CHAPTER-II

EXPERIMENTAL

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2.1

The "Infrared spectroscopy Technique" is commonly used to study the hyrogen bonding in some individual compounds or in their complexes. In the present work, the same technique has been used to study the hydrogen bonding in the complexes formed by (1:1) addition of P-nitrophenol and few amines.

2.2 MATERIALS AND THEIR PURIFICATIONS :

2.2.1. Chloroform :

The chloroform was washed with dilute sodium hydroxide and then with water, dried over fused calcium chloride and then over phosphorus pentoxide and fractionally distilled (1), (B.P. = 61°c).

2.2.2. Acetonitrile :

The acetonitrile was dried over calcium chloride, refluxed repeatedly over phosphorous pentoxide until no colour appeared on the oxide, distilled into freshly fused potassium carbonate, distilled from it and finally fractionally distilled (2), (B.P. = 56°c).

2.2.3 Acetone :

The acetone was treated with potassium permangnet solution and allowed it to stnad for 3 - 4 days. The mixture was distilled. The distilled product dried over calcium chloride and fractionally distilled (3), (B.P. = 81°c).

2.2.4 Aniline :

The Aniline was dried over calcium choride and distilled under reduced pressure (B.P. = 182°c).

2.2.5 Para-toluidine :

The solid para-toluidine is recrystallised from pure benzene and dried in vaccum dessicator. The purity was tested by melting point (M.P. = 43°c).

2.2.6 Para-anisidine :

The solid para-anisidine was recrystallised in pure benzene and dried in vaccum dessicator. The purity was tested by melting point. (M.P. = 58°c).

2.2.7 Para-Nitrophenol :

The solid para-nitrophenol was recrystallised from pure benzene and dried appropriately. The purity was confirmed by melting point (M.P. = 114°c).

2.3 PREPERATION OF SOLUTIONS :

The solutions were prepared as given below :

2.3.1 Para-nitrophenol (PNP) solutions in chloroform :

0.4M. PNP Solution - 1.39 g.of PNP dissolved and diluted to 25 ml. by chloform.

0.3M PNP Solution - 7.5ml. 0.4M PNP solution+2.5ml. chloroform

0.2M PNP Solution - 5ml. 0.4M.PNP Solution+5ml. chloroform.

0.1M PNP solution - 2.5ml. 0.4M PNP solution+7.5ml. chloroform.

2.3.2 Aniline solutions in chloroform :

0.4M Aniline solution - 1.83ml. aniline mixed and diluted to 50ml. by chloroform.

0.3M Aniline solution-7.5ml. 0.4M aniline solution+2.5ml.$CHCl_3$

0.2M Aniline solution-5ml. o.4M.aniline solution+5ml. $CHCl_3$

0.1M Aniline solution-2.5ml.0.4M aniline solution+7.5ml.$CHCl_3$.

2.3.3 Para-toluidine (PT) solutions in chloroform($CHCl_3$).

0.4M PT solution-1.072 g. of PT dissolved and diluted to 25ml. by chloroform.

0.3 M PT. Solution-7.5ml.0.4M PT solution+2.5ml. $CHCl_3$.

0.2M PT. Solution-5ml. 0.4M PT Solution+5ml. $CHCl_3$.

0.1M PT Solution-2.5ml. 0.4M PT solution+7.5ml. $CHCl_3$.

2.3.4 Para-anisidine (PA) solutions in chloroform

0.4M PA solution-1.23 g. of PA dissolved and diluted to 25ml. by chloroform.

0.3M PA. solution-7.5ml. 0.4M PA solution+2.5ml. $CHCl_3$.

0.2M PA. Solution-5ml. 0.4M PA Solution+5ml. $CHCl_3$.

0.1 M PA.Solution-2.5ml.0.4M PA solution+7.5ml. $CHCl_3$.

By using the same procedure 0.4M, 0.3M, 0.2M, 0.1M. solutions of P-nitrophenol, aniline, P-toluidine, and P-anisidine were prepared in the solvents ACETONITRILE and ACETONE respectively.

2.4

All weighings were made on a single pan balance having an accuracy of ± 0.1mg.. The volumetric apparatus were cleaned and calibrated. Appropriate precautions were taken to remove moisture.

2.5 INSTRUMENTATION :

The general principles of infrared spectrometer construction and the expected performance of commercial instruments, as well as a suitable basis for assesing them, has been discussed by Williams (5), Hawes and GAllaway (6), and Golay (7).

In the present work the infrared spectra of the compounds and complexes have been obtained with the help of Perkin Elmer - 783 infrared spectrophotometer which can be described in brief as follows :

2.5.1 PERKIN ELMER - 783 INFRARED SPECTROPHOTOMETER :

The 783 spectrophotometer provides a continous record of infrared transmitance or absorbance of a sample as a function of frequency (expressed in wave number units). A chart is driven in synchronism with the monochromator so that a pen moving latterally across the chart, records the smaple transmitance or absorbance as a function of wave number.

The wave number scan motor drives the grating monochromator scan mechanism, which is synchronised with the recorder drive by the abscissa microprocessor so that the wavenumber settings are thus accurately reproduce on the chart.

The radiation emitted by the source is devided into two beams. One beam passes through the sample, which absorbs radiation of wave number corrosponding to its characteristic molecular vibrational frequencies, while the other serves as a reference. In the photometer section of the two beams are combined by a rotating sector mirror to form a single beam consisting of pulses of radiation from the sample and reference beams. The combined pulses beam passes into the monochromator. Where it is dispersed by the gratting into its spectral components. As the gratting

is rotated the dispersed spectrum is scanned across the monochromator exit slit. The mechanical width of the monchromator slit determined the width of the wave number band emerging from monochromator.

Decreasing the slit width therefore decreases both this band width (i.e. improves the resolution) and the intensity of the imerging radiation (i.e. decreases the signal to noise ratio). The slit width is selected by means of the slit switch on the front panel. After leaving the monochromator, the radiation passes through one set of optical filters, the correct filter being automatically selected for the spectral region being scanned. This filter rejects unwanted radiation diffracted from the gratting at the same angle as the component of the desired wavenumber. Finally the transmitted radiation is foccused on to the thermocouple detector.

The resultant signal from the detector is applied via a pure amplifier to an analogue to digital converter. The digital data produced are applied to the ordinate microprocessor, which control the ordinate function of the instrument. The microprocessor output is converted to an analogue form, which is applied to the rervo system.

To maintain an uniform signal to noise response for the instrument, the detector output is maintained at an approximately constant level. Over the range of the instrument by programing the widths of the monochromator slit by means of cam drive.

2.5.2 SPECIFICATION OF THE INSTRUMENT :

The following specification refers to the full range scan mode of the 783 spectrophotometer, the figures quoted corrospond to maximum tolerance limits permitted in the manufacture of the instrument. Calibration was made using a polystyrene film.

Principle	: Double beam, ratio recording with duel microprocessor electronics and single beam facility. The model 783 includes per sample chopping.
Optics	: F/5 filter gratting monochromator purgeable.
Abscissa range	: 4000 cm^{-1} to 200 cm^{-1}.
Abscissas accuracy	: 4000 cm^{-1} to 2000 cm^{-1} ± 4 cm^{-1} 2000 cm^{-1} to 200 cm^{-1} ± 2 cm^{-1}
Abscissa repeatability	: Better than ± 0.05 cm^{-1}± run to run.

Abscissas expansion : x 0.25, x 0.5, x 1, x 5.

Chart dispersion cm^{-1}/cm :

Range	Expansion			
	x0.25	x0.5	x1	x5
4000-2000 cm^{-1}	400	200	100	20
2000-200 cm^{-1}	200	100	50	10

Ordinate accuracy : ± 0.2 % T linearity.

Ordinate repeatability : ± 0.05 % T.

Ordinate expansion : From 0.1 to 100 in steps of 0.1 by keyboard entry.

I_0 corrector : Standard feature.

I_0 fatness : ± 0.5 % T, ± 1.5 % T below 300 cm^{-1}

I_0 noise : Less than 0.5 % on medium slit and 6. min. scan.

Scan times : 5 nominal times for each of 4 slit programmes. 3,3,6(5) and 30(25)minutes. with x0.5,x1,x2,x4 and x16 multiples.

Scan speed(cm^{-}_1/cm)

Range	Scan time (nominal)		
	3min.	6min.	30min.
4000-2000 cm^{-}_1	2000	1000	200
2000-200 cm^{-1}	1000	500	100

Time drive speeds : 0.25, 0.5, 1.0, and 5.0 cm/min.

Slit programmers :

Resolution at 1000 cm^{-1}	Slit setting	Resolution
	1 wide	5.5 cm^{-1}
	2 wide	4.0 cm^{-1}
	4 narrow	1.2 cm^{-1}

Stray light (purged)	: 4000-420 cm^{-1} less than 0.5 % T. 420-280 cm^{-1} less than 1 % T. 280-250 cm^{-1} less than 2 % T. 50-200 cm^{-1} less than 3 % T.
"Flow Chart" recorder	: Microprocessor controlled analogue ordinate.
Chart Size (calibrated)	: 15 cm^{-1}x56 cm-40% roll(corrosponds to x 1 abscissa expantion). 15 cm^{-1}x28 cm^{-1}-75 % roll corrosponds to x0.5 abscissa expantion.
Ordinate readout	: 0 to 1V (full scale).
Overall dimensions	: 980 mm wide x 535 mm deep x 400 mm high.
Weight	: 65 Kg.
Voltage requirement	: 50 H_z version, 200 to 250 V
Power requirement	: 200 VA.
Ambient temperature range	: 15°c to 35°c
Relative humidity	: 75 % maximum.
Specific accessaries.	: Multisampler. Interface.

2.6 INFRARED SPECTRA OF THE SAMPLES :

Sodium chloride cell with path length 0.01cm. was used as the sample holder. With the help of Perkin-Elmer-783 infrared spectrophotometer. IR spectra of the following samples were obtained.

