CHAPTER-III

RESULTS & DISCUSSION

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In order to assess the reliability of the IR spectrophotometer handled in this work, the IR spectrum of a polystyrene film was initially obtained. The spectrum is depicted in Fig. 1.

The examinastion of the figure 1. reveals following peaks (transmission minima) and their assignments asre given below.

Table No. : 1

Vibrational frequencies (in cm^{-1}) of polystyrene :

Vibrational Frequencies (cm^{-1})	Assignments (1)
3080 (w), 1070 (w), 1028 (sh), 755 (s) and 700 (s).	monosubstituted benzene rings.
3080 (w), 3060 (w) and 3020 (w).	aromatic C-H stretching.
1600 (s)	aromatic C-C multiple bond stretching.

w=weak, sh=sharp, s=strong.

The comparison of the observed IR characteristics for polystyrine with literature data reveals a good correlation. Thus it is extablished that good and reliable measurements can be done with the available IR spectrophotometer.

In a simmilar manner, the measurements of pure solvents (liquid samples) chloroform, acetonitrile and acetone were carried out. The spectral data are summarised in figures 2,3 and 4 respectively. The peak wavenumbers and their asssignments are collected in table 2,3 and 4 for chloroform, acetonitrile and acetone respectively.

Table No. : 2

Vibrational frequencies (in cm^{-1}) of chloroform :

Vibrational frequencies (cm^{-1})	Assignments (1)
2900 (sh)	trisubstituted methane.
670 (s) and 760 (vs)	C-Cl stretching.

sh=sharp, s=strong, v=very.

Table No. 3 :

Vibrational frequencies (in cm^{-1}) of acetonitrile

Vibrational frequencies (cm^{-1})	assignments (1)
3005 (ms), 2950 (ms)	$-CH_3$ stretching.
2270 (ms), 2250 (ms)	alkyl nitrile ($-C\equiv N$) stretching.

ms=medium strong.

Table No. 4 :

Vibrational frequencies (in cm^{-1}) of acetone :

Vibrational frequencies (cm^{-1})	assignments (1)
3000 (w)	$-CH_3$ stretching.
1370 (w), 1430 (w)	$-CH_3$ bending, (symmetric and asymmetric)
1724 (s)	-, C=O

w=weak, s=strong.

The spectra of solid samples of P-nitrophenol, P-toluidine and P-anisidine were obtained using KBr pellet technique. The traces are shown in figures 5,6 and 7 respectively. The vibrational frequencies and their assignments asre collected in table number 5,6 and 7 respectively.

Table No. 5

Vibrational frequencies (in cm^{-1}) of solid P-nitrophenol :

Vibrational frequencies (cm^{-1})	Assignments (1)
3360 (VS and b)	-OH STRETCHING (Phenolic)
1290 (b)	-OH bending (Phenolic)
1340 (m)	Aromatic $C-NO_2$
3080 (w)	Aromatic C-H stretching
1510 (sh)	N=O anymmetric stretching.

v=very, s=strong, b=broad, m=medium, w=weak, sh=sharp.

Generally the free -OH absorption occurs at about 3600 cm^{-1}. The observation of peak at 3360 signifies that in solid, considerable lewering occurs because of the intermolecular association. (2)

Table No. 6 :

Vibrational frequencies (in cm^{-1}) of solid P-toluidine :

Vibrational frequencies (cm^{-1})	Assignments (1)
3340 (sh) and 3420 (sh)	-NH stretching (primary amine)
1625 (m h)	-NH bending.
2920 (m) and 2860 (m)	methyl C-H stretching
3010 (m)	aromatic C-H stretching.

sh=sharp, m=medium.

Table No.7 :

Vibrational frequencies (in cm^{-1}) of solid P-anisidine.

Vibrational frequencies (cm^{-1})	Assignments (1)
3430 (sh) and 3350 (sh)	-NH stretching (primary amine)
1635 (msh)	-NH bending
3080 (w), 3040 (w), 3010 (w)	aromatic C-H stretching.
2840 (sh)	methyl C-H stretching.

sh=sharp, msh=medium sharp, w=weak, sh=sharp

The spectra of P-nitrophenol, aniline, P-toluidine and P-anisidine in solution phase in different solvents e.g. chloroform, acetonitrile and acetone were obtained. The spectra of above mentioned solutions (0.4M) in diferent solvents are depicted in figures 8 to 19 respectively. The vibrational frequencies and their assignments are collected in table numbers 8 to 19 respectively.

Table No. 8 :

Vibrational frequencies (in cm^{-1}) of P-nitrophenol solution (0.4M) in chloroform :

Vibrational frequencies (cm^{-1})	Assignments (1)
3580 (s)	Free phenolic -OH stretching
3400 (b,s)	-OH stretching (phenolic) (H-bonded)

..cont.

1285 (s)	-OH bending (phenolic)
1345 (s)	Aromatic C-NO_2
1530 (m)	asymmetric -N=O stretching.
870 (Vsh)	-NO_2 in plane bending.

b=broad, s=strong, m=medium, Vsh=very sharp.

