31	0.75	0.256	87000.58	0.008
Ethanol	367	448.2	0.83	0.77	0.54	0.260	87618.59	0.008
DMF	369	442.2	0.00	0.69	0.88	0.191	82307.77	0.010
Chloroform	365	442.2	-	-	-	0.246	82407.67	0.008
Dioxane	366	415.0	0.00	0.37	0.55	0.258	81649.38	0.007
DCE	366	459.8	0.00	0.00	0.81	0.246	80342.91	0.008

Anthracene in ethanol has been taken as a fluorescence standard. The quantum yield = 0.27 ± 0.036. absorbance at 363nm = 0.03 and peak area= 324448.77.

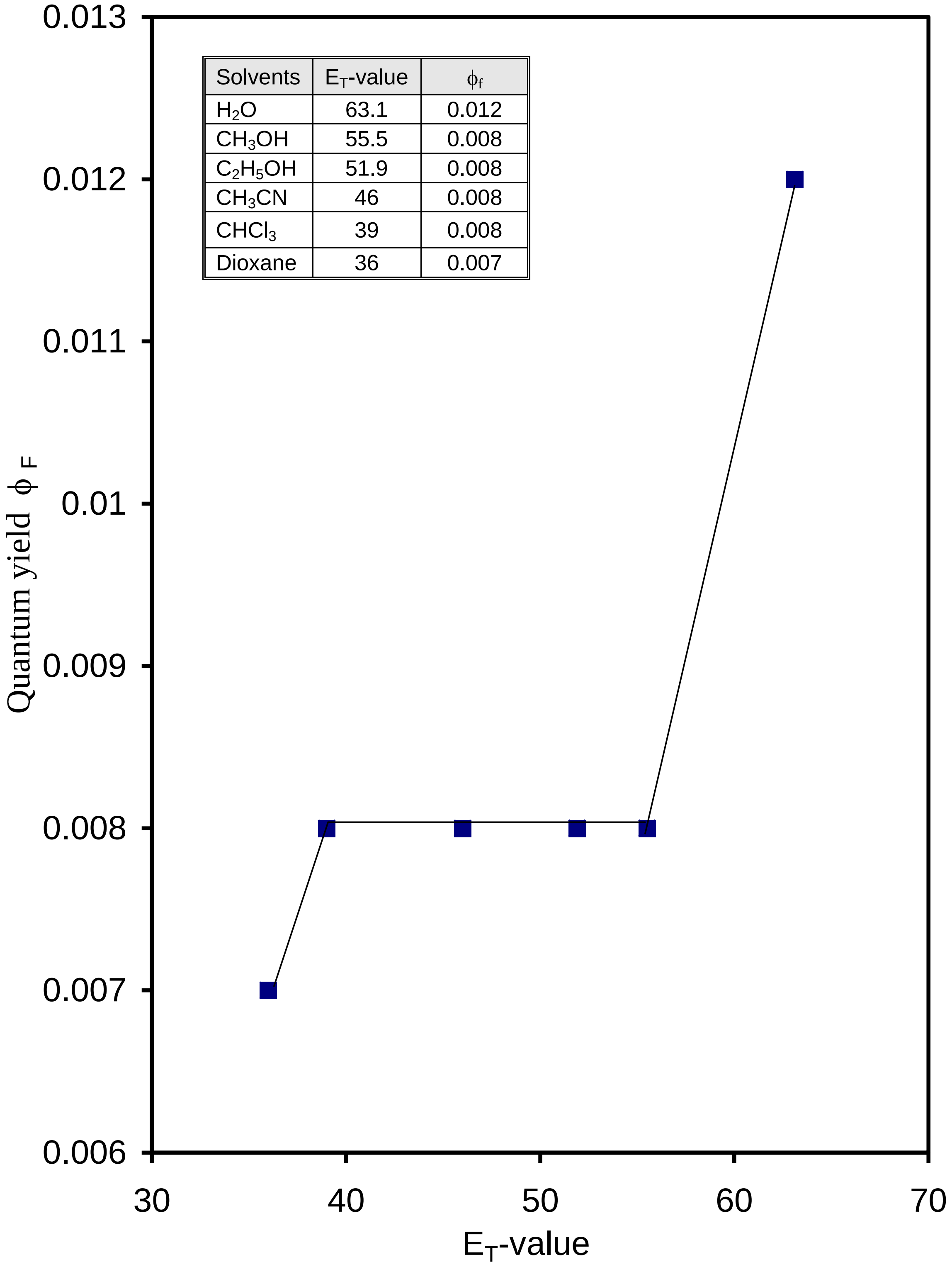
Table (10): Spectral data of dye IV_c in different solvents :

Solvent	α	β	π	E_T	λa^{max}	λf^{max}	$\bar{\nu}_A$	$\bar{\nu}_F$	$\Delta\bar{\nu} = \bar{\nu}_A - \bar{\nu}_F$	**ε x 10^4**
H_2O	1.17	0.18	1.09	63.1	369	458.8	27100	21795	5305	1000
MeOH	0.93	0.62	0.60	55.5	367	452.8	27247	22084	5163	1380
EtOH	0.83	0.77	0.54	51.9	367	448.2	27247	22311	4936	1300
Glycerol	-	-	-	-	372	448	26881	22321	4560	640
MeCN	0.19	0.31	0.71	46	367	448.6	27247	22291	4956	1280
DMF	0.00	0.69	0.88	43.8	369	442.2	27100	22614	4486	955
$CHCl_3$	-	-	-	39	365	442.2	27397	22614	4783	1230
Dioxane	0.00	0.37	0.55	36	366	415	27322	24096	3226	1290
DCE	0.00	0.00	0.81	-	366	459.8	27322	21748	5574	1230



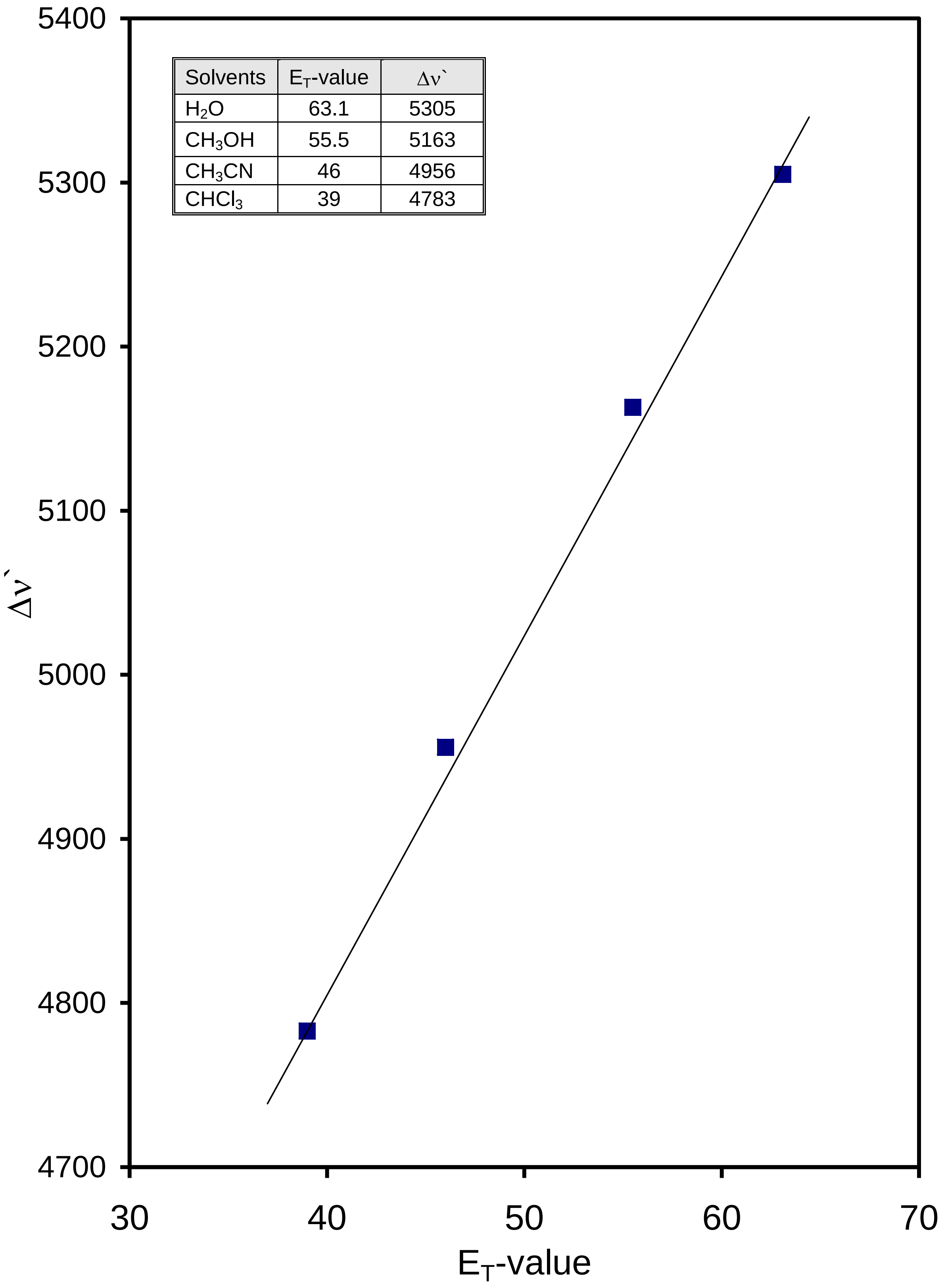
Solvents	E_T-value	λ_f
H_2O	63.1	458.8
CH_3OH	55.5	452.8
C_2H_5OH	51.9	448.2
CH_3CN	46	448.6
DMF	43.8	442.2
$CHCl_3$	39	442.2

Fig. (40): Relationship between fluorescence wavelength λ_f and E_T-value of the solvents for dye IVc.



Solvents	E_T-value	ϕ_f
H_2O	63.1	0.012
CH_3OH	55.5	0.008
C_2H_5OH	51.9	0.008
CH_3CN	46	0.008
$CHCl_3$	39	0.008
Dioxane	36	0.007

Fig. (41): Relationship between fluorescence quantum yield ϕ_f and E_T-value of the solvents for dye IV_c.



Solvents	E_T-value	Δν\`
H_2O	63.1	5305
CH_3OH	55.5	5163
CH_3CN	46	4956
$CHCl_3$	39	4783

Fig. (42): Relationship between Δν\` and E_T-value of the solvents for dye IVc.

Effect of temperature on the absorption and emission spectra of dye (IV_b):

The effect of temp. on the absorption and emission spectra of dye (IV) was studied using the Williams, Landel and ferry equation (1).

$$\log\left(\frac{\eta}{\eta g}\right) = \frac{C_{1,g}(T - Tg)}{C_{2,g}(T - Tg)} \qquad \text{.......} (1)$$

Where

The viscosity is referred to the quantity η_g, i.e., to the value of viscosity at the glass- transition temperature (Tg), and the temperature is compared with the glass temperature since the argument in eq. (1) is the difference (T- Tg). The constants $C_{1,g}$ and $C_{2,g}$ are expressed in terms of the thermal expansion coefficients, and these constants have the following values: $C_{1,g}$ = -17.44 and $C_{2,g}$ = 51.6. and the glass-transition temperature Tg is chosen as the reference temperature. It is ordinarily assumed that the WLF equation is valid for temperature from the glass- transition. Temperature Tg to (Tg + 100 ^{o}C).

The fluorescence intensity, ϕ_f and absorption spectra of dye (IV) was identified as a function of viscosity of glycerol, where viscosity was calculated from WLF equation (1) since T_g= 190K^o and $\eta_g = 6.5 \times 10^{14}$CP.