SOLVENT CHLOROFORM

Pure chloroform		
Para-nitrophenol solution	:	0.1M, 0.2M, 0.3M, 0.4M
Aniline solution	:	0.1M, 0.2M, 0.3M, 0.4M
[Para-nitrophenol solution+Aniline solution (1:1)]	:	0.1M, 0.2M, 0.3M, 0.4M
Para-toluidine solution	:	0.1M, 0.2M, 0.3M, 0.4M
[Para nitrophenol solution + para toluidine solution (1:1)]	:	0.1M, 0.2M, 0.3M, 0.4M
Para anisidine solution	:	0.1M, 0.2M, 0.3M, 0.4M
[Para-nitrophenol solution + para anisidine solution (1:1)]	:	0.1M, 0.2M, 0.3M, 0.4M

SOLVENT ACETONIRTILE

Pure aetonitrile	:	
Para nitrophenol solution	:	0.1M, 0.2M, 0.3M, 0.4M
Aniline solution	:	0.1M, 0.2M, 0.3M, 0.4M
[Para-nitrophenol solution+Aniline solution (1:1)]	:	0.1M, 0.2M, 0.3M, 0.4M
Para-toluidine solution	:	0.1M, 0.2M, 0.3M, 0.4M
[Para nitrophenol solution + para toluidine solution (1:1)]	:	0.1M, 0.2M, 0.3M, 0.4M
Para anisidine solution	:	0.1M, 0.2M, 0.3M, 0.4M
[Para-nitrophenol solution + para anisidine solution(1:1)]	:	0.1M, 0.2M, 0.3M, 0.4M

SOLVENT ACETONE

Pure acetone	:	
Paranitrophenol solution	:	0.4M
Aniline solution	:	0.4M
[Para-nitrophenol solution+Aniline solution (1:1)]	:	0.4M
Para-toluidine solution	:	0.4M
[Para-nitrophenol solution + para toluidine solution (1:1)]	:	0.4M
Para-anisidine solution	:	0.4M
[Para-nitrophenol solution + para anisidine solution(1:1)]	:	0.4M

The spectra of solids were obtained using KBr pellet technique. The A.R.anhydrous dried KBr was used for preparation of pellet. The pellets were prepared using a pressure pump. The thickness of the pellet was of the order of 1 to 2 mm.. The solid spectra of P-nitrophenol, P-toluidine and P-anisidine are given in figures 5, 6, & 7.

The liquid sample spectra of three pure solvents e.g. chloroform, acetonitrile and acetone, simmilarly 0.4M P-nitrophenol solutions in three solvents, aniline solutions (0.4M) in three solvents, P-toluidine solutions (0.4M) in three solvents, [P-nitorphenol+aniline] 1:1 adduct in three solvents, [P-nitrophenol+P-toluidine] 1:1 adduct in three

solvents and [P-nitrophenol+P-anisidine] 1:1 adduct in three solvents are given in figures 2 to 28 respectively.

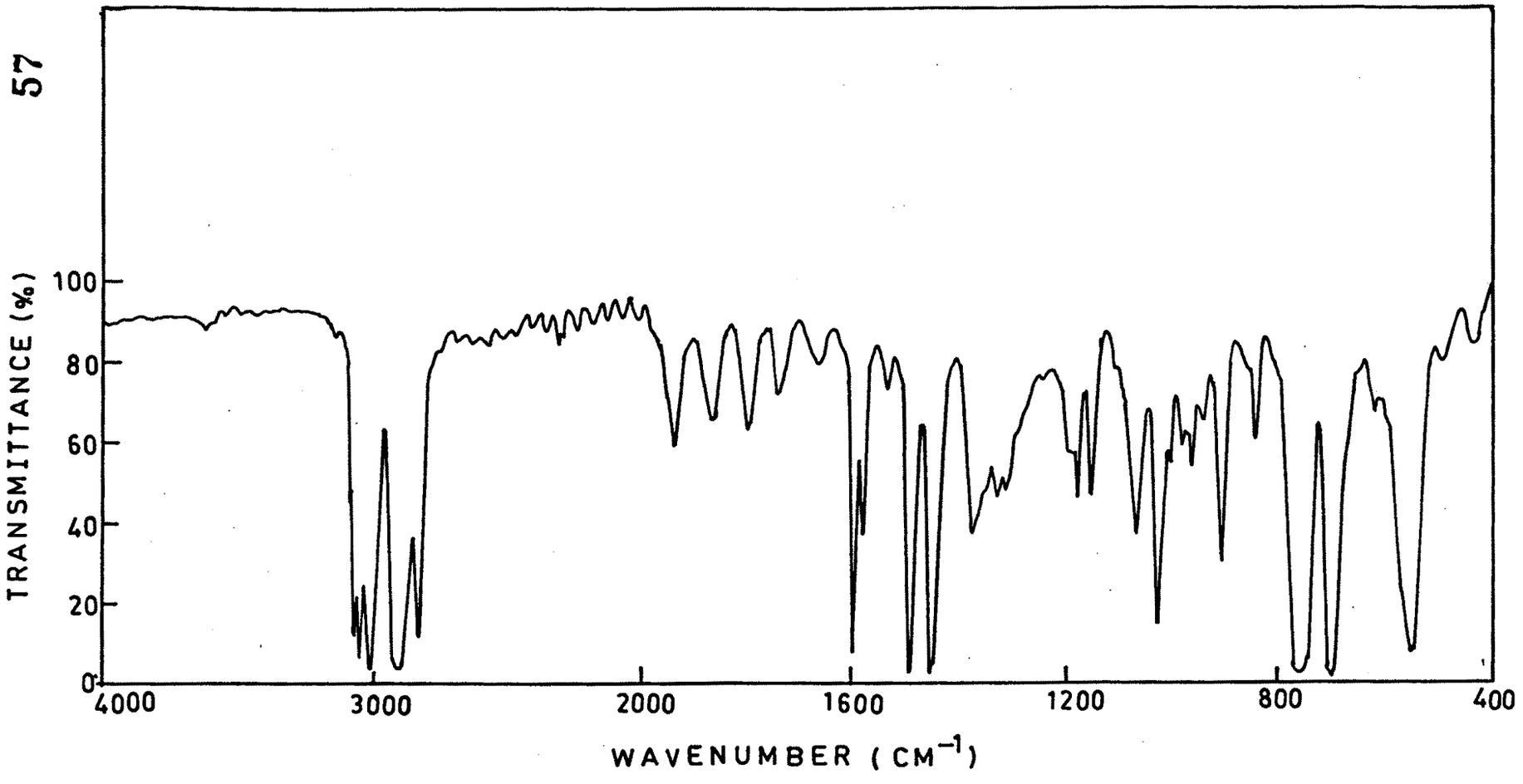

Fig. 1 — Infrared absorption spectrum of a thin polystyrene film.

(note that the abscissa scale changes at 2000 cm^{-1})

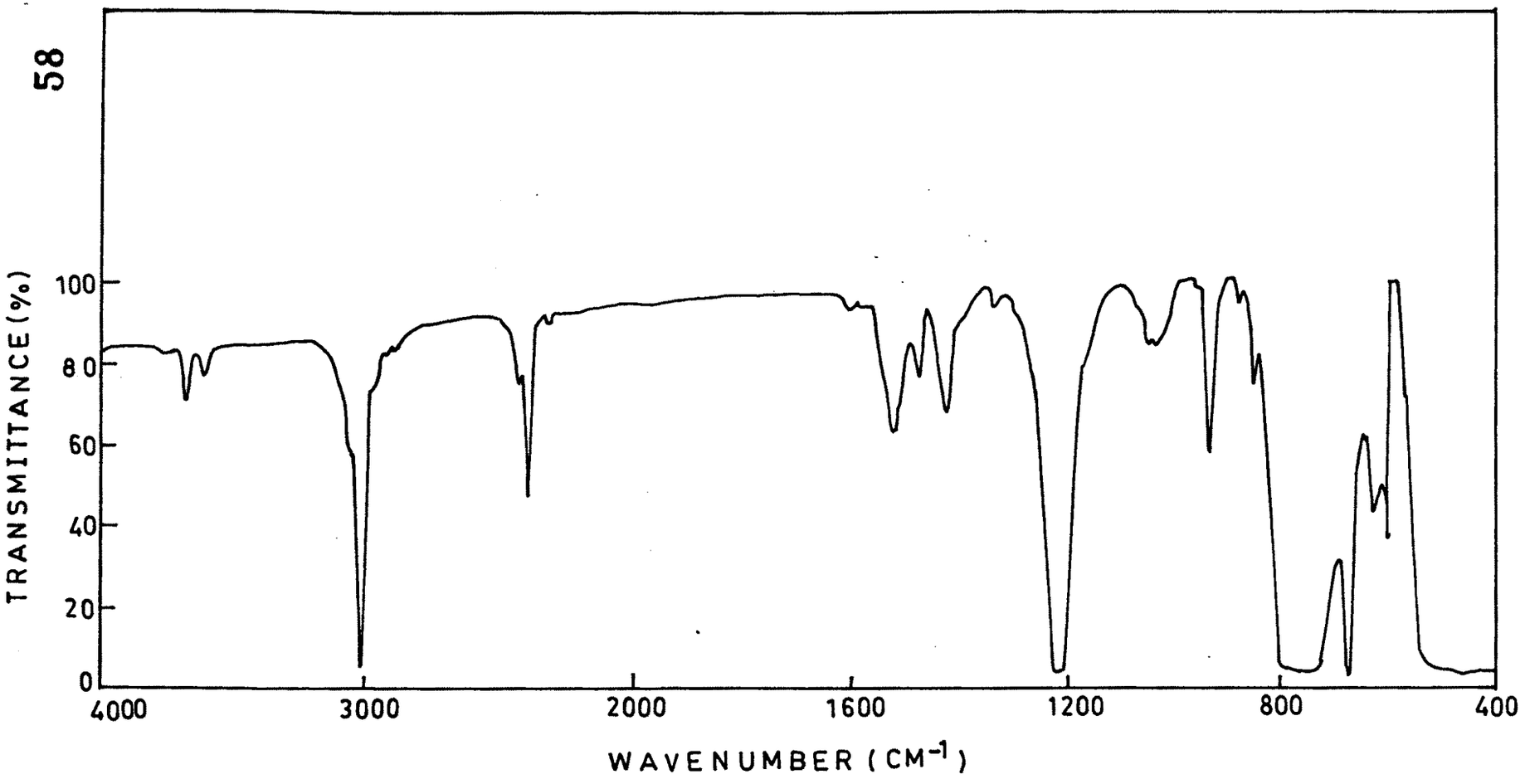

Fig. 2 — IR absorption spectrum of Chloroform.