Table No. 9 :

Vibrational frequencies (in cm^{-1}) of P-nitrophenol solution in acetonitrile :

Vibratioal frequencies (cm^{-1})	Assignments (1)
3320 (b.s)	-OH stretching (Phenolic)
1230 (s)	-OH bending (phenolic)
1340 (m)	C-NO_2 (aromatic)
860 (sh)	-NO_2 in plane bending.

b=bending, s=strong, m=medium, sh=sharp.

Table No. 10 :

Vibrational frequencies (in cm^{-1}) of P-nitrophenol solution (0.4M) in acetone :

Vibrational frequencies (cm^{-1})	Assignments (1)
3200 (b), (w)	-OH stretching (phenolic)
1165 (m)	Phenolic-OH bending
1290 (m)	aromatic C-NO_2
860 (sh)	-NO_2 in plane bending.

b=broad, m=medium, sh=sharp, w=weak

Table No. 11 :

Vibrational frequencies (in cm^{-1}) of aniline solution (0.4M) in chloroform :

Vibrational frequencies (cm^{-1})	Assignments (1)
3450 (s) and 3385 (s)	-NH stretching (primary amine)
1620 (m)	-NH bending
1270 (m)	-C≡N (aromatic primary amine)
3080 (w), 1045 (w), 995(w), 760(s), 690(s)	monosubstituted benzene ring.

sh=sharp, m=medium, w=weak, s=strong.

Table No. 12 :

Vibrational frequencies (in cm^{-1}) of aniline solution (0.4M) in acetonitrile :

Vibrational frequencies (cm^{-1})	Assigngments (1)
3470 (sh), 3388(sh)	-NH stretching (primary amine)
1635 (m)	-NH bending.
1290 (m)	-C≡N (aromatic primary amine)
3080 (w), 1000 (w), 760 (s), 700 (s).	monosubstituted benzen rings

sh=sharp, m=medium, w=weak, s=strong.

Table No. 13 :

Vibrational frequencies (in cm^{-1}) of aniline solution (0.4M) in acetone :

Vibrational frequencies (cm^{-1})	Assignments (1)
3455 (w), 3375 (w)	-NH stretching (primary amine)
1605 (w)	-NH bending
1285 (m)	C-N (aromatic primary amine)
1025 (w), 995 (w), 760 (w), 695 (s)	mono substituted benzene rings

w=weak, m=medium, s=strong.

Table No. 14 :

Vibrational frequencies (in cm^{-1}) of para toludine solution (0.4M) in chloroform :

Vibrational frequencies (cm^{-1})	Assignments (1)
3440 (m), 3370 (m)	-NH stretching (primary amine)
1620 (s)	-NH bending.
1265 (m)	C-N (aromatic primary amine)
2920 (w), 2860 (w)	$-CH_3$ stretching.

m=medium, s=strong, w=weak.

Table No. 15 :

Vibrational frequencies (in cm^{-1}) of P-toluidine solution (0.4M) in acetonitrile :

Vibrational frequencies (cm^{-1})	Asssignments (1)
3460 (s), 3380 (s)	-NH stretching (Primary amine)
1630 (s)	-NH bending.
1280 (s)	-NH bending.
2880 (w)	$-CH_3$ stretching.

s=strong , w=weak.

Table No. 16 :

Vibrational frequencies (in cm^{-1}) of P-toluidine solution (0.4M) in acetone :

Vibrational frequencies (cm^{-1})	Assignments (1)
3460 (w), 3375 (w)	-NH Stretching (Primary amine)
1595 (w)	-NH bending.
1285 (m)	C-N (aromatic amine)
2880 (V.W)	$-CH_3$ stretching.

w=weak, m=medium, v=very.

Table No. 17 :

Vibrational frequencies (in cm^{-1}) of P- anisidine solution (0.4M) in chloroform :

Vibrational frequencies (cm^{-1})	Assingnments (1)
3450 (m), 3378 (m)	-NH stretching (primary amine)
1610 (m)	-NH bending.
1300 (m)	C-N (aromatic amine)
1130 (sh), 1185 (sh)	Ar - OCH_3 Vibration.

m=medium, sh=sharp, Ar=aryl group.

Table No. 18 :

Vibrational frequencies (in cm^{-1}) of P-anisidine solution (0.4M) in acetonitrile :

Vibrational frequencies (cm^{-1})	Assignments (1)
3450 (m), 3370 (sh)	-NH stretchiing (primary amine)
1632 (s)	-NH bending.
1300 (m)	C-N (aromatic amine).
1185 (sh), 1130 (w)	Ar - OCH_3 vibration.

m=medium, sh=sharp, w=weak, Ar=aryle group.

Table No. 19 :

Vibrational frequencies (in cm^{-1}) of P-anisidine solution (0.4M) in acetone :

Vibrational frequency (cm^{-1})	Assignments (1)
3460 (w), 3375 (m)	-NH stretching (Primary amine)
1639 (sh)	-NH bending.
1290 (w)	C-N (aromatic amine).
1300 (VW)	Ar-OCH_3.

w=weak, sh=sharp, v=very weak.