2.4. The effect of temperature on the absorption spectra of dye IV_b.

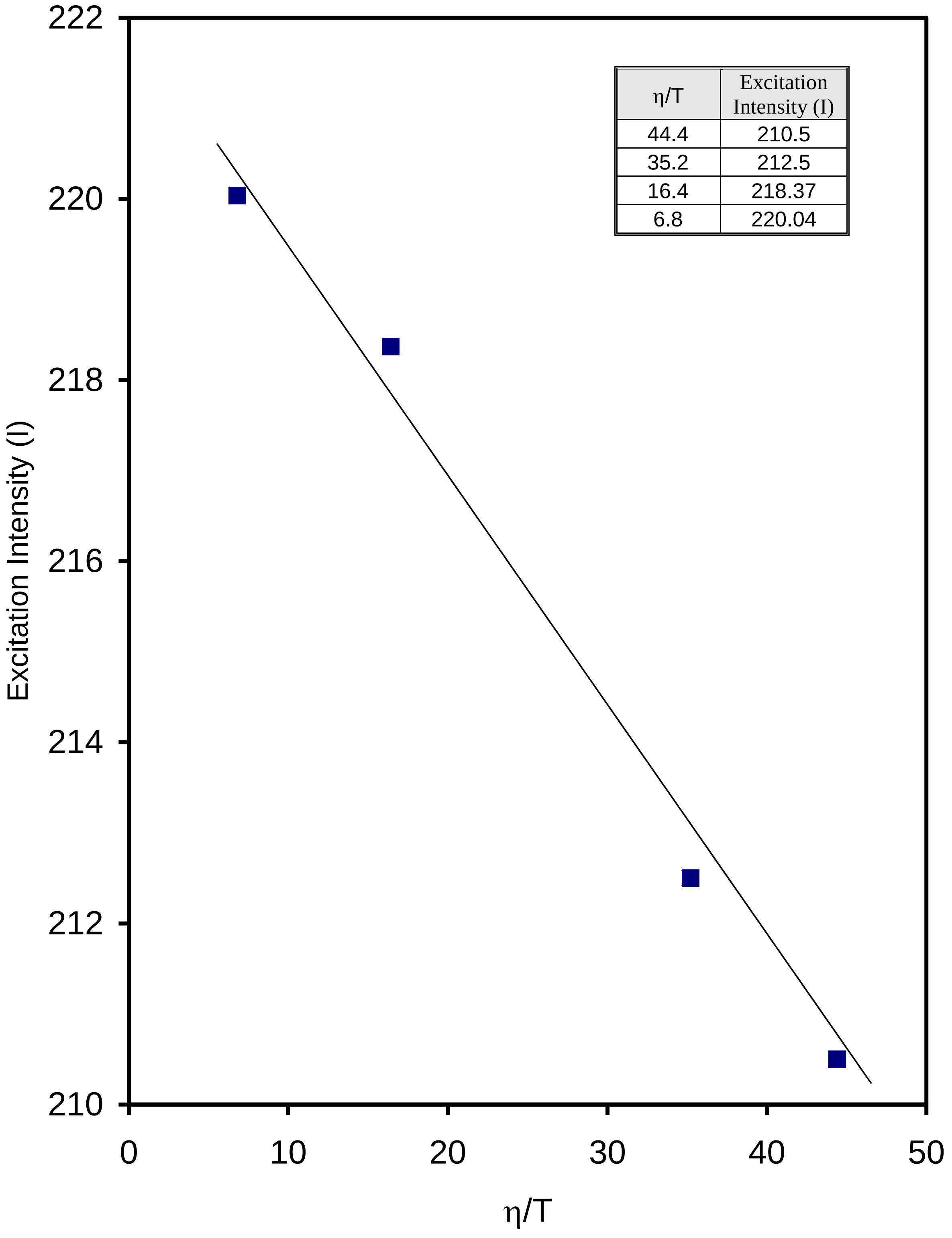
The viscosity effect on the excitation spectra of sample dye IV_b was shown in Figs. (43, 44). The fit linear relationship between excitation intensity and η/T is demonstrated at Figs. (45, 46). The data was tabulated in Table (11) which show that, the intensity of the absorption spectra was increased as the temperature increased from T = 273 K^o to T= 294 K^o then it was noticed that the intensity of absorption spectra was decreased as temperature increased from T= 296 K^o to T= 333 K^o.

This phenomena can be explained as ‘ complex process’ in which two opposed behviours can be observed. The phenomena may be due to that, the WLF equation (1) is valid for temperatures from glass (Tg = 190Ko) to (Tg + 100 ^oC). Or this effect is usually associated with specific interactions in ground state S_o. From the above we can conclude that, the WLF equation may be not valid on dye IV_b when temperature become higher than T= 294K^o.

Table (11): Effect of temperature on the excitation intensity and viscosity of glycerol.

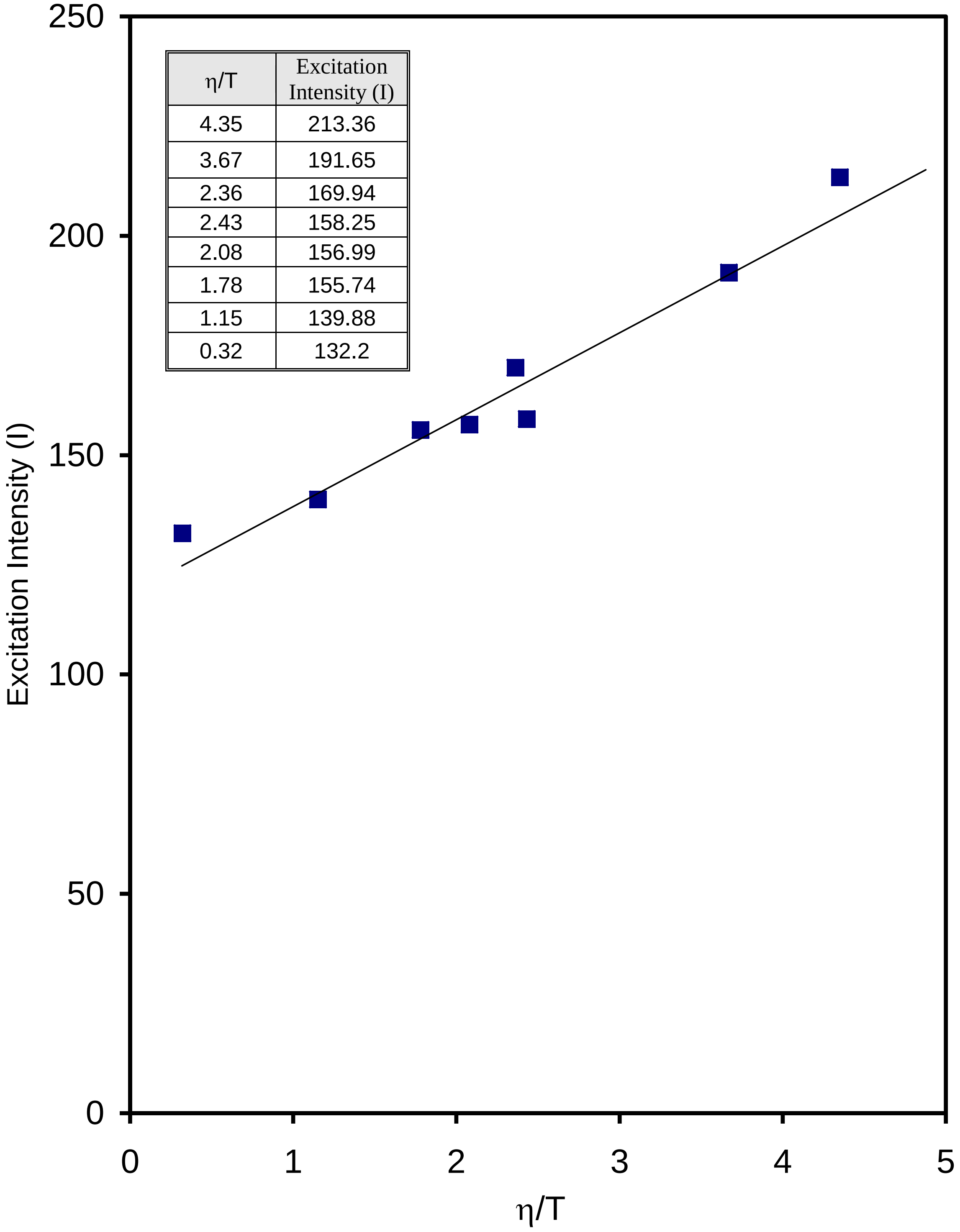
T (K^o)	η (CP)	η/T (CP/k)	Excitation intensity (a.u).
273	12115.6	44.4	210.50
275	9675.6	35.2	212.50
282	4626.8	16.4	218.37
291	1979.4	6.8	220.04
294	1524.4	5.18	227.56
296	1287.9	4.35	213.36
298	1092.6	3.67	191.65
301	860.4	2.86	169.94
303	737.2	2.43	158.25
305	634	2.08	156.66
307	547.2	1.78	155.74
313	359.1	1.15	139.88
333	106.3	0.32	132.20

Viscosity was calculated from WLF, equation, Since, $T_g = 190K^o$ and $\eta_g = 6.5 \times 10^{14}$CP.



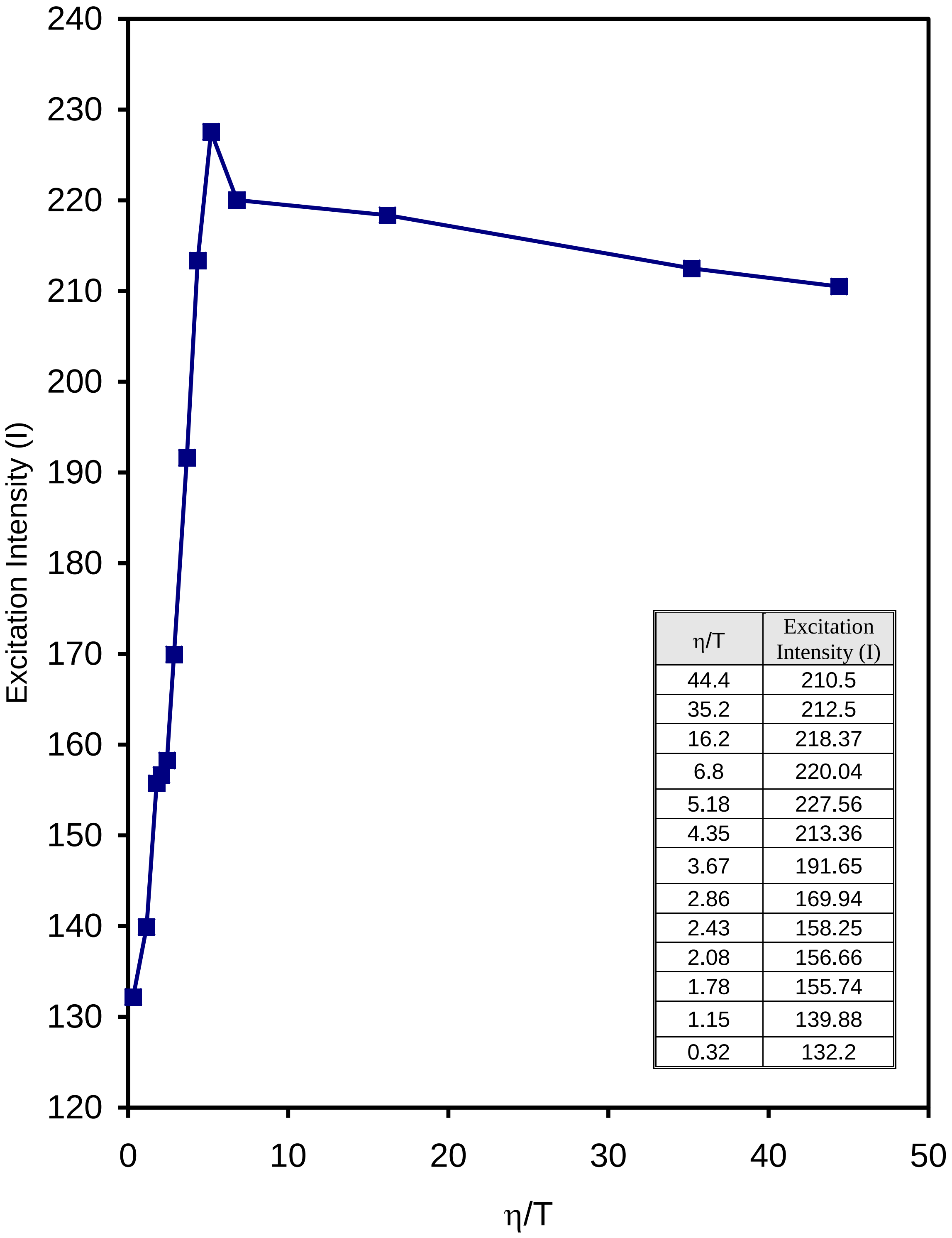
η/T	Excitation Intensity (I)
44.4	210.5
35.2	212.5
16.4	218.37
6.8	220.04

Fig. (45): Fit linear relationship between excitation intensity (I) of dye IV_b and η/T.