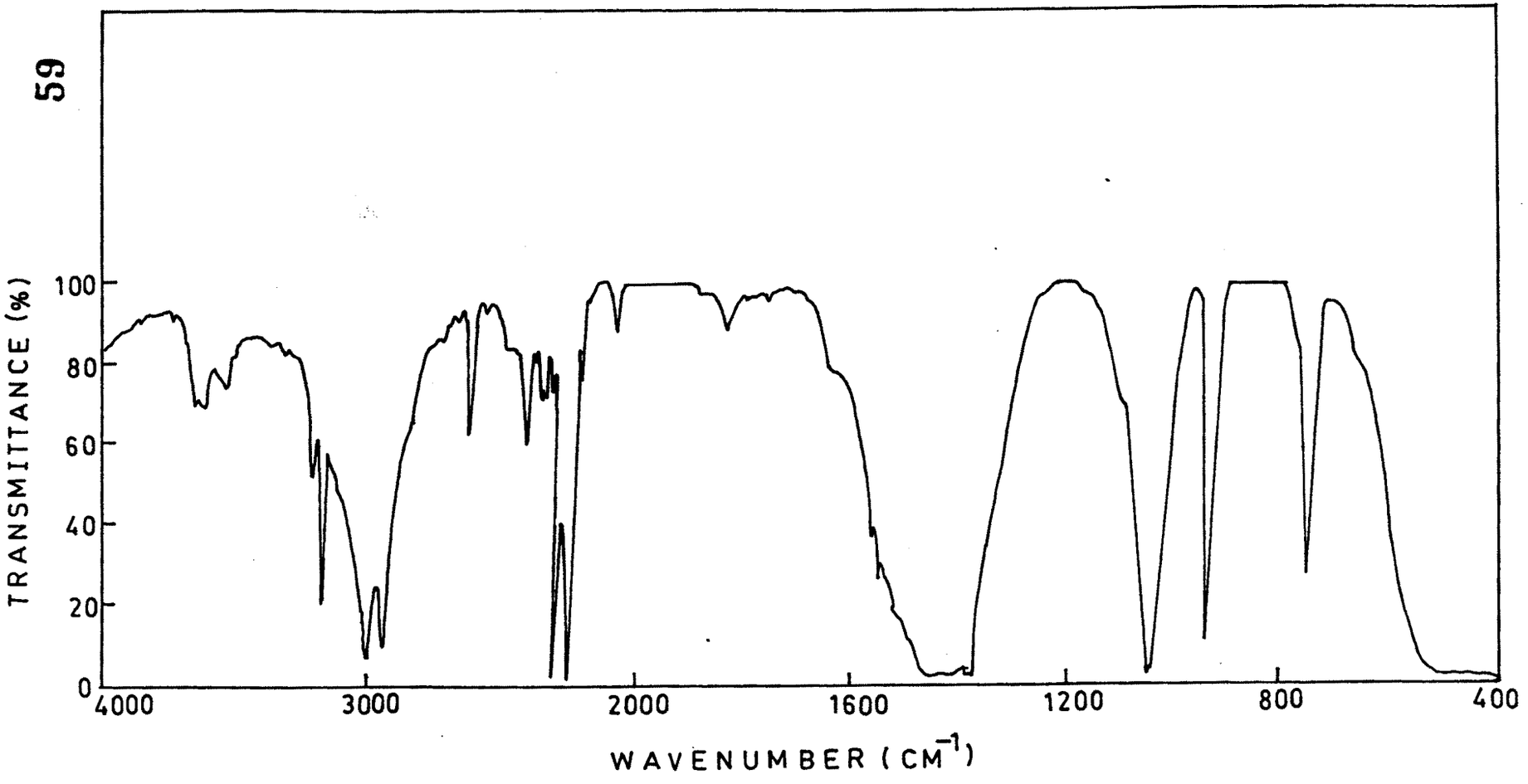

Fig. 3 — IR absorption spectrum of Acetonitrile.

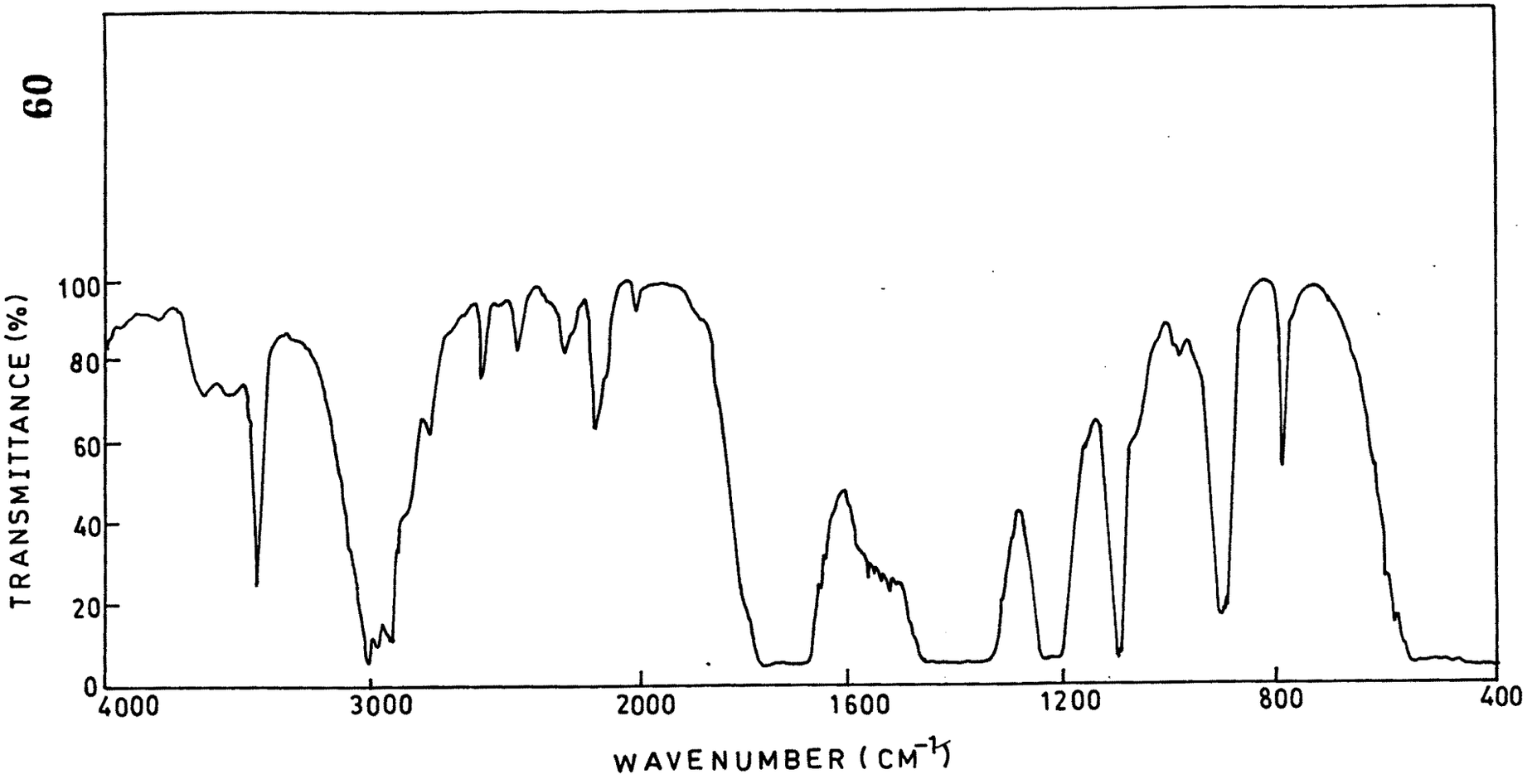

Fig. 4 — IR absorption spectrum of Acetone.

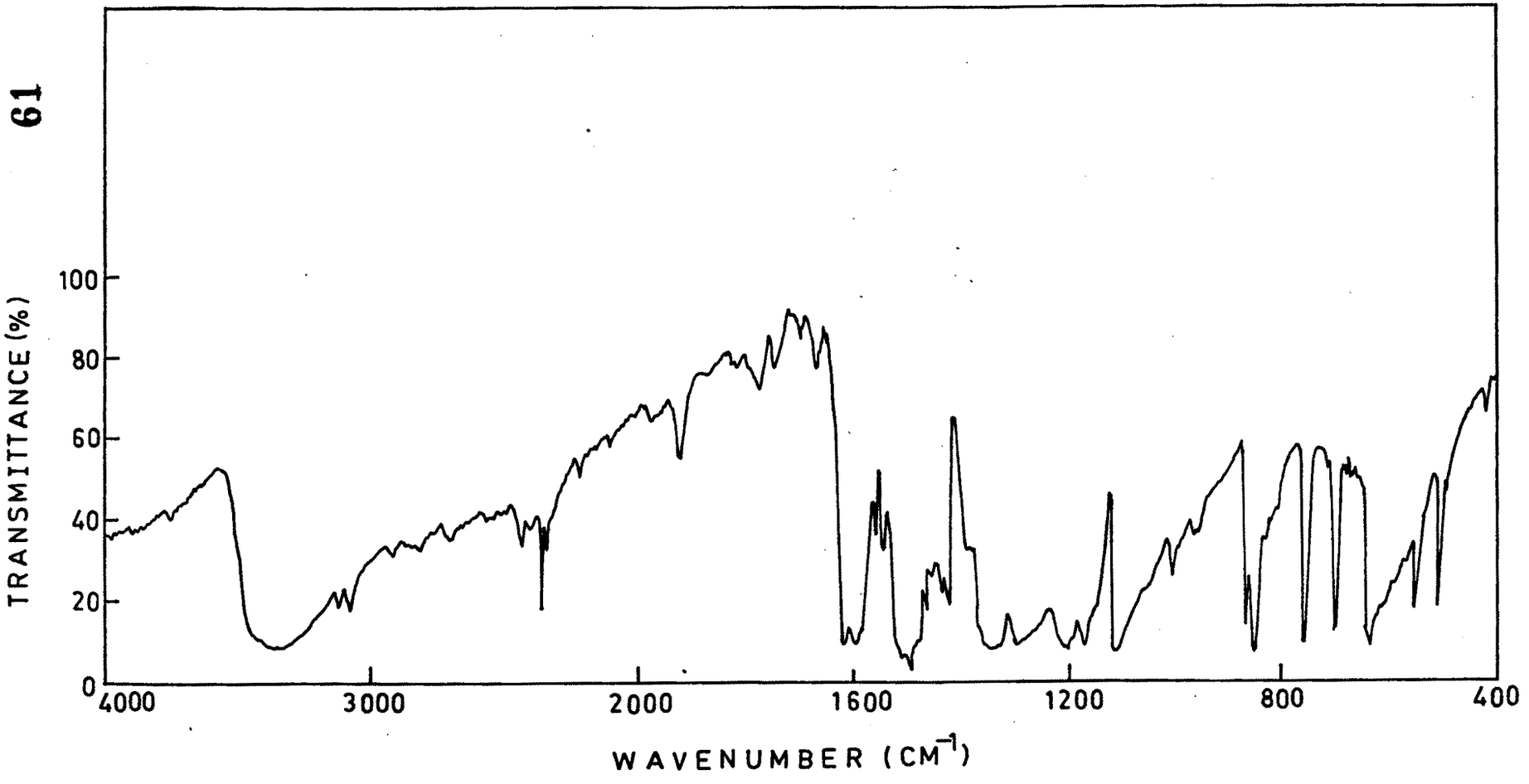

Fig. 5 — IR absorption spectrum of p-Nitrophenol (solid) .