From the comparative study of -OH stretching and -NH stretching vibration frequencies in solids and their solutions in different solvents (table No.25) it is observed that the -OH stretching vibration peak of para nitrophenol in solid phase appears at 3360 cm^{-1} while it occurs at 3400 cm^{-1} in chloroform, at 3320 cm^{-1} in acetonitrile and in acetone at 3200 cm^{-1} respectively for 0.4M concentration (3 to 10). It clearly indicate that in solid phase there is intermolecular association and the -OH stretching frequency goes on decreasing in solvents with increasing dielectric constant. There is no considerable change in -NH stretching frequencies in solid phase and solutioin phase in case of P-toluidine, P-anisidine and aniline solutions in different solvents like chloroform, acetonitrile and acetone.

BEER'S AND LAMBERT'S LAW :

To verify the Beer's and Lambert's law the variabion of absorbance as a function of concentration in case of P-ntrophenol, aniline, P-toluidine and P-anisidine solutions were plotted. All the plots of priviously mentioned sample solutions were found to be straight lines passing through the origine. This clearly indicates that in above mentioned samples the Beer's and Lambert's law is valid (figures 29, 30, 31 and 32. and Table no's. 20, 21, 22 and 23). Beer's and Lambert's law is obeyed in the concentrations of samples under study. The deviations in the laws are reported in P-nitrophenol and acetone on the basis of active equilibria.

The extinction coefficient values of samples mentioned above are calculated with respect to the traces of graphs shown in figures 29, 30, 31 and 32. The values of extinction coefficients are presented in table number 24. The coefficients values of P-nitrophenol, aniline, P-toluidine and P-anisidine solution prepared in solvent acetonitrile (Table No. 24) are always greater than that prepared in chloroform. It may be due to higher dielectric constant of acetonitrile than chloroform (11).

Table No. 20 (A) :

IR Spectra of P-nitrophenol in chloroform. :

Group vibration	Peak at wave number (cm^{-1})	Concetration [M]	Percentage transmitance		Optical density
			On spectrum	Actual	
-OH stret.	3400	0.1	75.00	88.2	0.054
-OH stret.	3400	0.2	70.00	82.3	0.084
-OH stret.	3400	0.3	55.00	64.7	0.189
-OH stret.	3400	0.4	48.9	57.5	0.240

Table No. 20 (B) :

IR Spectra of P-nitrophenol in acetonitrile :

-OH stret.	3320	0.1	53.00	62.3	0.20
-OH stret.	3320	0.2	36.00	42.3	0.37
-OH stret.	3320	0.3	23.60	27.7	0.55
-OH stret.	3320	0.4	16.00	18.8	0.72

Table No.21 (A) :

IR Spectra of aniline in chloroform :

Group vibration	Peak at wave number (cm^{-1})	Concetration [M]	Percentage transmitance		Optical density
			On spectrum	Actual	
-NH stret.	3385	0.1	70.6	83.05	0.080
-NH stret.	3385	0.2	65.9	77.5	0.110
-NH stret.	3385	0.3	59.0	69.4	0.158
-NH stret.	3385	0.4	53.0	62.3	0.205
-NH stret.	3450	0.1	70.2	82.5	0.083
-NH stret.	3450	0.2	67.2	79.05	0.102
-NH stret.	3450	o.3	62.0	72.9	0.137
-NH stret.	3450	0.4	57.5	67.6	0.169

Table No. 21 (B) :

IR Spectra of aniline in acetonitrile :

-NH stret.	3380	0.1	63.6	75.0	0.125
-NH stret.	3380	0.2	51.0	60.0	0.221
-NH stret.	3380	0.3	40.0	47.0	0.327
-NH stret.	3380	0.4	32.8	37.6	0.424
-NH stret.	3470	0.1	72.0	84.7	0.072
-NH stret.	3470	0.2	64.5	75.8	0.119
-NH stret.	3470	0.3	54.5	64.1	0.193
-NH stret.	3470	0.4	51.0	60.0	0.221

Table No. 22 (A) :

IR Spectra of P-toluidine in chloroform :

Group vibration	Peak at wave number (cm^{-1})	Conc-etration [M]	Percentage transmitance		Optical density
			On spectrum	Actual	
-NH stret.	3370	o.1	79.0	92.9	0.031
-NH stret.	3370	0.2	75.0	88.2	0.054
-NH stret.	3370	0.3	71.0	83.5	0.078
-NH stret.	3370	0.4	59.0	69.4	0.158
-NH stret.	3440	0.1	79.5	93.5	0.029
-NH stret.	3440	0.2	76.0	89.4	0.048
-NH stret.	3440	0.3	72.0	84.7	0.072
-NH stret.	3440	0.4	60.0	70.5	0.151

Table No. 22 (B) :

IR Spectra of P-toluidine in acetonitrile

-NH stret.	3380	0.1	69.0	81.1	0.090
-NH stret.	3380	0.2	54.0	63.5	0.197
-NH stret.	3380	0.3	47.0	55.2	0.257
-NH stret.	3380	0.4	37.5	44.1	0.355
-NH stret.	3460	0.1	76.0	89.4	0.048
-NH stret.	3460	0.2	65.5	77.0	0.113
-NH stret.	3460	0.3	60.0	70.5	0.151
-NH stret.	3460	0.4	52.0	61.1	0.213