η/T	Excitation Intensity (I)
4.35	213.36
3.67	191.65
2.36	169.94
2.43	158.25
2.08	156.99
1.78	155.74
1.15	139.88
0.32	132.2

Fig. (46): Fit linear relationship between excitation intensity (I) of dye IV_b and η/T.



η/T	Excitation Intensity (I)
44.4	210.5
35.2	212.5
16.2	218.37
6.8	220.04
5.18	227.56
4.35	213.36
3.67	191.65
2.86	169.94
2.43	158.25
2.08	156.66
1.78	155.74
1.15	139.88
0.32	132.2

Fig. (47): Fit linear relationship between excitation intensity (I) of dye IV_b and η/T.

2.5. The effect of temperature on the emission spectra of dye IV_b:

The effect of temperature on the emission spectrum of dye IV_b was also explored using of 1.05 x 10^{-5}M solution of the dye in glycerol. Where fluorescence intensity and fluorescence quantum efficiency ϕ_f as a function of viscosity of glycerol was reported using WLF equation (Table 12). It was found that both of fluoresence intensity and fluoresence quantum efficiency ϕ_f were increased as temperature increased from T = 273 K^o to T= 294 K^o this may be due to thermal population of the excited state, but it was noticed that both of fluorescence intensity and fluorescence quantum efficiency ϕ_f were decreased as temperature increased from T= 296 K^o to T= 333 K^o. This is usually encountered in many fluorophores and is attributed to the role of thermal energy in enhancing internal conversion and the other radiationless deactivation pathways at the expense of fluorescence (Fig. 48-56).

The master viscosity-temperature curve for sample dye IV_b Fig. (57) according to WLF equation which show that, the viscosity of the solution of the dye IV_b in glycerol were decreased as the temperature increased so this proved that the increase in temperature lead to decrease the rigidity of the medium (viscosity) which make the molecules in excited state loss its energy in collusion with each other as thermal energy, or as other radiationless deactivation process

Figure (58) showed that, the dependence of the viscosity of solution of dye IV_b on the temperature.

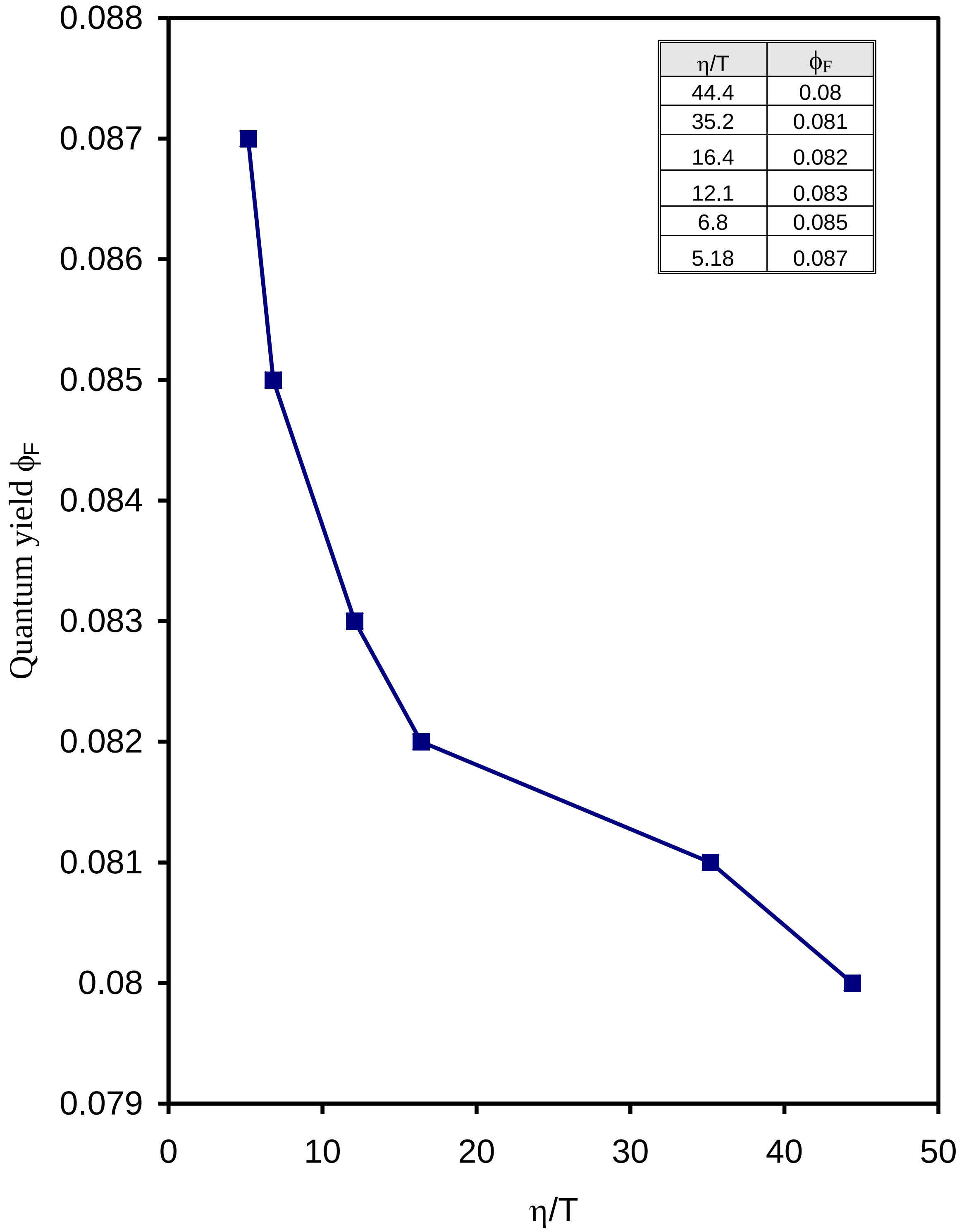
Finally we can concludes that, the study of the fluorescence intensity and fluorescence quantum efficiency ϕ_f of dye IV_b as a function of viscosity in glycerol over wide range of temperature T = 273K^o to T = 333= K^o. can be explained as (complex process).

Table (12): Effect of temperature on the fluorescence intensity and viscosity of glycerol for dye IV_b.

T [K^o]	η [cP]	η / T [cP/K]	Fluorescence intensity [a.u]	ϕ_f
273	12115.6	44.4	197.7	0.080
275	9675.6	35.2	201.3	0.081
282	4626.8	16.4	204.3	0.082
285	3446.1	12.1	205	0.083
291	1979.4	6.80	211.4	0.085
294	1524.4	5.18	216.9	0.087
296	1287.9	4.35	212.1	0.085
298	1092.6	3.67	191.7	0.077
301	860.4	2.86	183.5	0.074
303	737.2	2.43	165.8	0.067
305	634	2.08	153.1	0.062
307	547.2	1.78	148.8	0.060
313	359.1	1.15	147.6	0.0598
323	189.1	0.59	125.6	0.051
328	140.7	0.43	122.1	0.049
333	106.3	0.32	120.1	0.0487

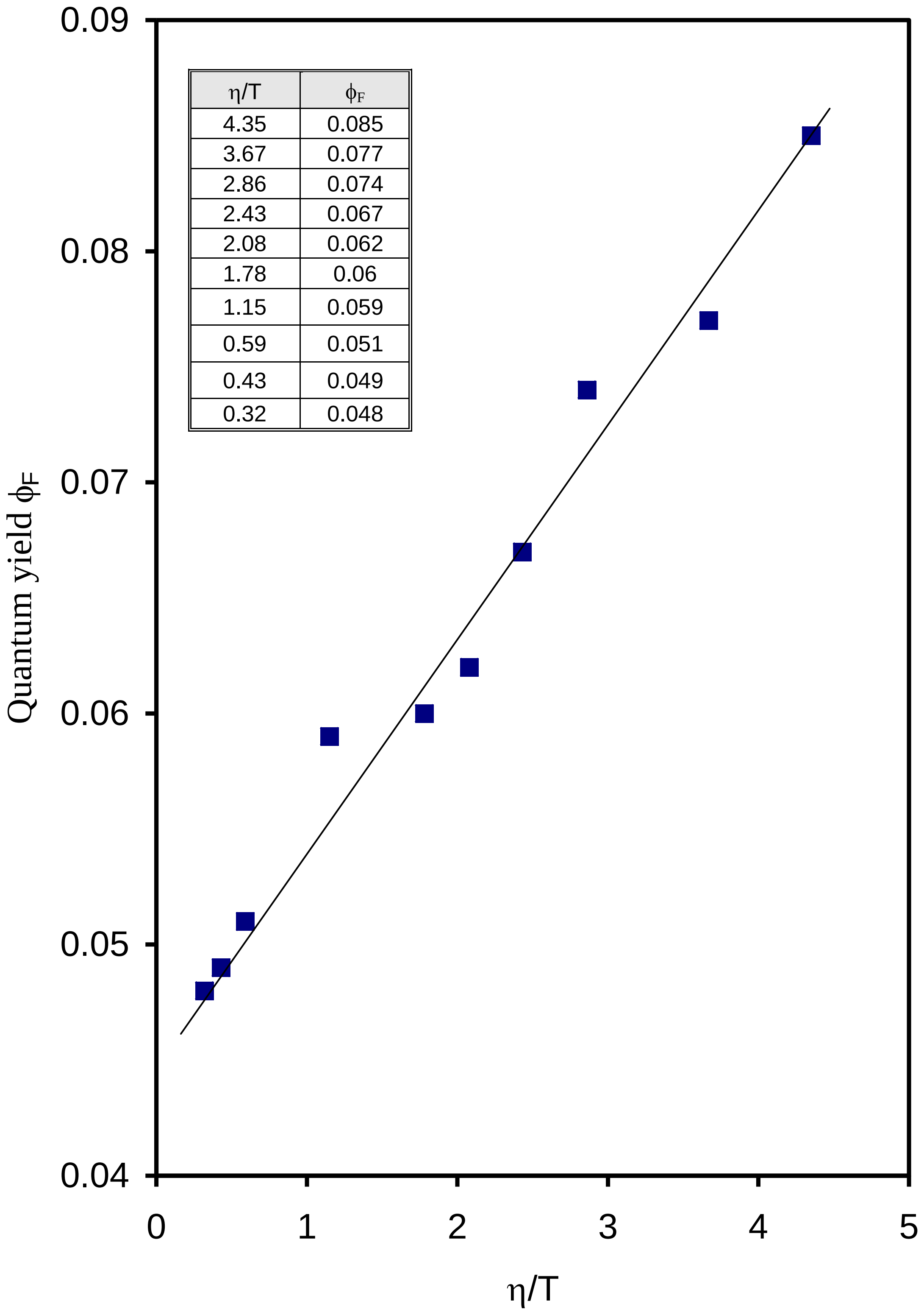
Viscosity was calculated from WLF equation, since Tg = 190 K^o and $\eta_g = 6.5 \times 10^{14}$ cP.