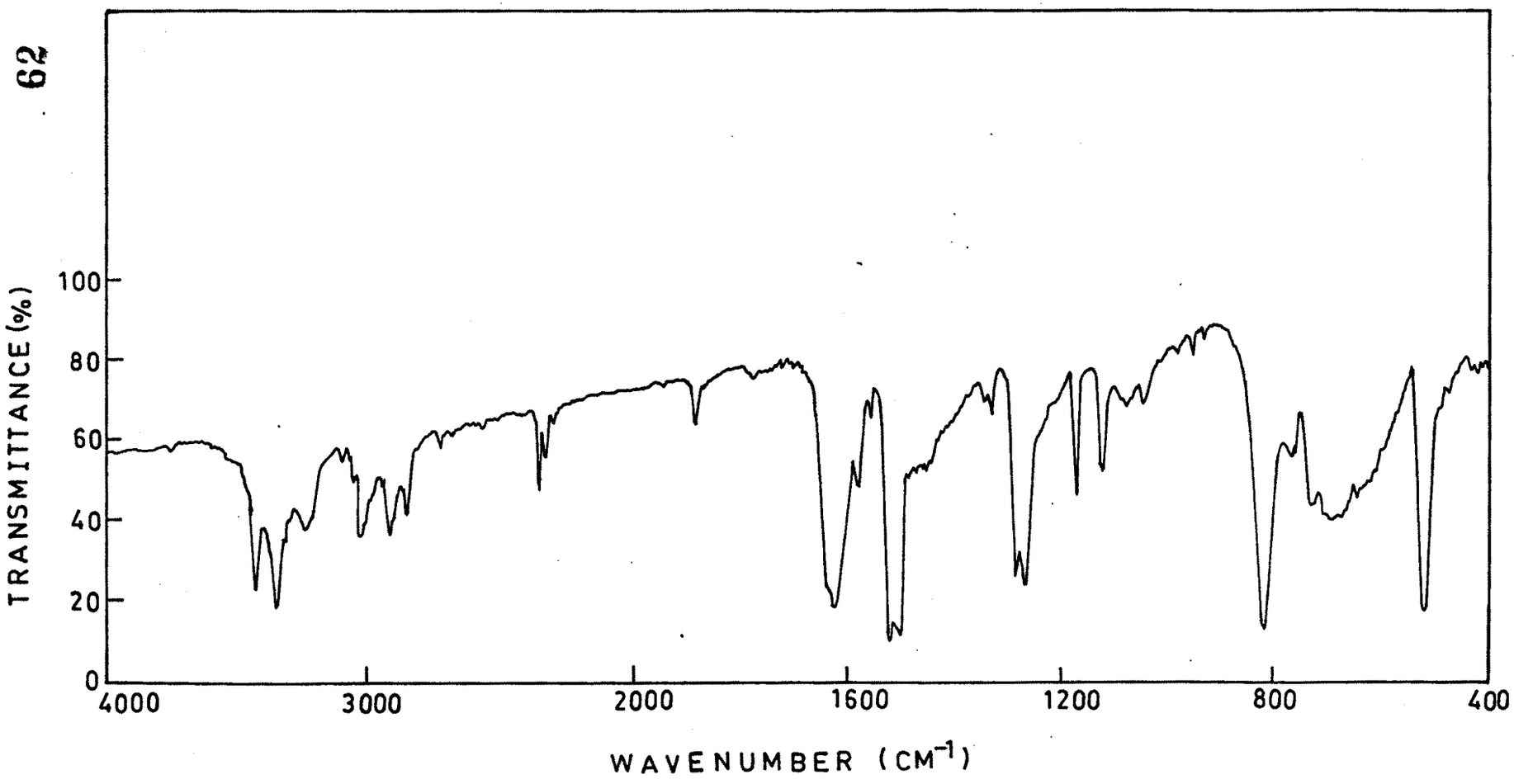

Fig. 6 — IR absorption spectrum of p—Toluidine (solid).

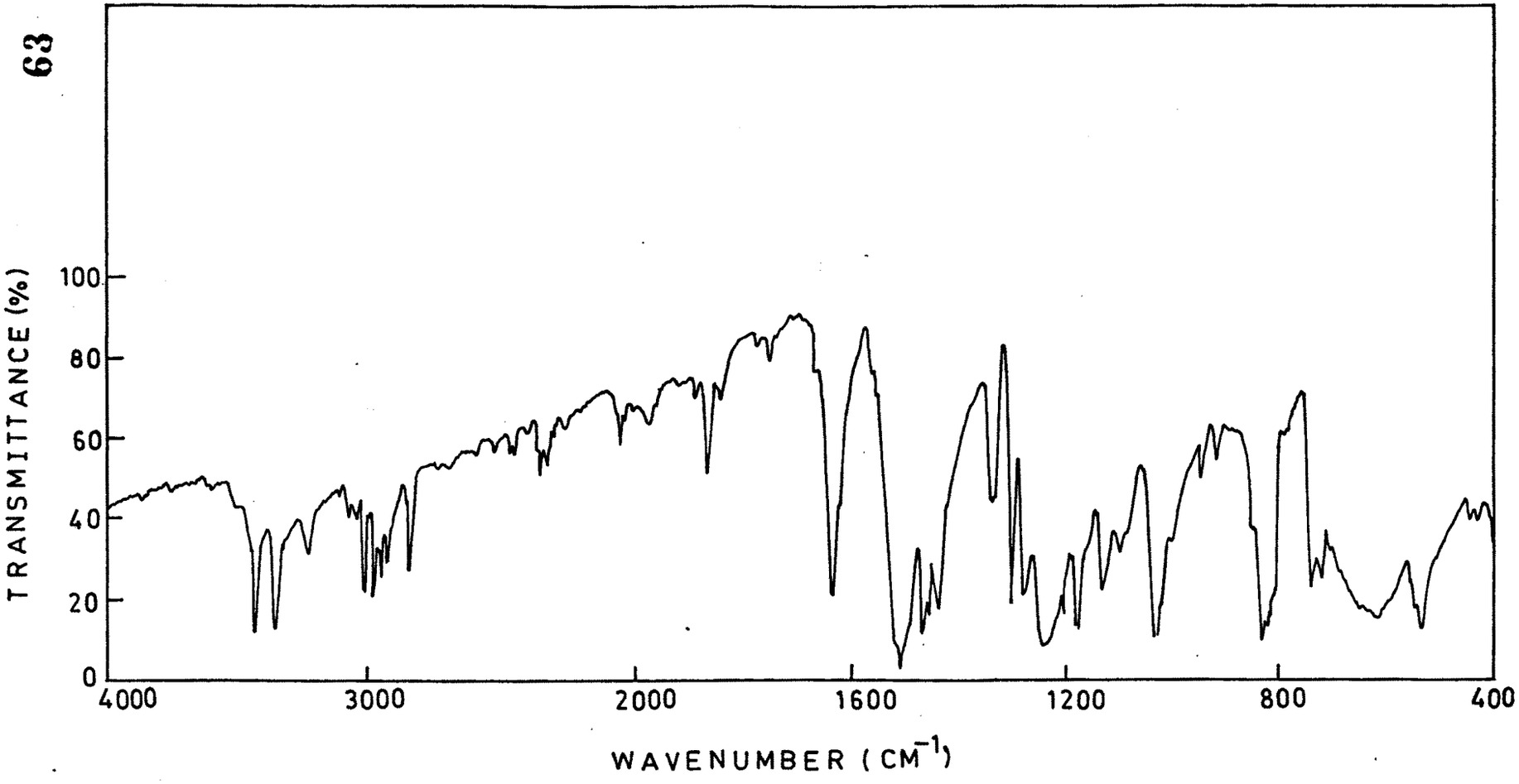

Fig. 7 — IR absorption spectrum of P—Anisidine (solid).

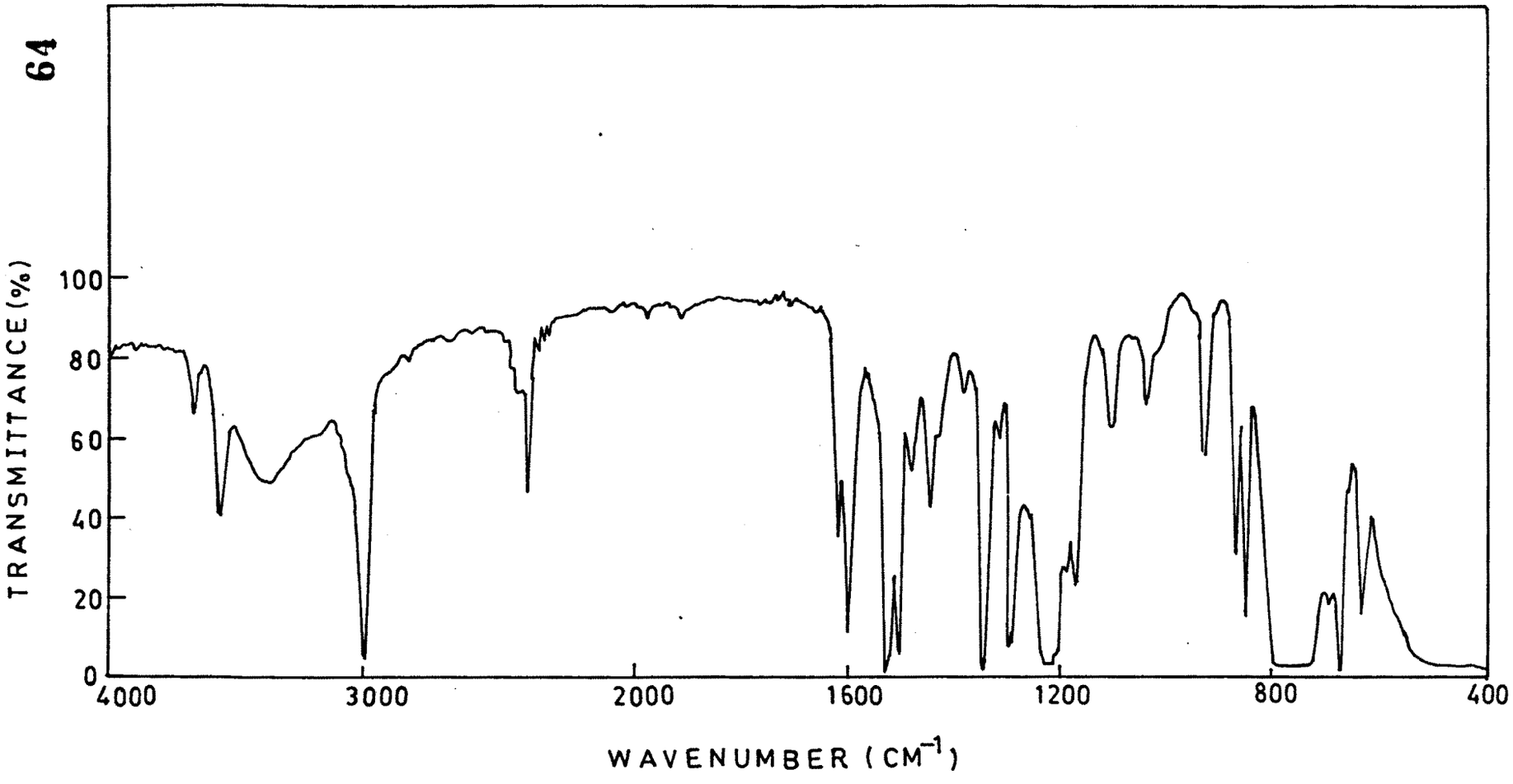

Fig. 8 — IR absorption spectrum of 0·4M solution of p-Nitrophenol in Chloroform.