Table No. 23 (A) :

IR Spectra of P-anisidine in chloroform :

Group Vibration	Peak at wave number (cm^{-1})	Conc-entrat-ion [M]	Percentage transmitance		Optical density
			On spectrum	Actual	
-NH stret.	3378	0.1	79.2	93.18	0.031
-NH stret.	3378	0.2	73.7	86.70	0.061
-NH stret.	3378	0.3	68.6	80.70	0.093
-NH stret.	3378	0.4	64.0	75.20	0.123
-NH stret.	3450	0.1	80.0	94.1	0.026
-NH stret.	3450	0.2	76.0	89.4	0.048
-NH stret.	3450	0.3	71.0	83.5	0.078
-NH stret.	3450	0.4	66.8	78.5	0.104

Table No. 23 (B) :

IR Spectra of P-anisidine in acetonitrile

-NH stret.	3370	0.1	71.00	83.53	0.078
-NH stret.	3370	0.2	58.60	68.94	0.161
-NH stret.	3370	0.3	45.30	53.29	0.273
-NH stret.	3370	0.4	38.20	44.94	0.347
-NH stret.	3450	0.1	77.00	90.59	0.042
-NH stret.	3450	0.2	69.00	81.18	0.090
-NH stret.	3450	0.3	59.00	69.41	0.158
-NH stret.	3450	0.4	54.00	63.53	0.197

Table No.24 :

Extinction coefficient values from figures 29, 30, 31, 32.

Sample solution	Group Vibrat-	Peak at Wave number (cm^{-1})	Extinction coefficient values ($lit. mol.^{-1} cm.^{-1}$)	
			In chloroform	In Acetonitrile
PNP	-OH stre.	3400	60.00	-
	-OH stre.	3320	-	178.57
Aniline	-NH stre.	3385	55.56	-
	-NH stre.	3388	-	110.00
	-NH stre.	3450	47.16	-
	-NH stre.	3470	-	60.60
PT	-NH stre.	3370	24.87	-
	-NH stre.	3380	-	87.5
	-NH stre.	3440	25.4	-
	-NH stre.	3460	-	52.42
PA	-NH stre.	3378	31.11	-
	-NH stre.	3370	-	86.66
	-NH stre.	3450	25.71	-
	-NH stre.	3450	-	48.27

PNP=P-nitrophenol. PT=P-toluidine. PA=P-anisidine.

Table No. 25 :

Table showing the comparison of -OH stretchig and -NH stretching vibration frequencies; in solids and their solutions. (1)

Name of the Compound	Mode of vibration	Peak at wave numbers (cm^{-1})			
		In solid	In 0.4M solution in chloroform.	In 0.4M solution in acetonitrile.	In 0.4M solution in acetone.
1) P-Nitrophenol.	-OH stretching.	3360(VS,b)	3400 (S,b)	3320 (S,b)	3200 (W,b)
2) Aniline.	-NH stret. i)	-	3450 (s)	3470 (sh)	3455 (w)
	ii)	-	3385 (s)	3388 (sh)	3375 (w)
3) P-toluidine.	-NH stret. i)	3420 (sh)	3440 (m)	3460 (s)	3460 (w)
	ii)	3340 (sh)	3370 (m)	3380 (s)	3375 (w)
4) P-anisidine.	-NH stret. i)	3430 (sh)	3450 (m)	3450 (m)	3460 (w)
	ii)	3350 (sh)	3378 (m)	3370 (sh)	3375 (m)

s=strong, w=weak, sh=sharp, b=broad, m=medium.

The spectra of complexes (1:1 adduct) of P-nitrophenol and three amines e.g. aniline, P-toluidine and P-anisidine in three solvents e.g. chloroform, acetonitrile and acetone (all 0.4M. solutions) are shown in Figures 20 to 28. The observations and conclusions from each spectrum are as follws.

I [P-nitrophenol (0.4M)] (1:1) adduct in chloroform. (fig :- 20) (1).

a) -OH stretching frequency peak at 3400 cm^{-1} dissappeared and appeared at 3200 cm^{-1}.

b) Free phenolic -OH peak at 3580 cm^{-1} has become very weak in the complex as compared to it in pure P-nitrophenol - free phenolic -OH peak.

c) -NH stretching frequency peak at 3450 cm^{-1} vanished but that at 3385 cm^{-1} has not vanished completely.

The dissappearence of -OH stretching peak and -NH stretching peak indicated the presence of hydrogen bond between P-nitrophenol and aniline. The appearence of new band at 3200 cm^{-1} confirms the presence of vibration of hydrogen bonded species (3).

II [P-nitrophenol (0.4M)+aniline(0.4M)] (1:1) adduct in acetonitrile. (fig.21) (1)

a) -OH stretching frequency peak at 3320 cm^{-1} completely dissappeared.

b) -NH stretching peak at 3380 and 3470 cm^{-1} were very sharp in aniline solution but in this complex these have become very very weak.

III <u>[P-nitrophenol(0.4M)+aniline(0.4M)] (1:1) adduct in acetone</u> : (fig.22) (1)

a) -OH stretchiing frequency peak at 3200 cm^{-1} dissappeared completely.

b) -NH stretching frequency peaks at 3455 and 3375 cm^{-1} have become very very weak.