$\log \eta/\eta g = - 17.4 [T-Tg]/ 51.6 [T-Tg]$



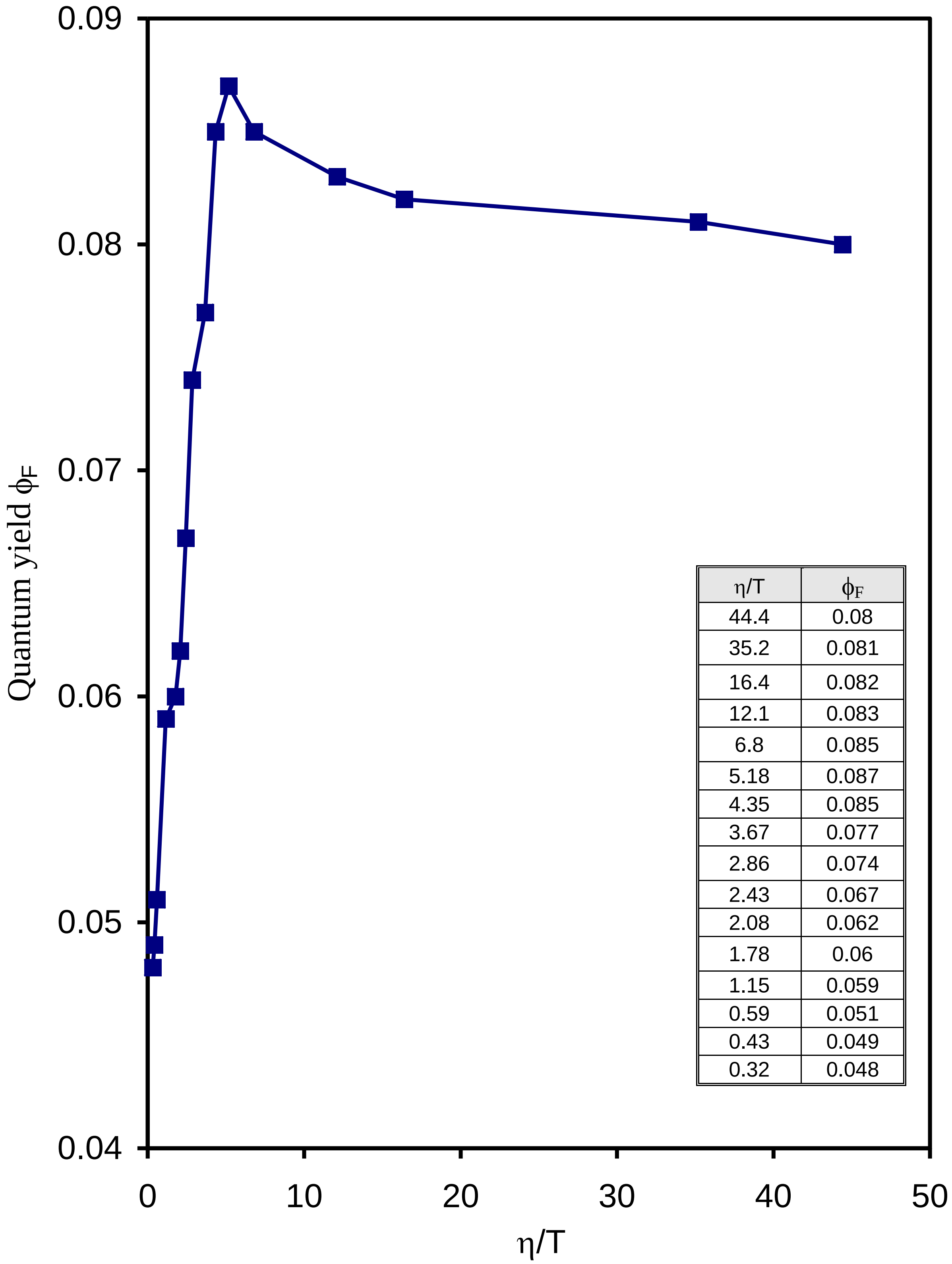
η/T	ϕ_F
44.4	0.08
35.2	0.081
16.4	0.082
12.1	0.083
6.8	0.085
5.18	0.087

Fig. (54): Relationship between fluorescence quantum yield ϕ_f of dye IV_b and η/T.



η/T	ϕ_F
4.35	0.085
3.67	0.077
2.86	0.074
2.43	0.067
2.08	0.062
1.78	0.06
1.15	0.059
0.59	0.051
0.43	0.049
0.32	0.048

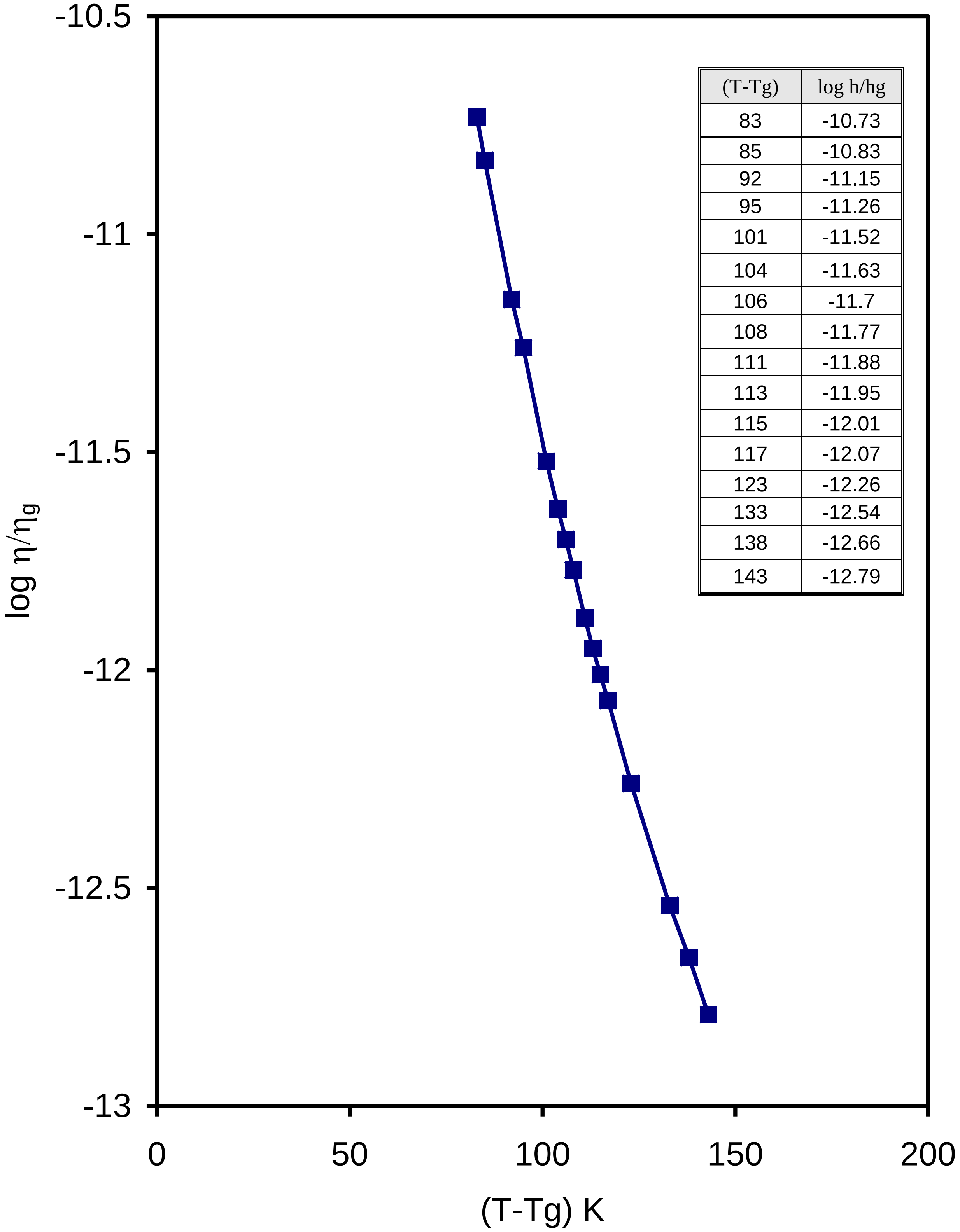
Fig. (55): Relationship between fluorescence quantum yield ϕ of dye IV_b and η/T.



η/T	ϕ_F
44.4	0.08
35.2	0.081
16.4	0.082
12.1	0.083
6.8	0.085
5.18	0.087
4.35	0.085
3.67	0.077
2.86	0.074
2.43	0.067
2.08	0.062
1.78	0.06
1.15	0.059
0.59	0.051
0.43	0.049
0.32	0.048

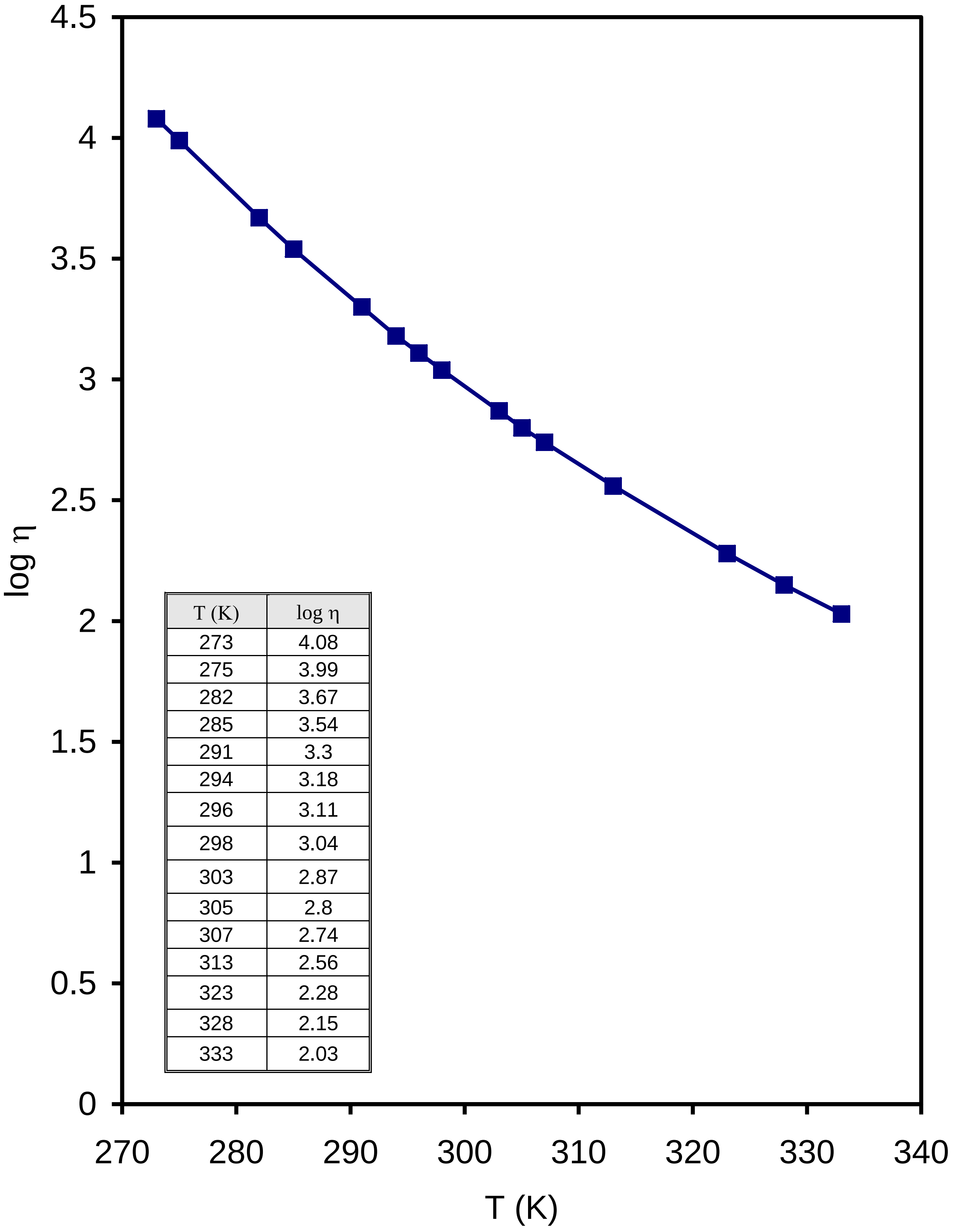
Fig. (56): Relationship between fluorescence quantum yield

ϕ of dye IV_b and η/T.