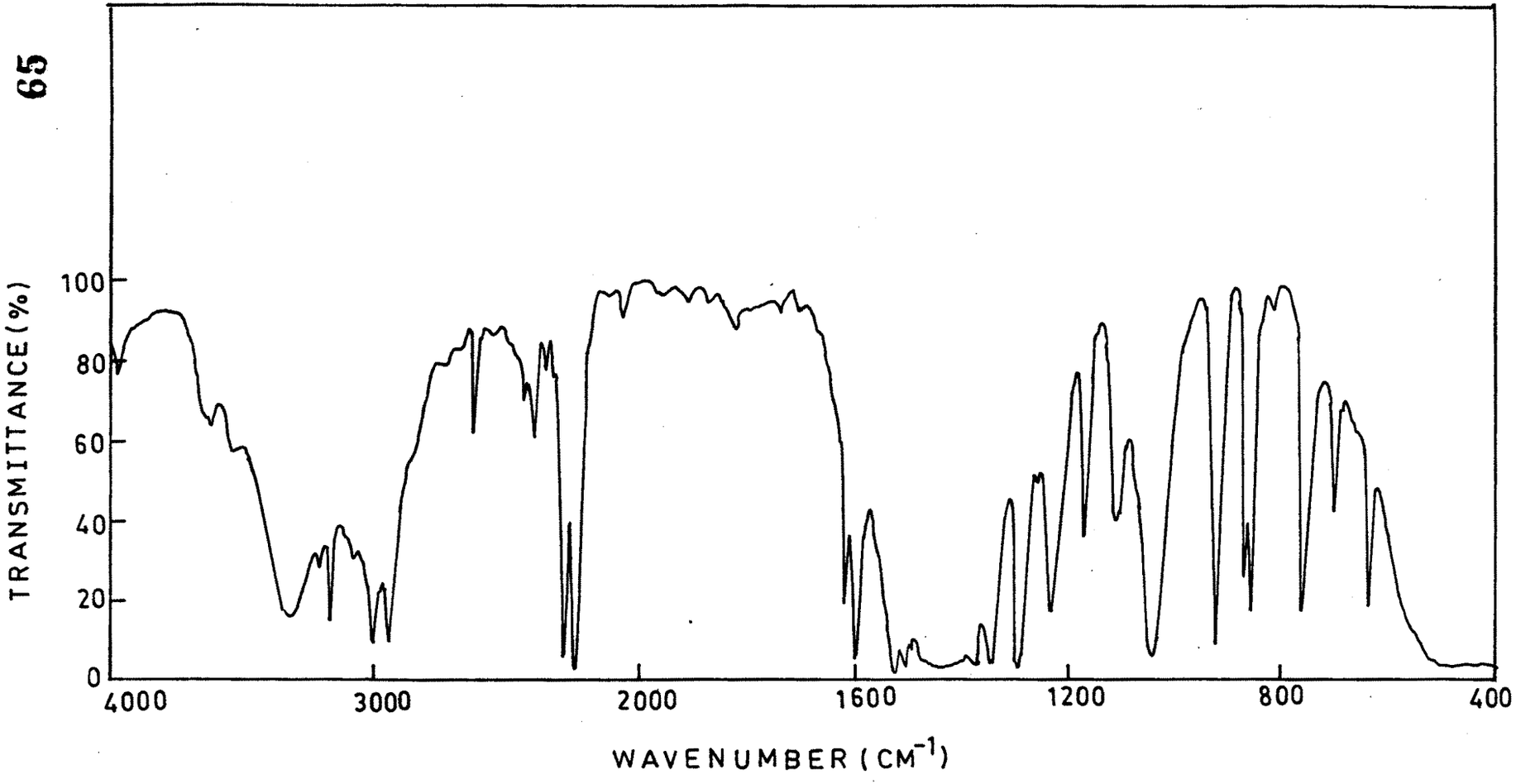

Fig. 9 — IR absorption spectrum of 0·4M solution of p-Nitrophenol in Acetonitrile.

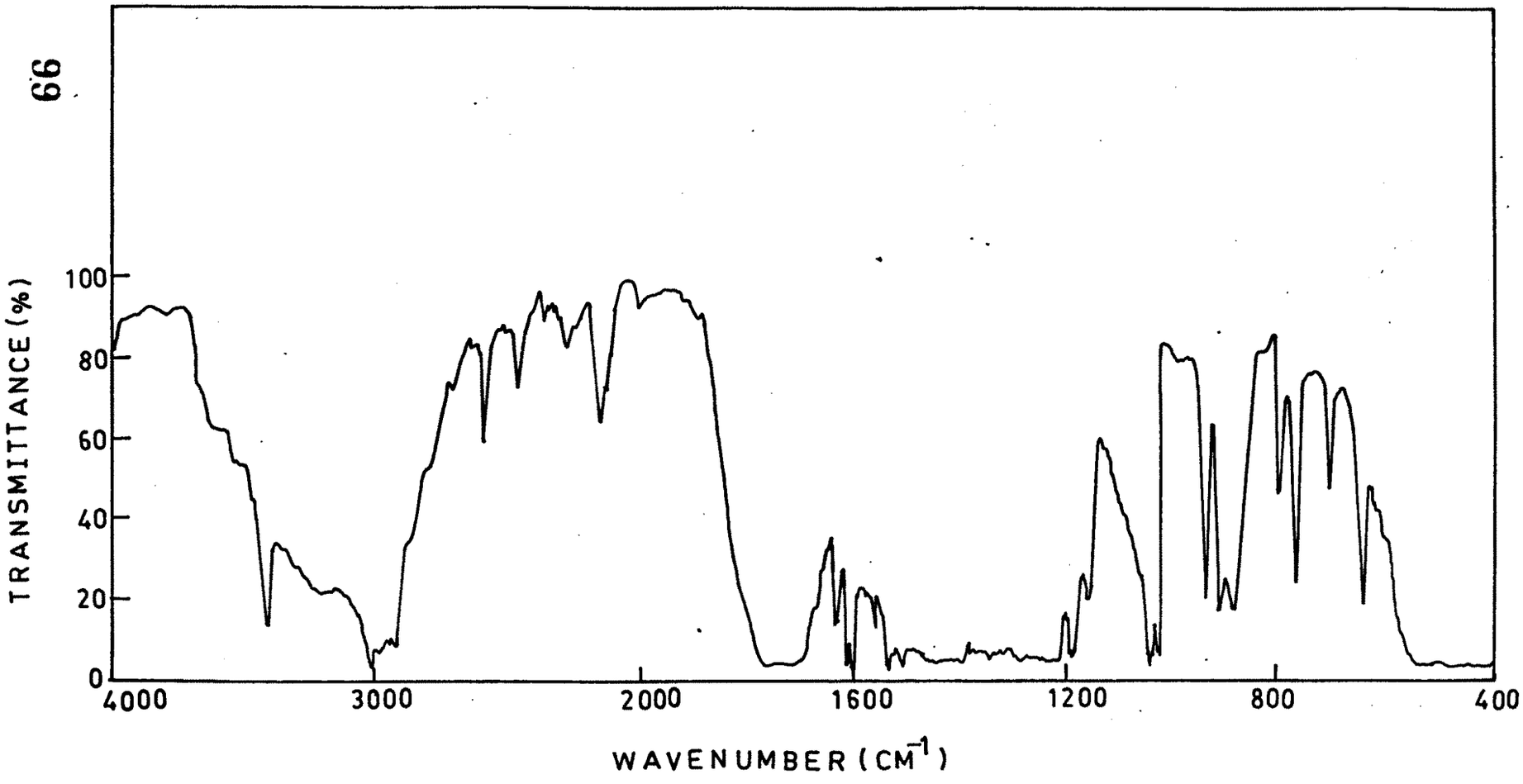

Fig. 10 — IR absorption spectrum of 0·4 M solution of p—Nitrophenol in Acetone.

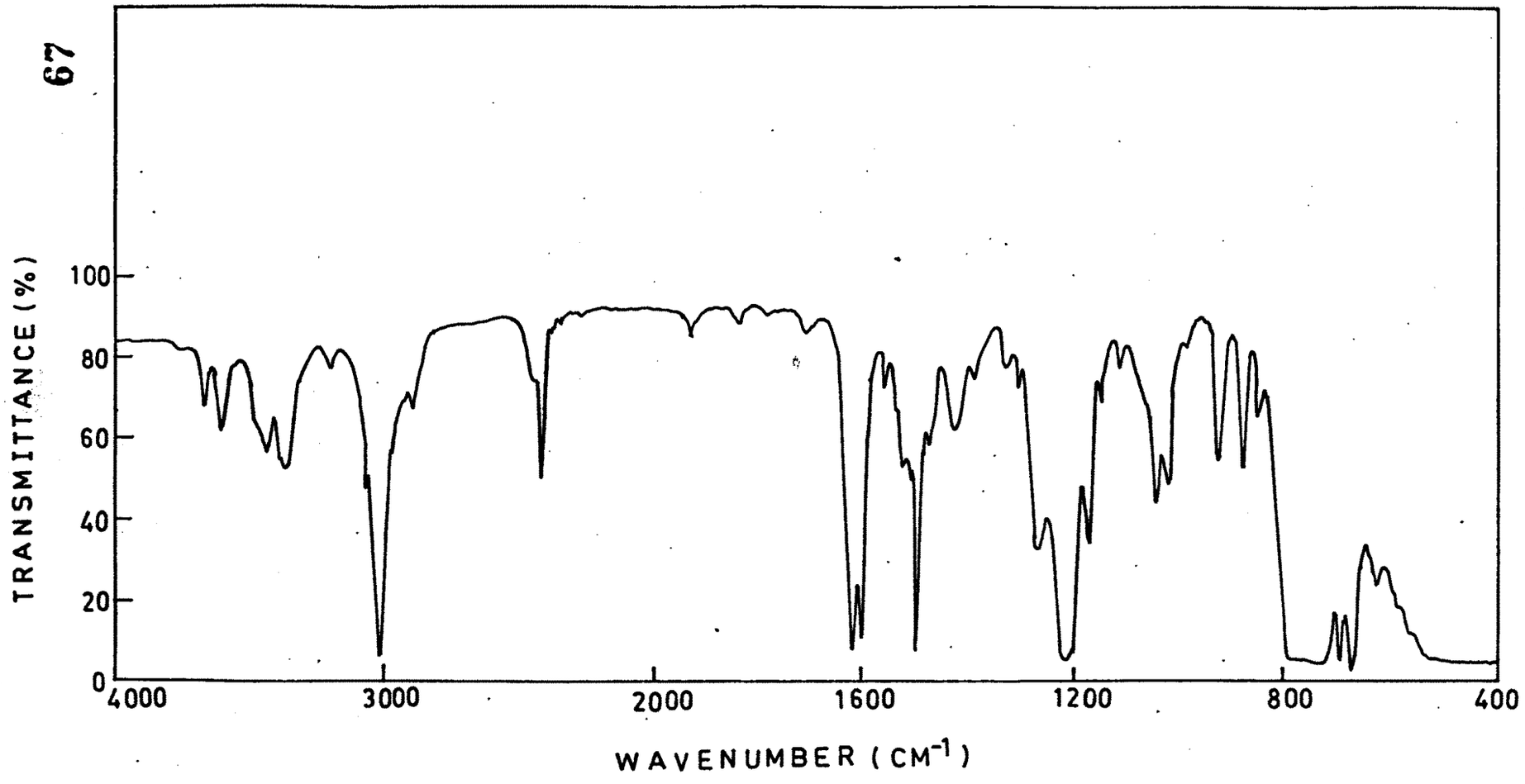

Fig. 11 — IR absorption spectrum of 0·4 M solution of Aniline in Chloroform.