In the above two cases i.e. II and III no new band appeared because of hydrogen bonding. This tentatively can be explained in terms of equilibria, either solute-solvent or acid-base which are faciliated by the polar nature and comparatively higher dielectric constants of the solvents used.

IV <u>[P-nitrophenol (0.4M)+P-toluidine(0.4M)] (1:1) adduct in chloroform (fig. 23)</u> (1)

a) Small effect on phenolic free -OH stretching frequency at 3580 cm^{-1}.

b) -OH stretching frequency peak at 3400 cm^{-1} has not dissappeared completely but became very very weak (12).

c) -NH stretching frequency peak at 3378 cm^{-1} dissappeared completely.

The dissappearence of -NH stretching peak suuggests the hyydrogen bonding between the two. However, very small effect on free -OH suggest that in solution some concentration of free -OH still exit. To explain these one has to do the calculations of equilibrium constant which has not become possible in this work.

V [P-nitrophenol (0.4M)+P-toluidine (0.4M)] (1:1) adduct in acetonitrile. (fig. 24) (1)

a) -OH stretching peak at 3320 cm^{-1} dissappeared.

b) -NH stretching peaks at 3460 cm^{-1} and 3380 cm^{-1} not completely vanished but he became very weak.

c) -NH bending peak at 1630 cm^{-1} dissappeared.

VI [P-nitrophenol (0.4M)+P-toluidine (0.4M) (1:1) adduct in acetone (fig. 25).

a) -OH stretchig peak at 3200 cm^{-1} completely vanished.

b) -NH stretching peaks at 3460 and 3365 cm^{-1} have become very very weak.

The observations of above V and VI suggest the hydrogen bond formation but the vibration of the corrosponding hydrogen bond are very weak. This further indicate a stronger bond having comparatively higher equilibrium constant. This in turn can be explained in terms of adduct (ionic) formation via-acid-base equilibria.

VII [P-nitrophenol (0.4M)+P-anisidine (o.4M)] (1:1) adduct in chloroform. (fig. 26).

a) -OH stretching peak at 3580 cm^{-1} (free phenolic) became weak.

b) -OH stretching vibration peak at 3400 cm^{-1} completely vanished.

c) -NH stretching vibration peaks at 3450 cm^{-1} and 3378 cm^{-1} completely dissappeared.

d) -NH bending vibration peak at 1630 cm^{-1} dissappeared and shifted to 1710 cm^{-1}.

VIII< [P-nitrophenol(0.4M)+P-anisidine (0,4M)] (1:1) adduct in acetonitrile (fig. 27).

a) -OH stretching vibration at 3320 cm^{-1} completely dissappeared.

b) -NH stretching peaks at 3450 and 3378 cm^{-1} became very very weak.

IX [P-nitrophenol (0.4M)+P-anisidine(0.4M)] (1:1) adduct in acetone (fig. 28).

a) -OH stretching vibration peak at 3200 cm^{-1} completely dissappeared.

b) -NH stretching vibration peaks at 3460 and 3375 cm^{-1} dissappeared.

Similar arguments as that of IV, V and VI can be made on these observations. The substitution of $-OCH_3$ in place of $-CH_3$ does not influence the stretching characteristics of the hydrogen bonded species but only the -NH bending vibrations are shifted to higher value. On the basis of inductive effect the $-OCH_3$ is expected to weaken the hydrogen bond tendancy. However because of the para position of $-OCH_3$ group, the desired effect is not observed.