(T-Tg)	log h/hg
83	-10.73
85	-10.83
92	-11.15
95	-11.26
101	-11.52
104	-11.63
106	-11.7
108	-11.77
111	-11.88
113	-11.95
115	-12.01
117	-12.07
123	-12.26
133	-12.54
138	-12.66
143	-12.79

Fig. (57): Master viscosity-temperature curve for dye IV_b according to the WLF equation.



T (K)	log η
273	4.08
275	3.99
282	3.67
285	3.54
291	3.3
294	3.18
296	3.11
298	3.04
303	2.87
305	2.8
307	2.74
313	2.56
323	2.28
328	2.15
333	2.03

Fig. (58): Temperature dependence of the viscosity of solution of dye IV_b in glycerol.

2.6. Effect of concentration on fluorescence of dye II and dye IV$_b$:

The relationship between the fluorescence intensity of dyes II and IV$_b$ and concentration was described and the verification of beer's lambert law on fluorescence of dyes II and IV$_b$ at different concentrations was proved by plot fluorescence intensities against concentrations.

Where

$I_f = 2.303\ I_o\ \phi_f\ \in bc.$ ………[Beers Lambert law] …..(2)

and

I_f = fluorescence intensity

I_o = intensity of incident light beam

ϕ_f = fluorescence quantum efficiency

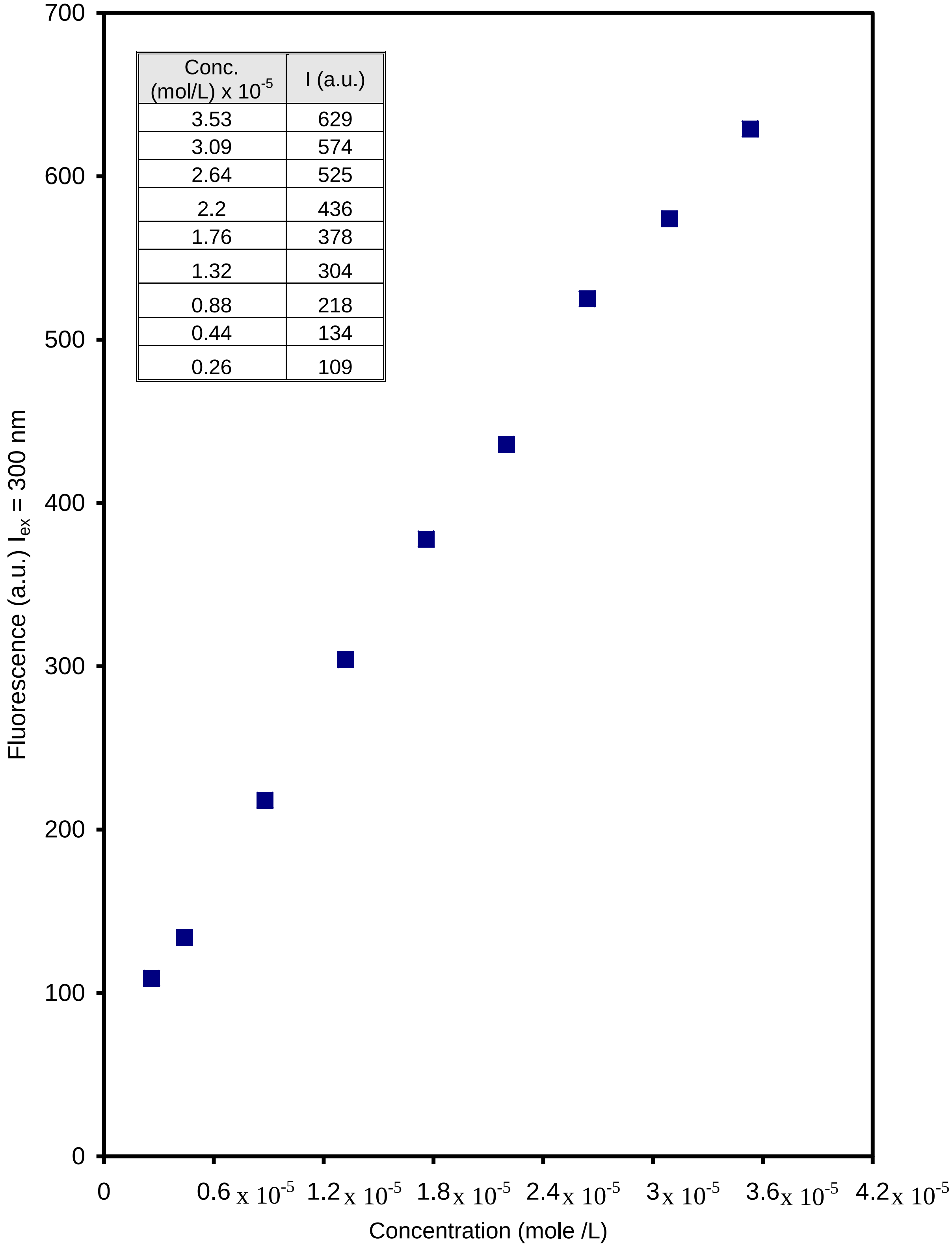
$\in$ = molar absorptivity [1 mole^{-1} cm^{-1}]

b = bath length in cm

c = molar concentration

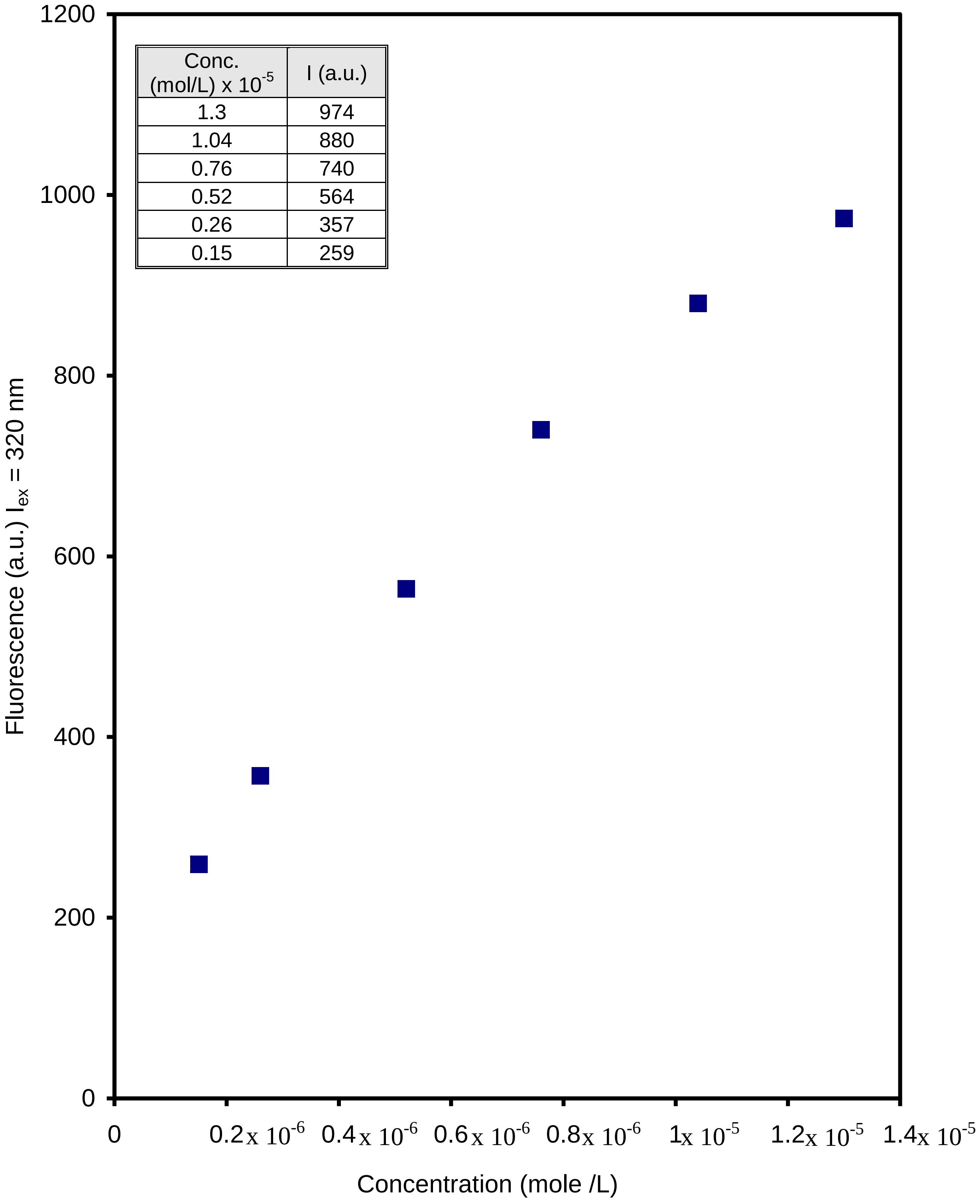
for dye II, it was found that an increase of the concentration from 0.26 x 10^{-5} Mol/L to 3.53 x 10^{-5} Mol/L in aqueous solution resulted in an increased of fluorescence intensities I_f with no significant shifts in λ_{max} emission Fig. (59) also the fluorescence spectra over different concentration show that, no excimer [excited dimer] or higher aggregation formation by increase concentration, also linear relationship between the fluorescence intensity I_f and the concentration i.e. I_f direct preoperational with concentration which obey Beer's Lambert law with slight deviation Fig. (60).

For dye IV$_b$, it was found that on increasing in the concentration from 0.15 x 10^{-5} Mol/L to 1.30 x 10^{-5} Mol/L in aqueous solutions resulted in an increasing of fluorescence intensities with no significant shifts in λ_{max} emission, Fig. (61) show that, no emission band for excimer or higher aggregation in the excited state by increase the concentration. Fig. (62) show that, verification of Beer's Lambert law on the fluorescence spectrum of dye IV_b at different concentrations by plot fluorescence intensity against concentration and proved that I_f direct preoperational with concentration which obey Beer's Lambert law with slight deviation.



Conc. (mol/L) x 10^{-5}	I (a.u.)
3.53	629
3.09	574
2.64	525
2.2	436
1.76	378
1.32	304
0.88	218
0.44	134
0.26	109

Fig. (60): Verification of Beer's Lambert law on the fluorescence spectrum of dye II at different concentrations.