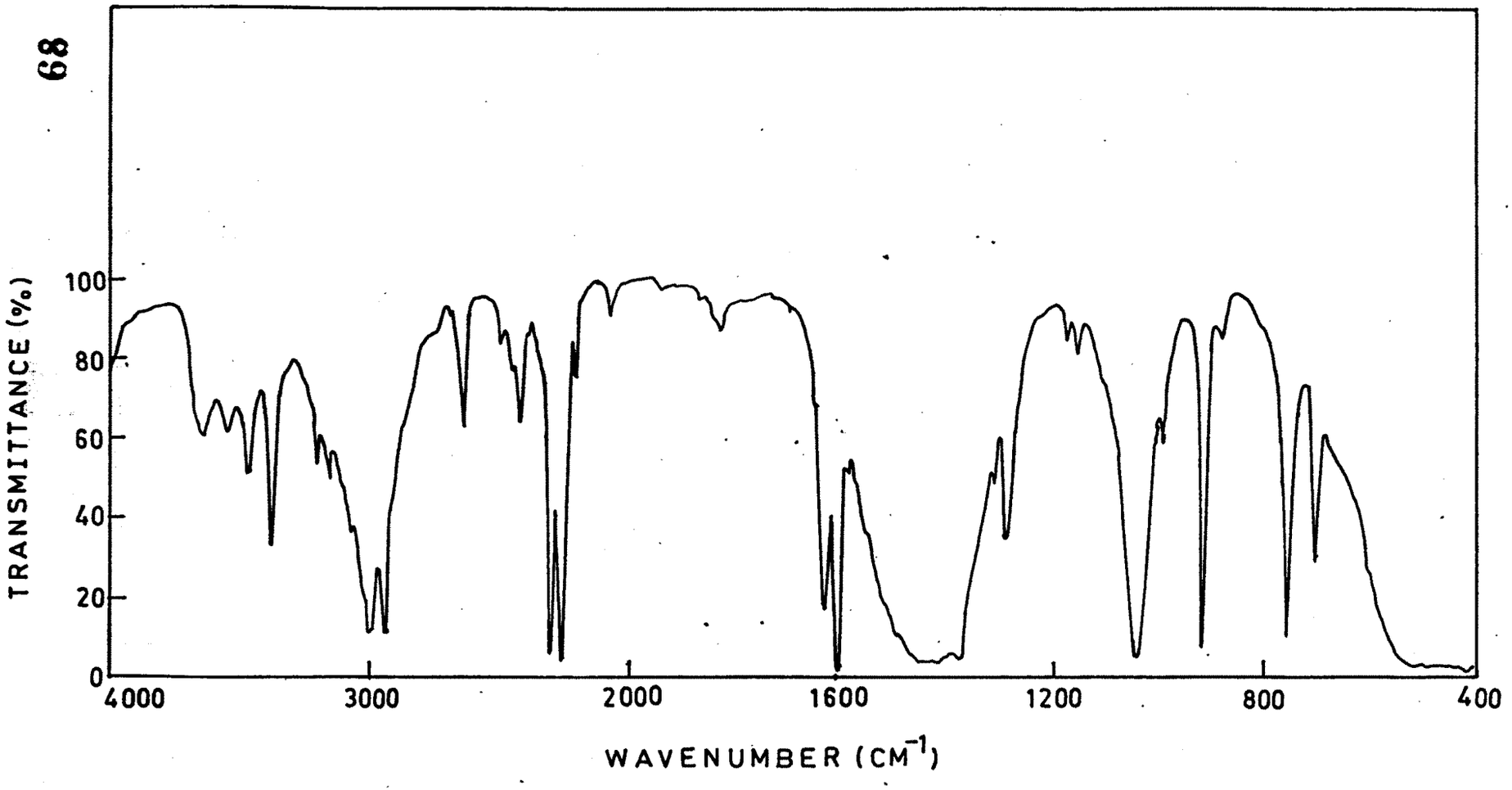

Fig.12 — IR absorption spectrum of 0·4 M solution of Aniline in Acetonitrile.

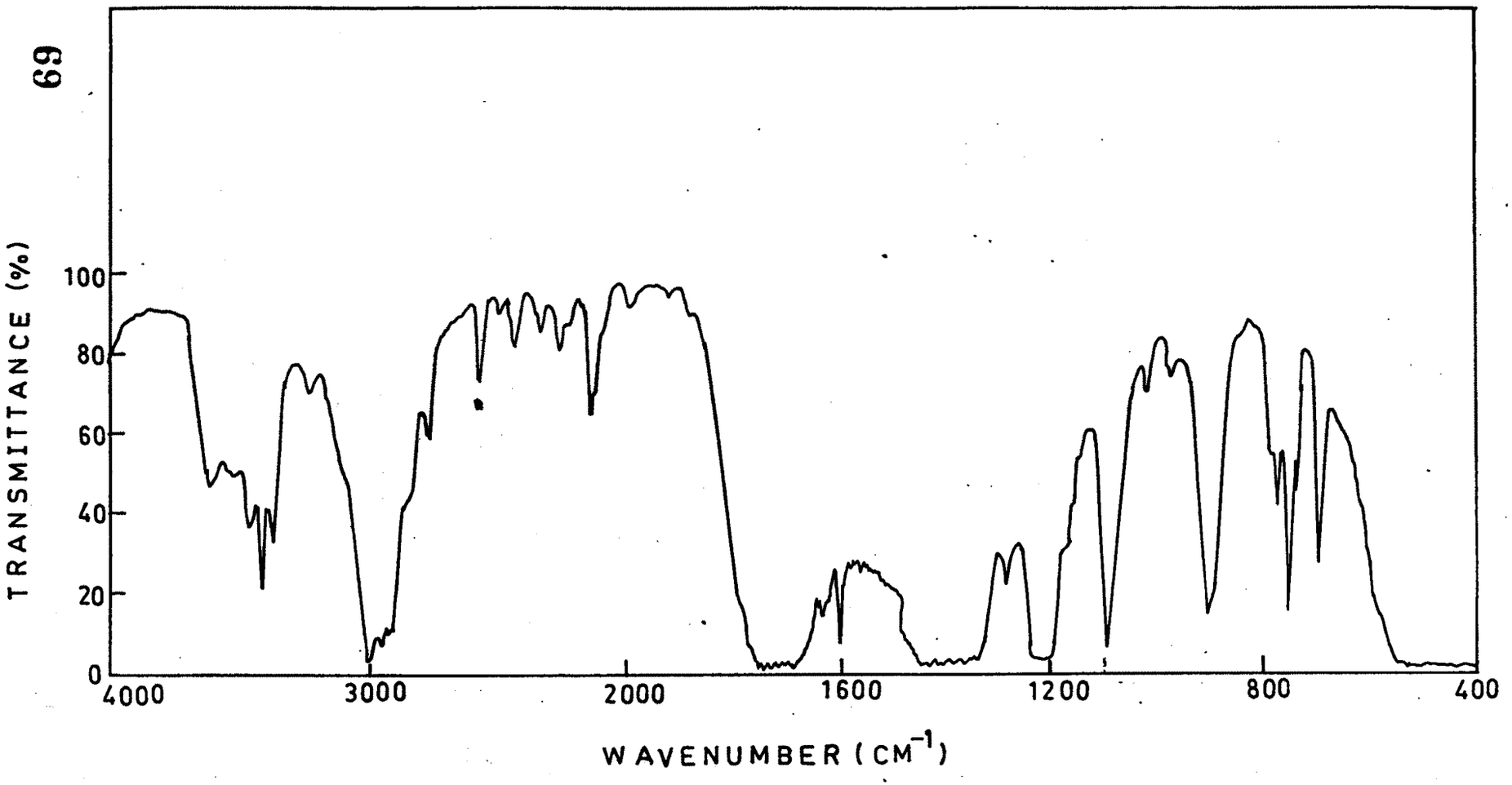

Fig. 13 — IR absorption spectrum of 0·4 M solution of Aniline in Acetone.