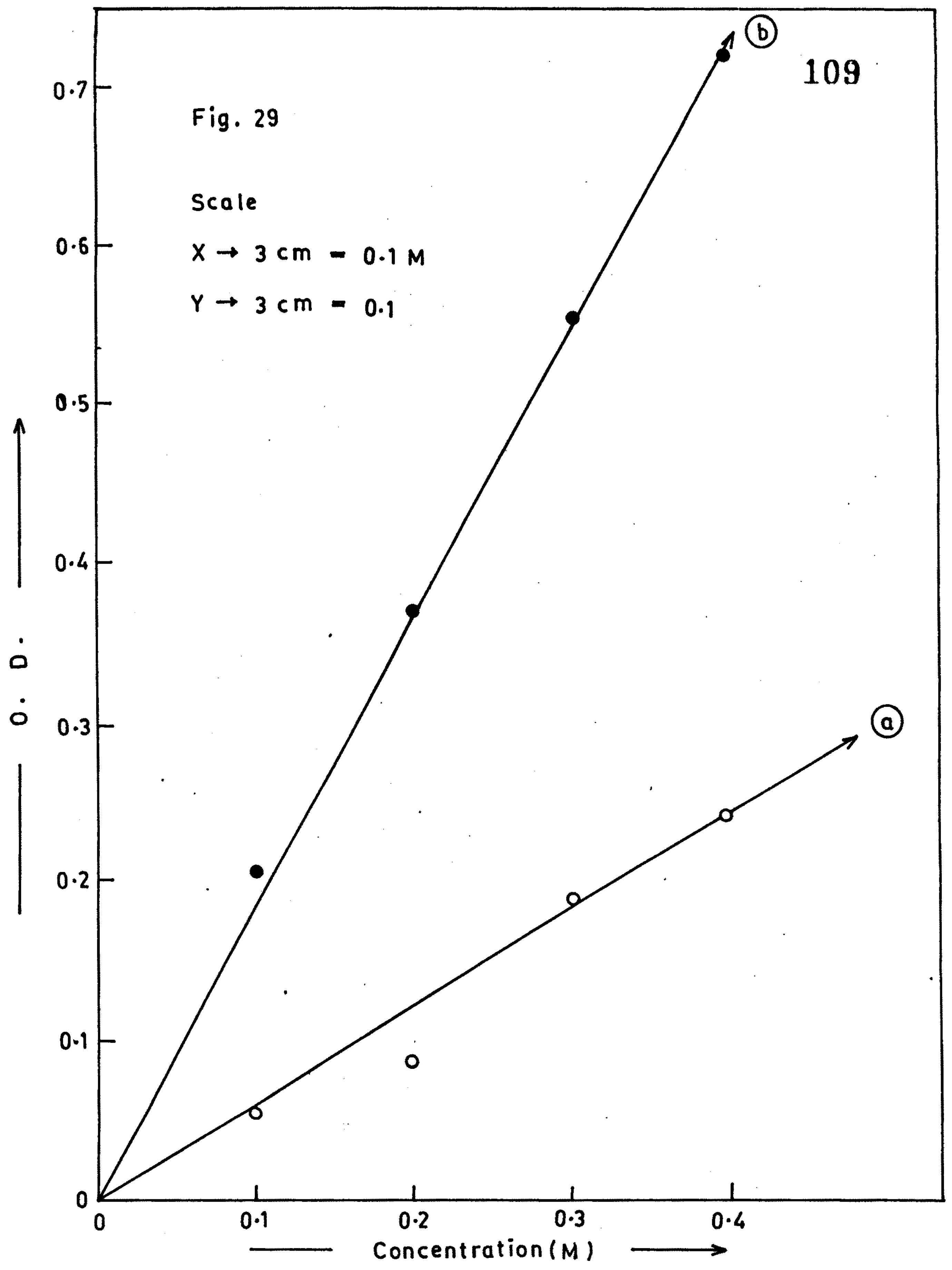


Fig. 29

ⓐ P-nitrophenol in Chloroform → -OH stretching at 3400 cm^{-1}.

ⓑ P-nitrophenol in Acetonitrile → -OH stretching at 3320 cm^{-1}.