Conc. (mol/L) x 10^{-5}	I (a.u.)
1.3	974
1.04	880
0.76	740
0.52	564
0.26	357
0.15	259

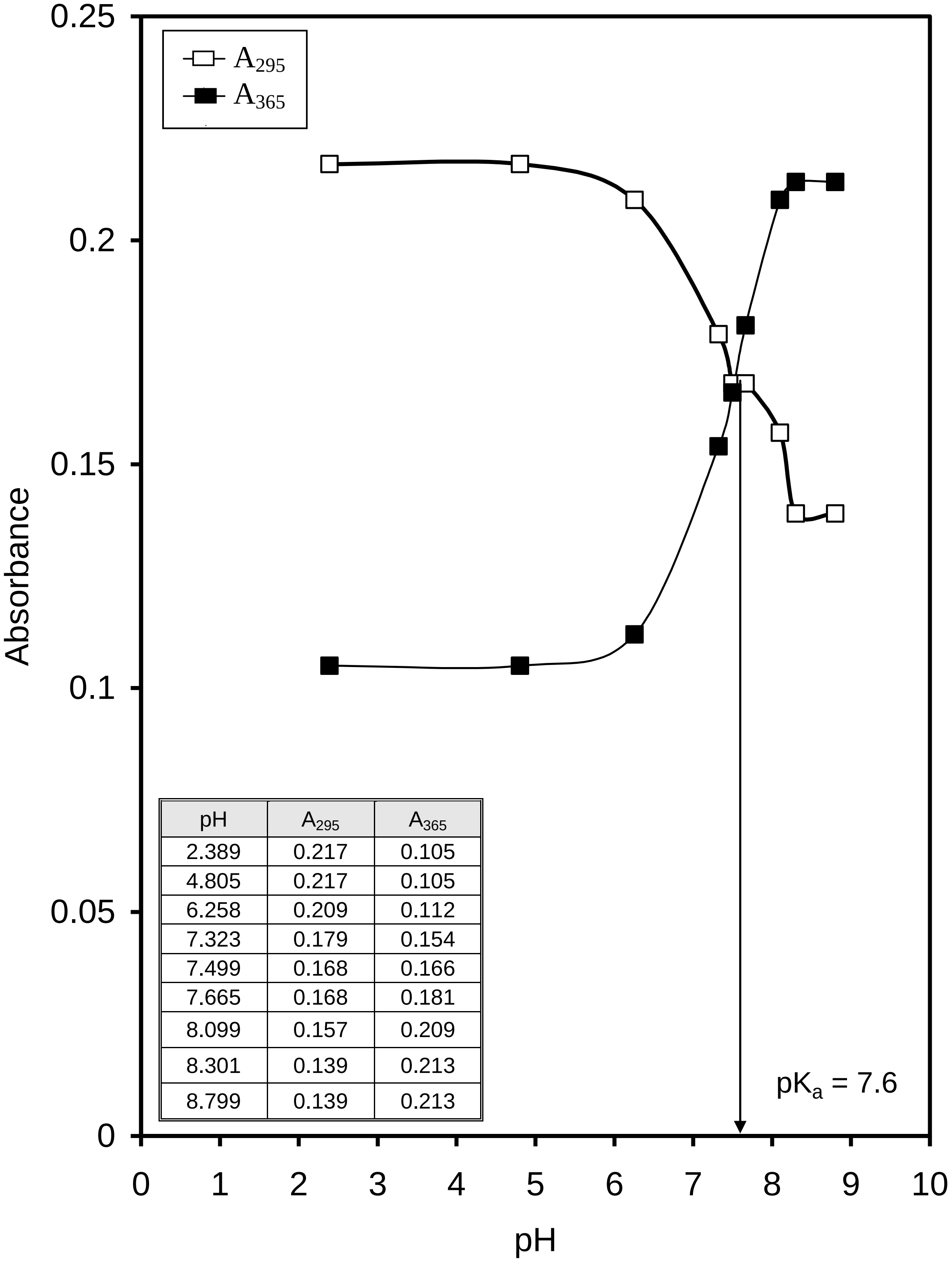
Fig. (62): Verification of Beer's Lambert law on the fluorescence spectrum of dye IV_b at different concentrations.

2.7. Effect of pH on the absorption spectra of dye IV_b and dye IV_c:

For Dye IV_b:

The affect of pH of the medium on the absorption spectrum of 4 x 10^{-8} M of dye IV_b was studied Figs. (65, 64). This study was performed over wide range of pH’s ranged from pH = 4.80 to pH = 9.80, the absorption band at 324 nm was slightly shifted around its value but its intensity was decreased as the pH increased which indicate that as the acidity of the medium increased the ground state S_o become less stable and the molecules of dye IV_b become easily promoted to excited state i.e., population of the excited state by absorption energy become more allowed in acidic medium also we noticed that, another absorption band appeared at 332 nm where its intensity increase with decreasing of the pH value, till it become more intense than the absorption band at 324nm. That is attributed to the possibility of existence of more than one species at different pH values.

The absorption bands at 295 nm and 365 nm were selected for determination of the pKa of the dye IV_b the value of the pKa of dye IV_b was determined by using different methods such as S-shape method Fig. (65), half-wave hight Fig. (66) and limiting absorbance methods Fig. (67). The value of pKa was summarized in Table (13).



pH	A_{295}	A_{365}
2.389	0.217	0.105
4.805	0.217	0.105
6.258	0.209	0.112
7.323	0.179	0.154
7.499	0.168	0.166
7.665	0.168	0.181
8.099	0.157	0.209
8.301	0.139	0.213
8.799	0.139	0.213

Fig. (65): Determination of the pK_a-value of dye IV_b by S-shape method.

The half-wave height methods:

This methods depends on the fact that, Pka= pH at which the two equilibrium species coexist in equivalent amounts at which half-length of A-pH curve for ionization.

$$HL = L^{-} + H^{+} \qquad , \qquad C_{HL} = C_{L^{-}}$$

Where:

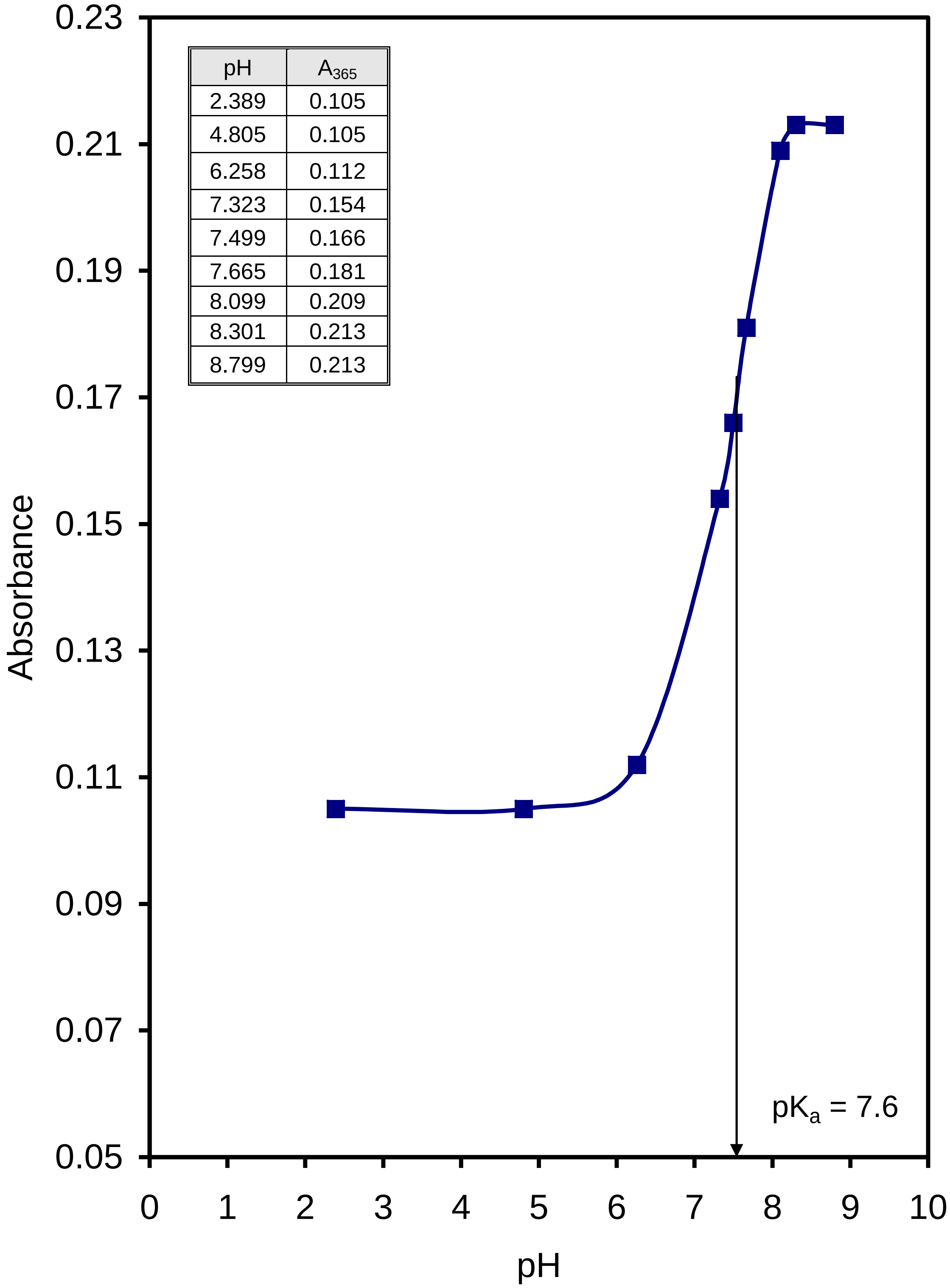
C_{HL} , C_{L}^{-} are the concentration of protonated and nonprotonated form

and,

$$A_{\frac{1}{2}} = \left(\frac{A_{\max} - A_{\min}}{2} \right) + A_{\min} \quad \ldots\ldots (3)$$

where

A_{max} , A_{min} are max and min absorbance on A-pH curve.



pH	A_{365}
2.389	0.105
4.805	0.105
6.258	0.112
7.323	0.154
7.499	0.166
7.665	0.181
8.099	0.209
8.301	0.213
8.799	0.213

Fig. (66): Determination of the pK$_a$-value of dye IV$_b$ by half-wave height method.

The limiting absorbance method:

This method depends on the fact that,

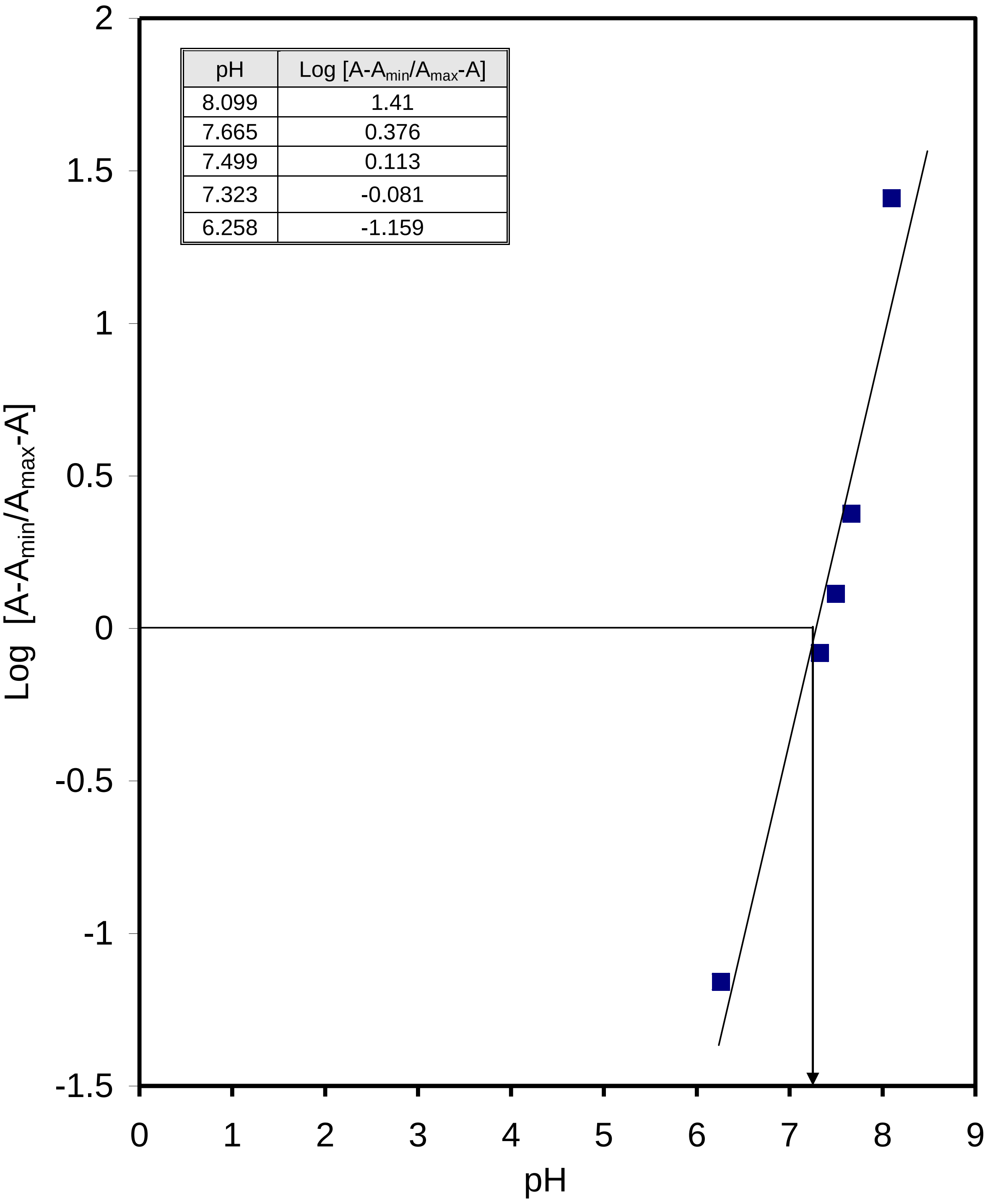
$$pH = pKa + \log\gamma + \log\frac{A - A_{\min}}{A_{\max} - A} \quad \ldots\ldots(4).$$

Where $A_{max.}$, $A_{min.}$, are max and min absorbances at given pH, and γ is the activity coefficient of ions which present in equilibrium, in very dilute solution $\log\gamma = 0$. Hence from the above equation by plotting log $\frac{A - A_{\min}}{A_{\max} - A}$ against pH values, the pKa value can be obtained from the fact pKa= pH when term log $\frac{A - A_{\min}}{A_{\max} - A} = 0$

Table (13): Calculation of pKa of dye IV_b by using the limiting absorbance method :

pH	**A**	**$A-A_{min}$**	**$A_{max}-A$**	$\frac{A - A_{\min}}{A_{\max} - A}$	**Log** $\frac{A - A_{\min}}{A_{\max} - A}$	**PKa**
8.301	0.213	-	-	-	-	-
8.099	0.209	0.104	0.004	26	1.41	6.689
7.665	0.181	0.076	0.032	2.375	0.376	7.289
7.499	0.166	0.061	0.047	1.298	0.113	7.386
7.323	0.154	0.049	0.059	0.831	-0.081	7.404
6.258	0.112	0.007	0.101	0.069	-1.159	7.417
4.805	0.105	0.00	0.108	0.00	-	-

Average calculated pKa = 7.24 found pKa = 7.25.



pH	Log [A-A_{min}/A_{max}-A]
8.099	1.41
7.665	0.376
7.499	0.113
7.323	-0.081
6.258	-1.159

Fig. (67): Determination of the pK_a-value of dye IV_b

Using the limiting absorbance method where at

log [A-A_{min}/A_{max}-A] = 0, The pH = pK_a = 7.25

For dye IV_c:

The effect of pH of the medium on the absorption spectrum of 4 x 10^{-8} M of dye IV_c was explored Fig. (68). The study was performed over wide range of pH's ranged from pH= 6.258 to pH= 11.037 and it was found that, with increasing pH value, the absorption band at 375 nm was slightly red shifted around its value by about 2-4 nm, but its intensity was decreased as pH increased which indicated that the promotion of dye IV_c molecules become more allowed in more acid medium (less pH). So, the interaction between the molecules of dye IV_c with each other or with the medium become more in basic medium (stabilize ground state) i.e., population of the excited state by absorption energy become more allowed in acidic medium. Also, we notice that, another absorption band at about 392 nm which increase in its intensity with the increase in the pH, till it become more intense than the absorption band at 375nm. This indicated that there are more than one species exist at different pH values which allowed to promote from ground state to excited state. The absorption bands at 320 nm and 450nm were selected for determination of the pKa value for dye IV_c.

The pKa of dye IV_c was determined by using different methods such as S-shape method Fig. (69) by ploting absorption against pH with respect to absorption band 320 nm and 450 nm we found that the pKa = 10.9. Also the half wave height method Fig. (70) which indicate that pKa= 10.4 finally the limiting absorbance method Fig. (71). Table (14) indicates that, the average calculated pKa = 10.38 and that found pK = 10.19.

The values of pKa of dyes IV_b and IV_c were summarized in Table (15).

CONCLUSIONS

From the pervious study which focused on the effect of pH on absorption spectrum of dyes IV_b and IV_c we notice that:

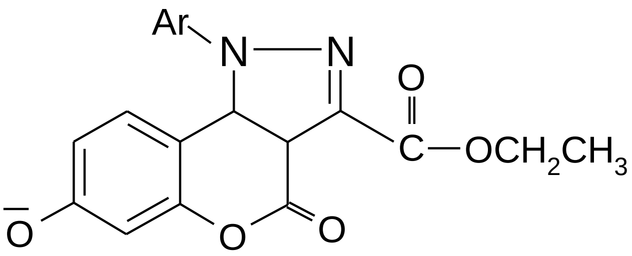
1- The absorption spectrum of both dye IV_b and dye IV_c were affected by pH value of the medium.

2- The introducing nitro group to dye IV_c cause red shifted more than dye IV_b.

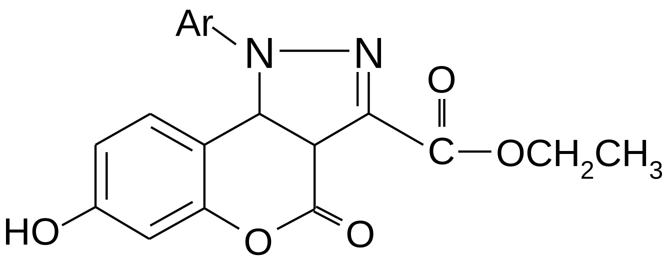
3- The intensities of absorption bands of both dye IV_b and dye IV_c. were affected by change pH value more than the its position.

4- Introducing nitro group to dye IV_c make its pKa is greater than that of dye IV_b.

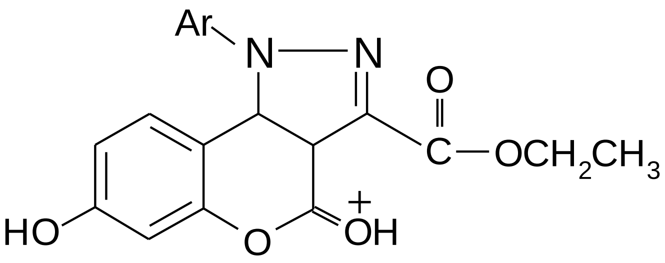
5- More investigation of absorption spectra of dyes IV_b and IV_c at various pH values, led to the assignment of structures which appear successively on going from basic to acidic media. This are, the basic anion (B^-), the neutral species (N) and the cation (C^+).



($\overline{B}$)

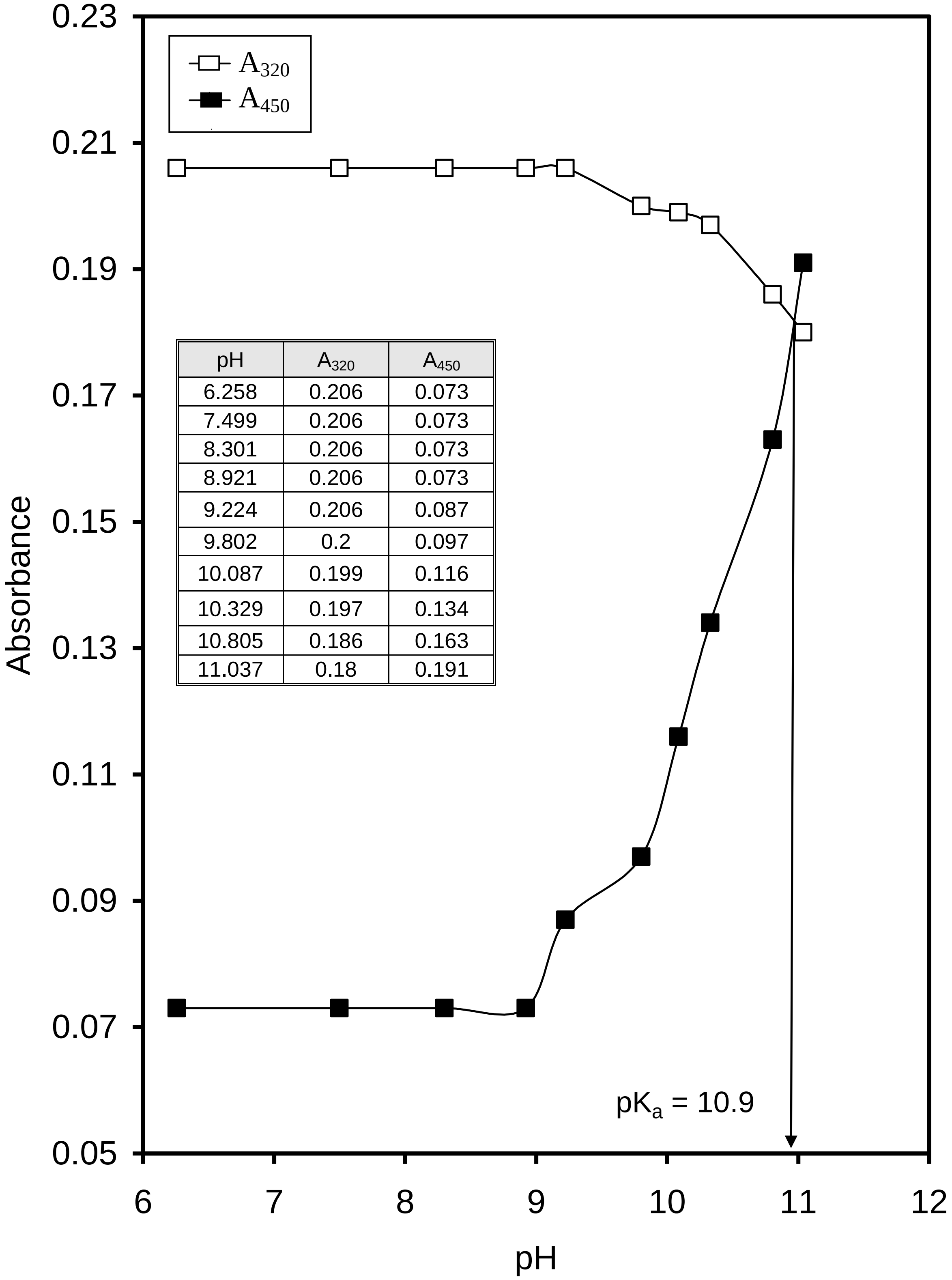


(N)