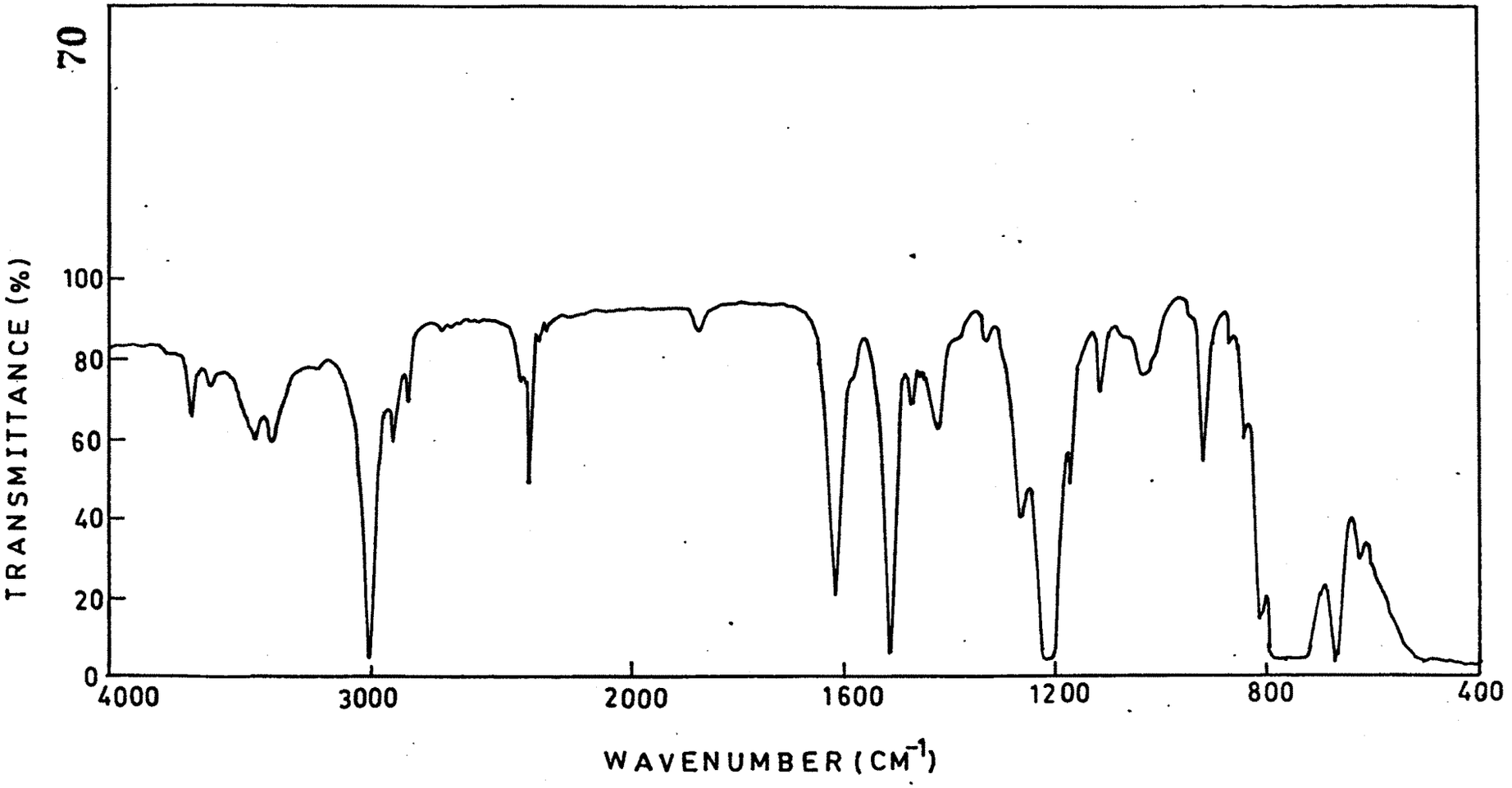

Fig. 14 — IR absorption spectrum of 0·4 M solution of p—Toluidine in Chloroform.

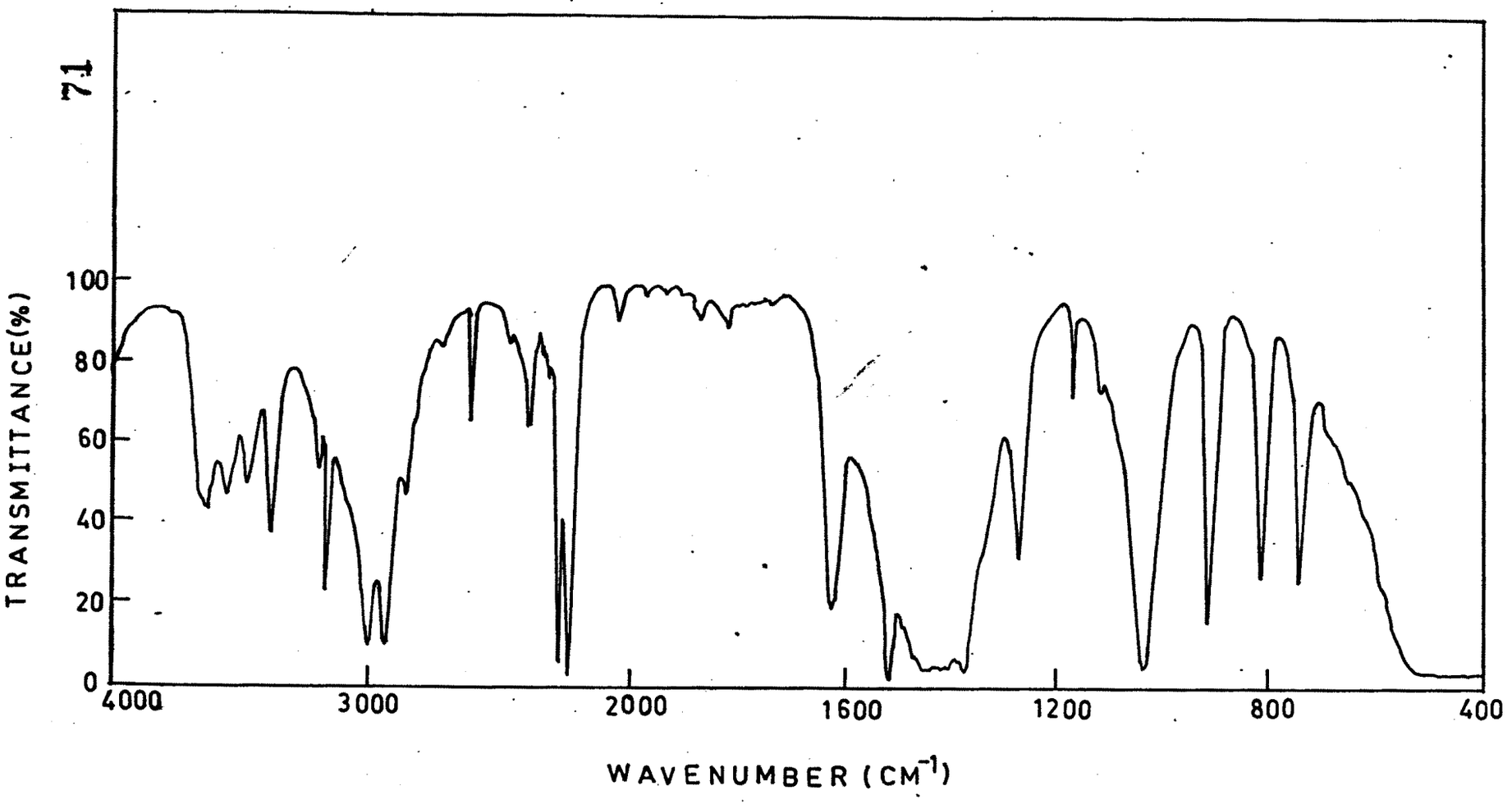

Fig.15 — IR absorption spectrum of 0·4 M solution of p–Toluidine in Acetonitrile .

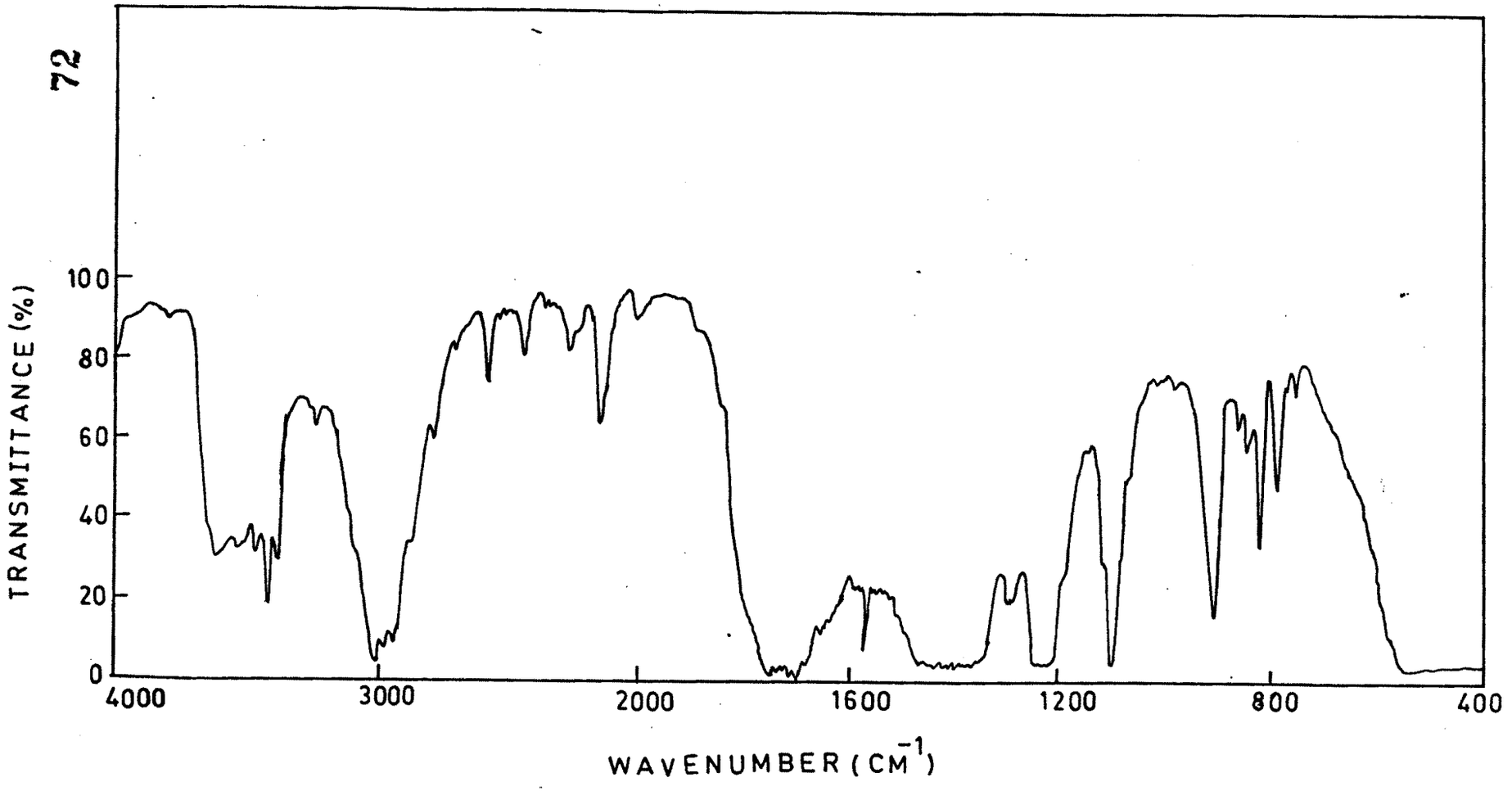

Fig. 16 — IR absorption spectrum of 0·4 M solution of P-Toluidine in Acetone .