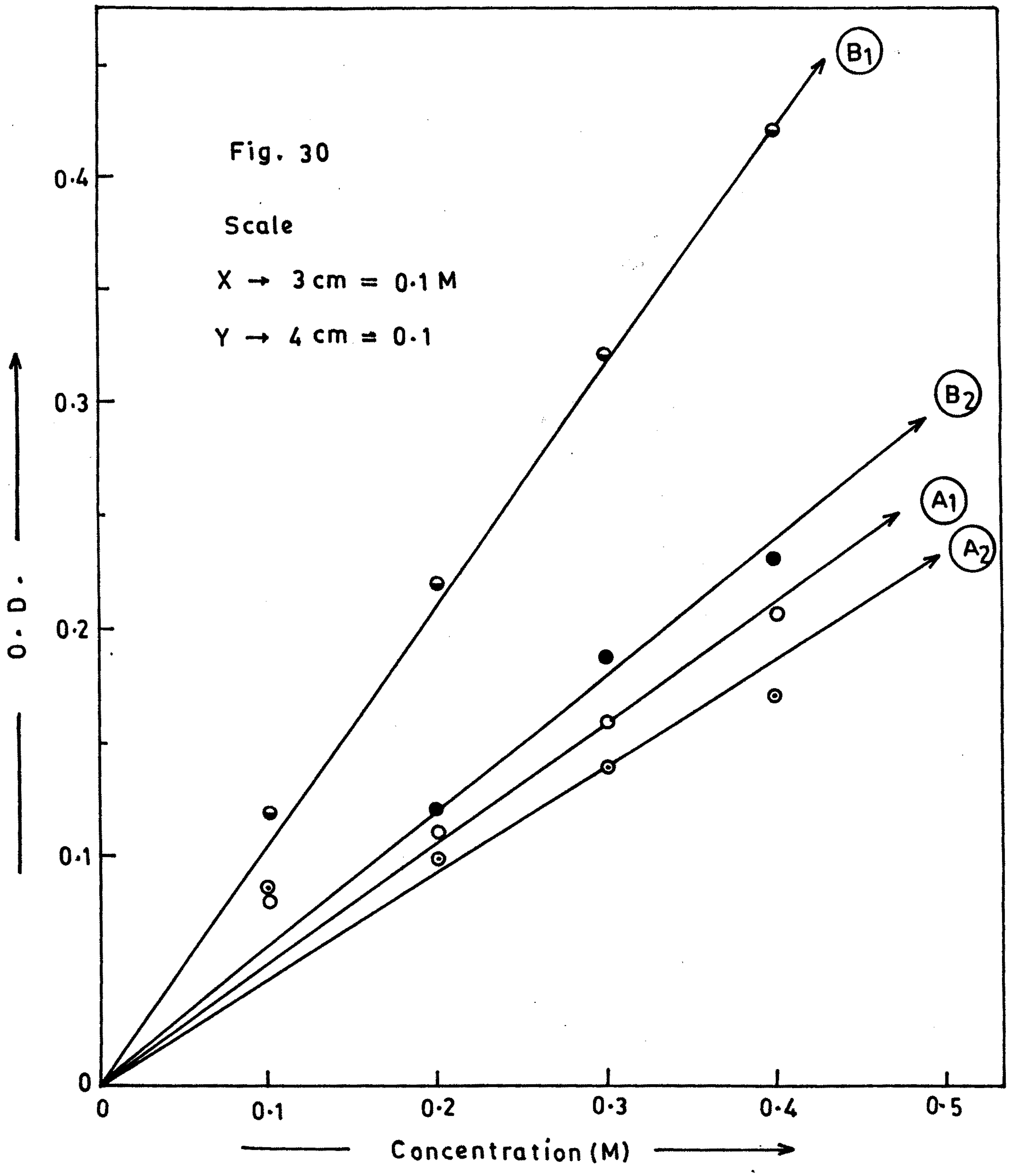


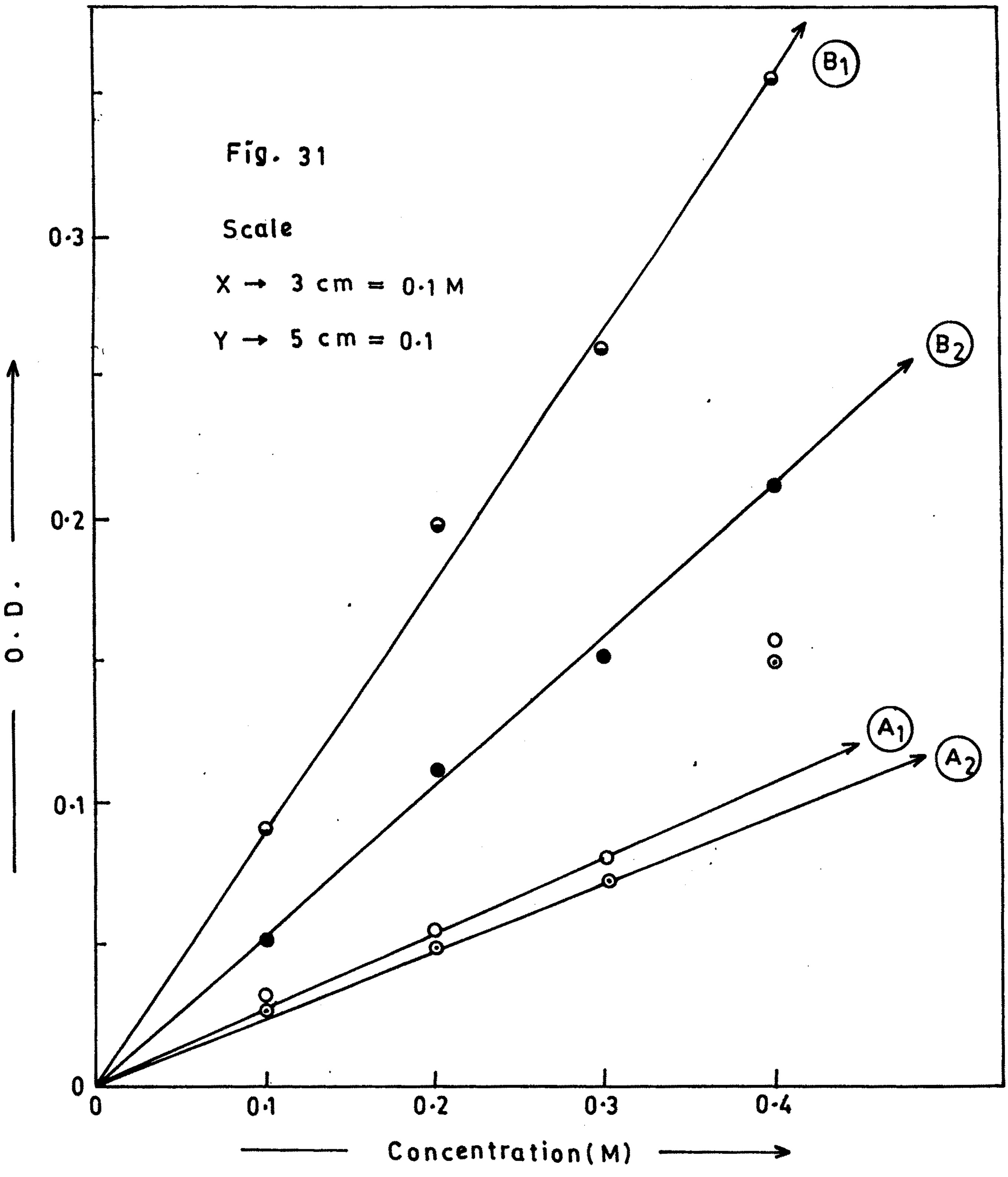
Fig. 30

A_1 Aniline in Chloroform → –NH stretching at 3385 cm^{-1}.