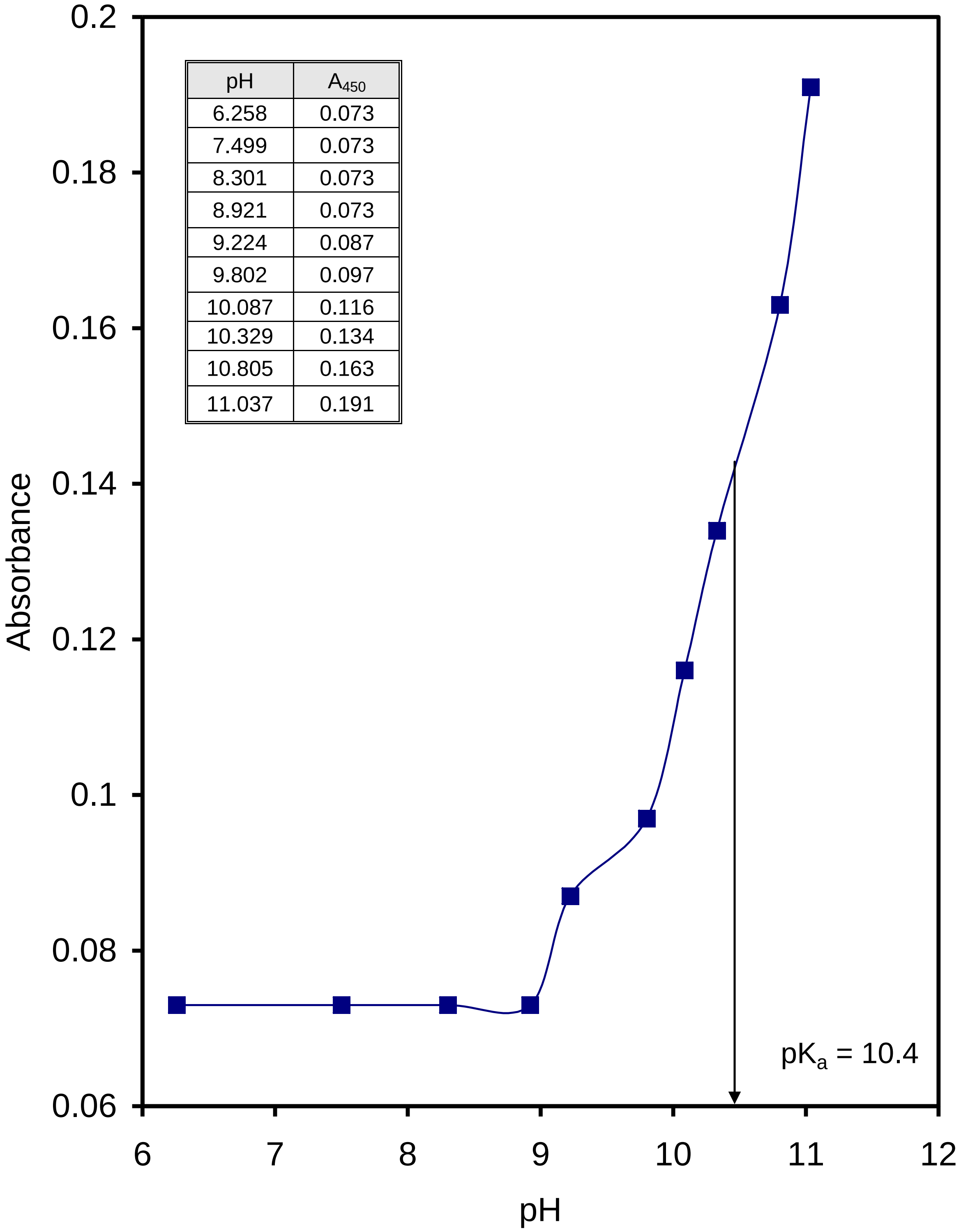
(C^+)

Dye	Ar
IV_b	$C_6H_5^-$
IV_c	$C_6H_4^-$ NO_2(*p*-).



pH	A_{320}	A_{450}
6.258	0.206	0.073
7.499	0.206	0.073
8.301	0.206	0.073
8.921	0.206	0.073
9.224	0.206	0.087
9.802	0.2	0.097
10.087	0.199	0.116
10.329	0.197	0.134
10.805	0.186	0.163
11.037	0.18	0.191

Fig. (69): Determination of the pK_a-value of dye IV_C by using S-shape method.



pH	A_{450}
6.258	0.073
7.499	0.073
8.301	0.073
8.921	0.073
9.224	0.087
9.802	0.097
10.087	0.116
10.329	0.134
10.805	0.163
11.037	0.191

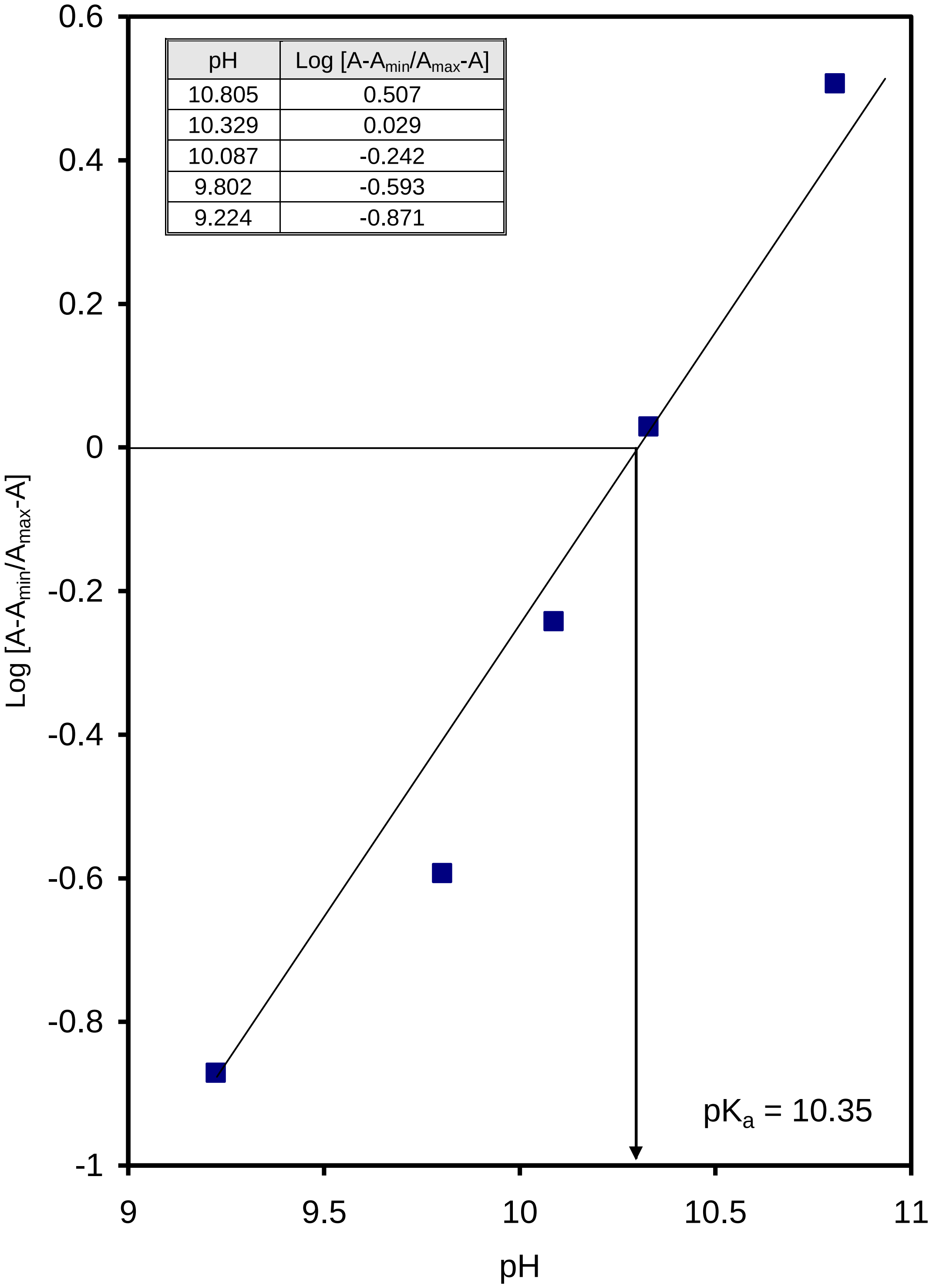
Fig. (70): Determination of the pK$_a$-value of dye IV$_C$ by half-wave height method.

Table (14): Calculation of pKa value of dye IV$_c$ using limiting absorbance method:

PH	A	A-A$_{min}$	A$_{max}$-A	$\frac{A-A_{\min}}{A_{\max}-A}$	Log $\frac{A-A_{\min}}{A_{\max}-A}$	PKa
11.037	0.191	0.028	0.00	-	-	-
10.805	0.163	0.090	0.028	3.214	0.507	10.298
10.329	0.134	0.061	0.057	1.070	0.029	10.776
10.087	0.116	0.043	0.075	0.573	- 0.242	10.329
9.802	0.097	0.024	0.094	0.255	- 0.593	10.395
9.224	0.087	0.014	0.104	0.135	-0.871	10.095
8.921	0.073	-	-	-	-	-

Average calculated pKa = 10.37

Found pKa = 10.35

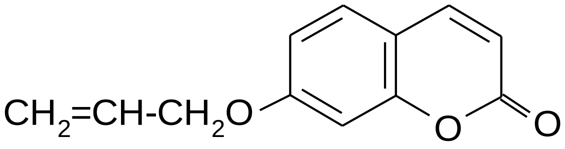


pH	Log [A-A$_{min}$/A$_{max}$-A]
10.805	0.507
10.329	0.029
10.087	-0.242
9.802	-0.593
9.224	-0.871

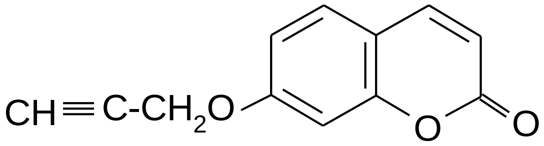
Fig. (71): Determination of the pK$_a$-value of dye IV$_C$
Using the limiting absorbance method where at
log [A-A$_{min}$/A$_{max}$-A] = 0, The pH = pK$_a$ = 10.35.

Table (15): pKa values of dyes IV_b and IV_c:

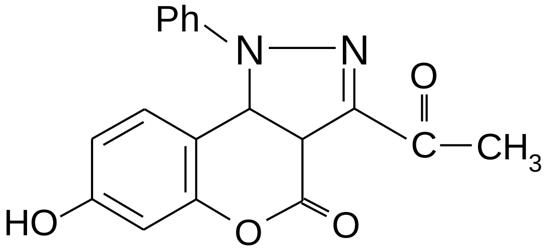
Compd.	S. shape method	Limiting absorance method	Half –wave high	Average pKa
IV	7.6	7.36	7.6	7.51
V	10.9	10.36	10.4	10.53


CH2=CH-CH2O
O
O

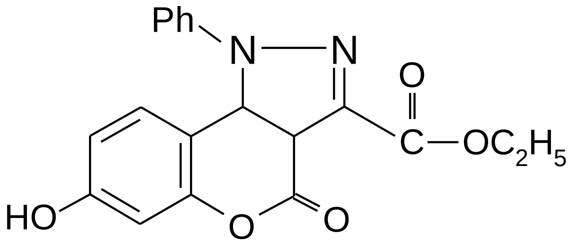
I


CH≡C-CH2O
O
O

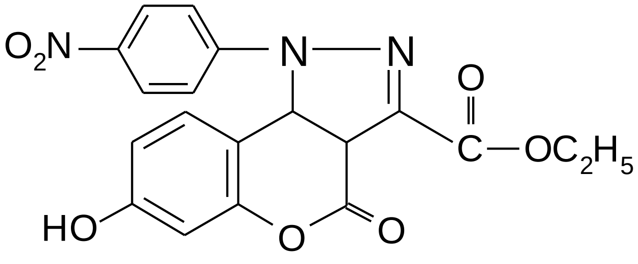
II


Ph
N
N
O
C
CH3
HO
O
O

III


Ph
N
N
O
C
OC2H5
HO
O
O

IV


O2N
N
N
O
C
OC2H5
HO
O
O

V