A_2 Aniline in Chloroform → –NH stretching at 3450 cm^{-1}.

B_1 Aniline in Acetonitrile → –NH stretching at 3388 cm^{-1}.

B_2 Aniline in Acetonitrile → –NH stretching at 3470 cm^{-1}.



(A_1) P-Toluidine in Chloroform → —NH stretching at 3370 cm^{-1} .

(A_2) ,, ,, ,, → ,, ,, ,, 3440 cm^{-1} .

(B_1) P-Toluidine in Acetonitrile → ,, ,, ,, 3380 cm^{-1} .

(B_2) ,, ,, ,, → ,, ,, ,, 3460 cm^{-1} .

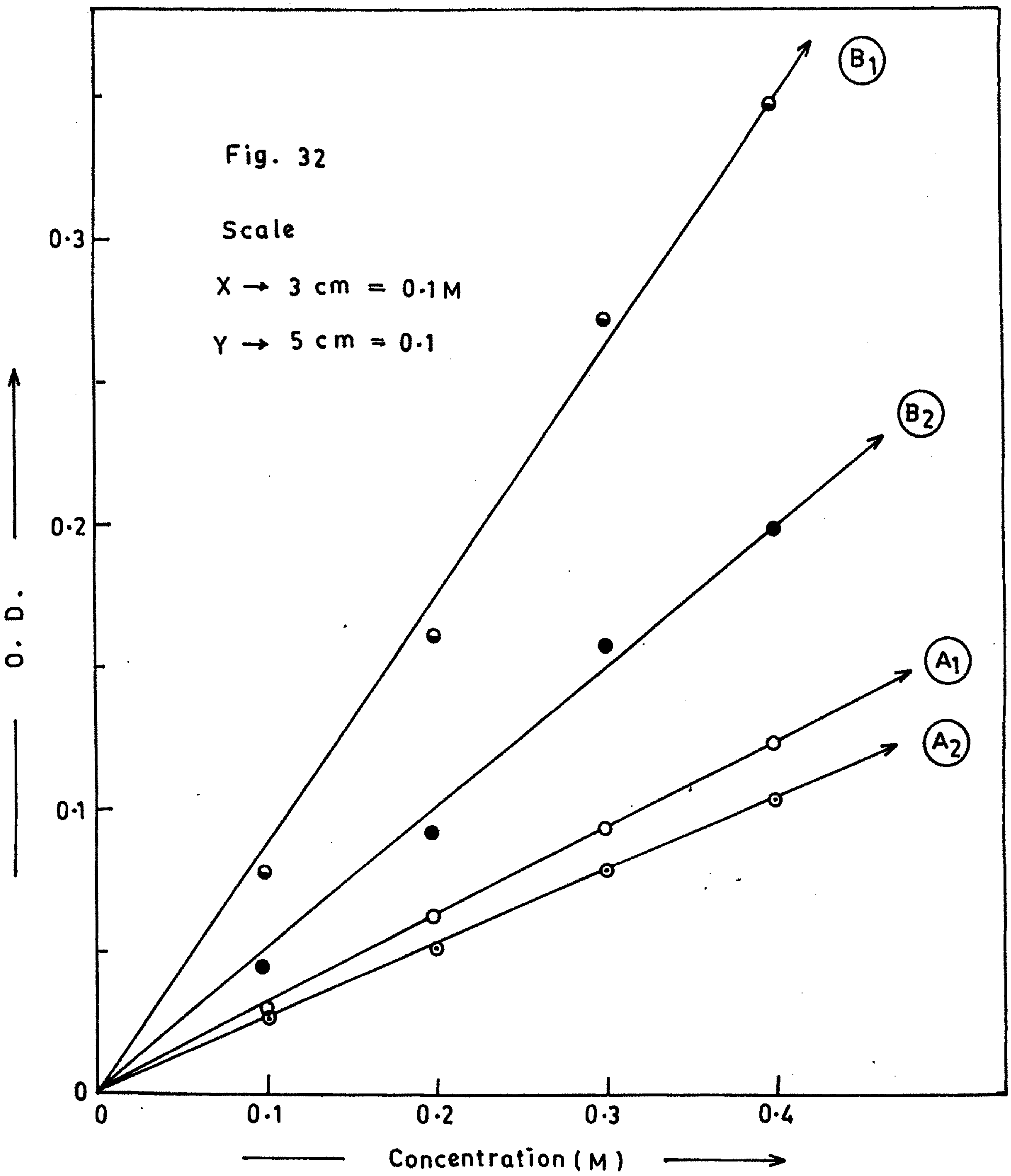


Fig. 32

(A1) P – Anisidine in Chloroform → –NH stretching at 3378 cm^{-1}.

(A2) ,, ,, ,, ,, → ,, ,, ,, 3450 cm^{-1}.

(B1) P – Anisidine in Acetonitrile → ,, ,, ,, 3370 cm^{-1}.

(B2) ,, ,, ,, ,, → ,, ,, ,, 3450 cm^{-1}.

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