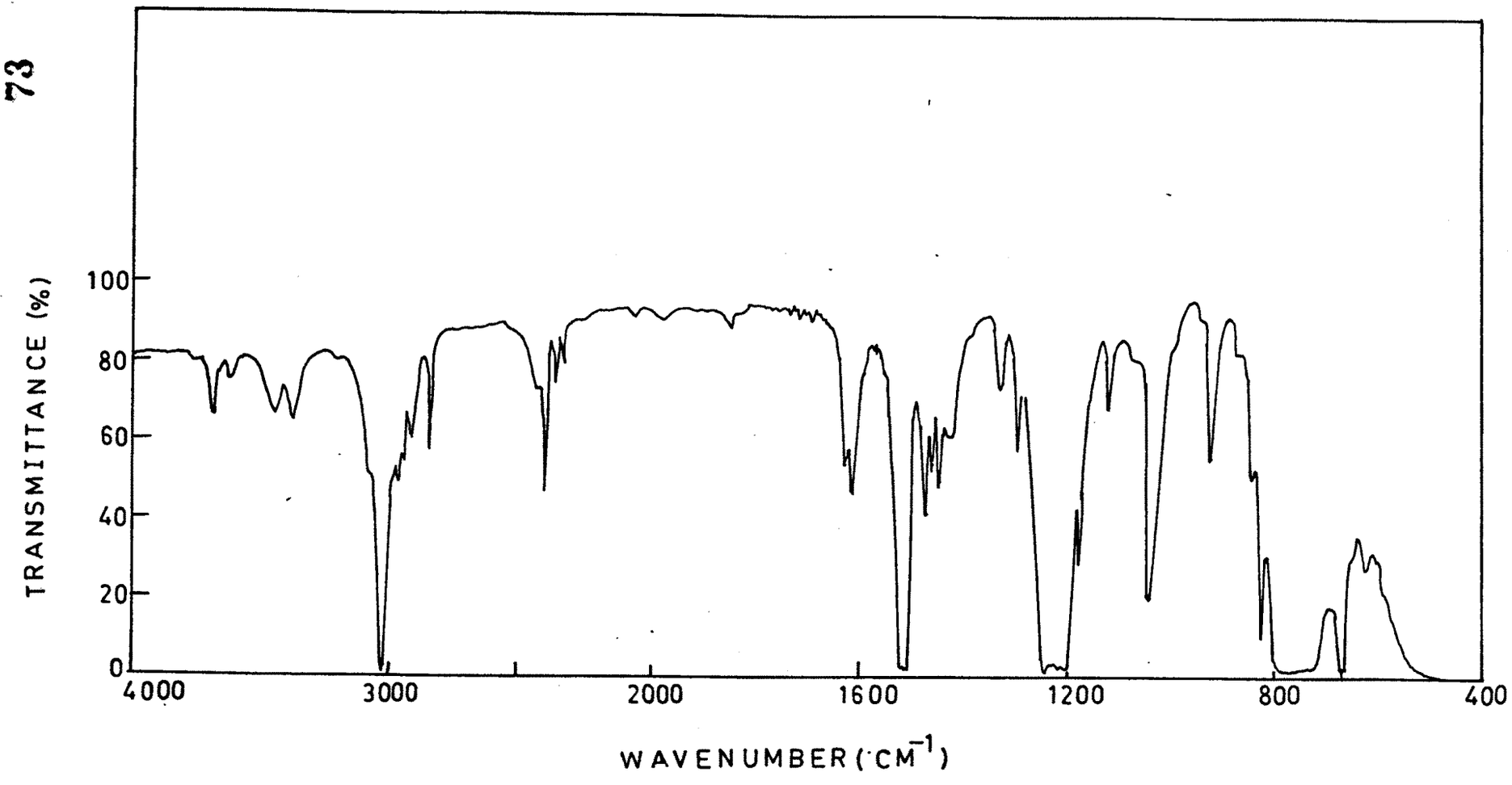

Fig. 17 — IR absorption spectrum of 0·4 M solution of p-Anisidine in Chloroform.

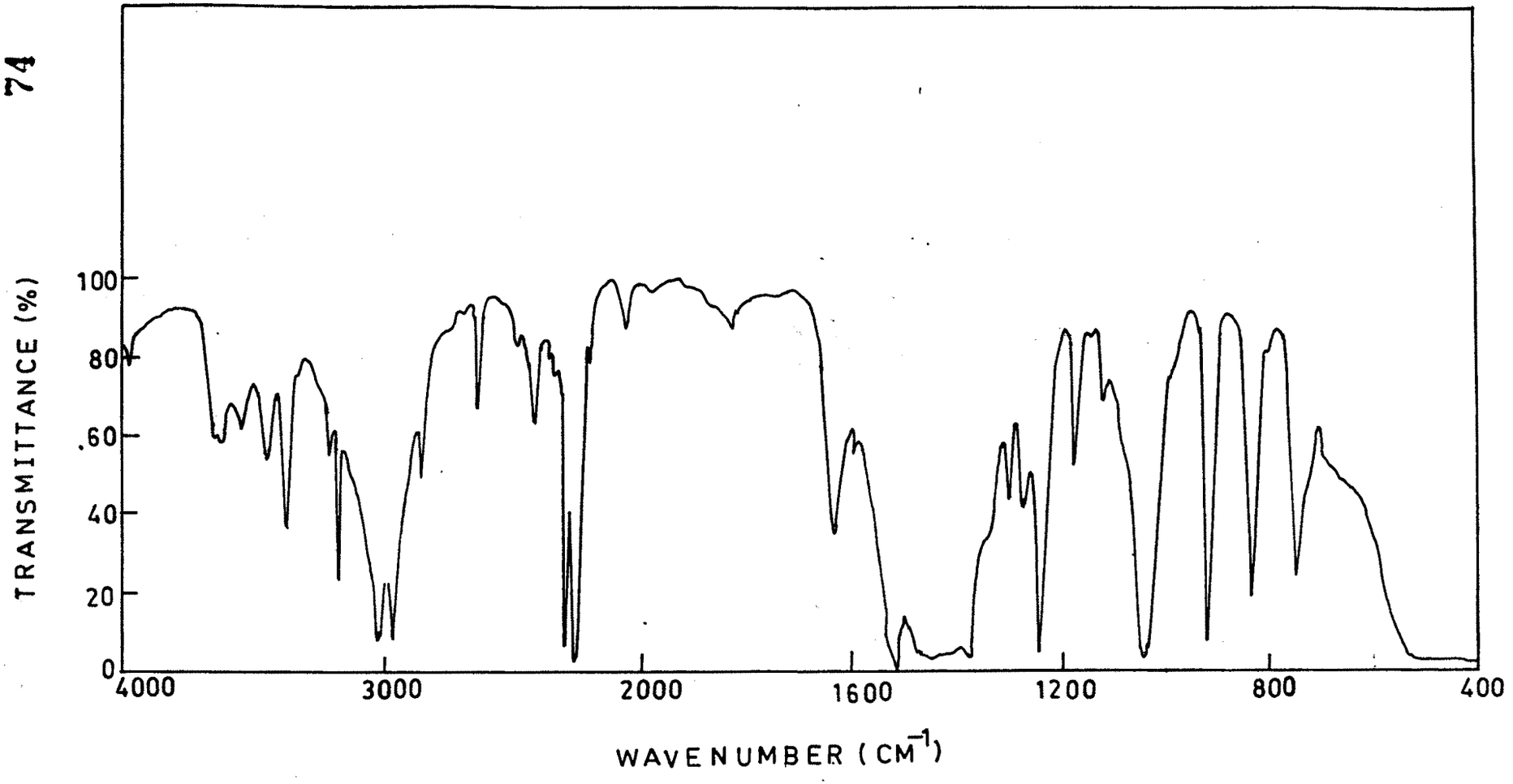

Fig. 18 — IR absorption spectrum of 0·4 M solution of p-Anisidine in Acetonitrile.

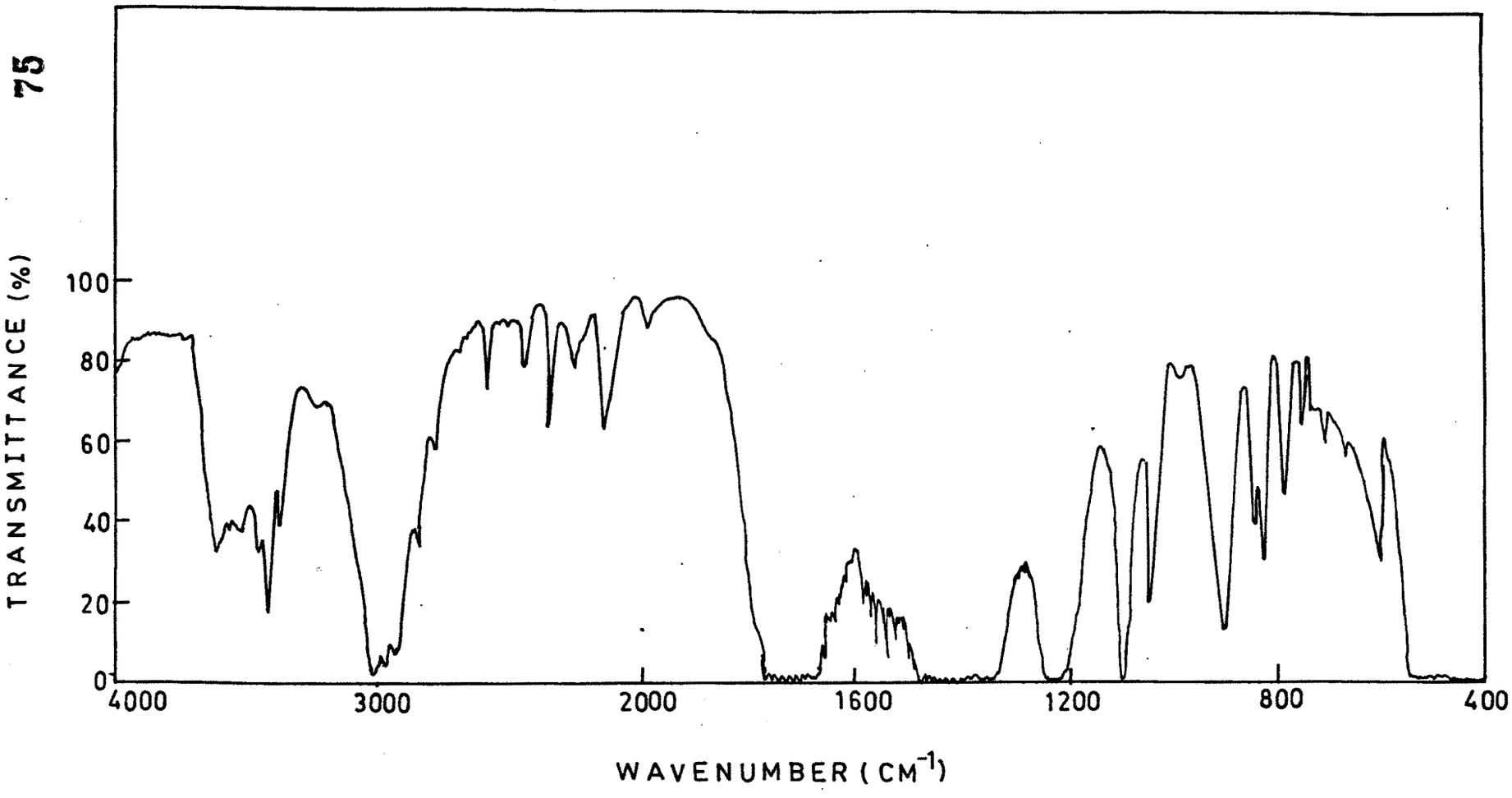

Fig. 19 — I R absorption spectrum of 0·4 M solution of p-Anisidine in Acetone.

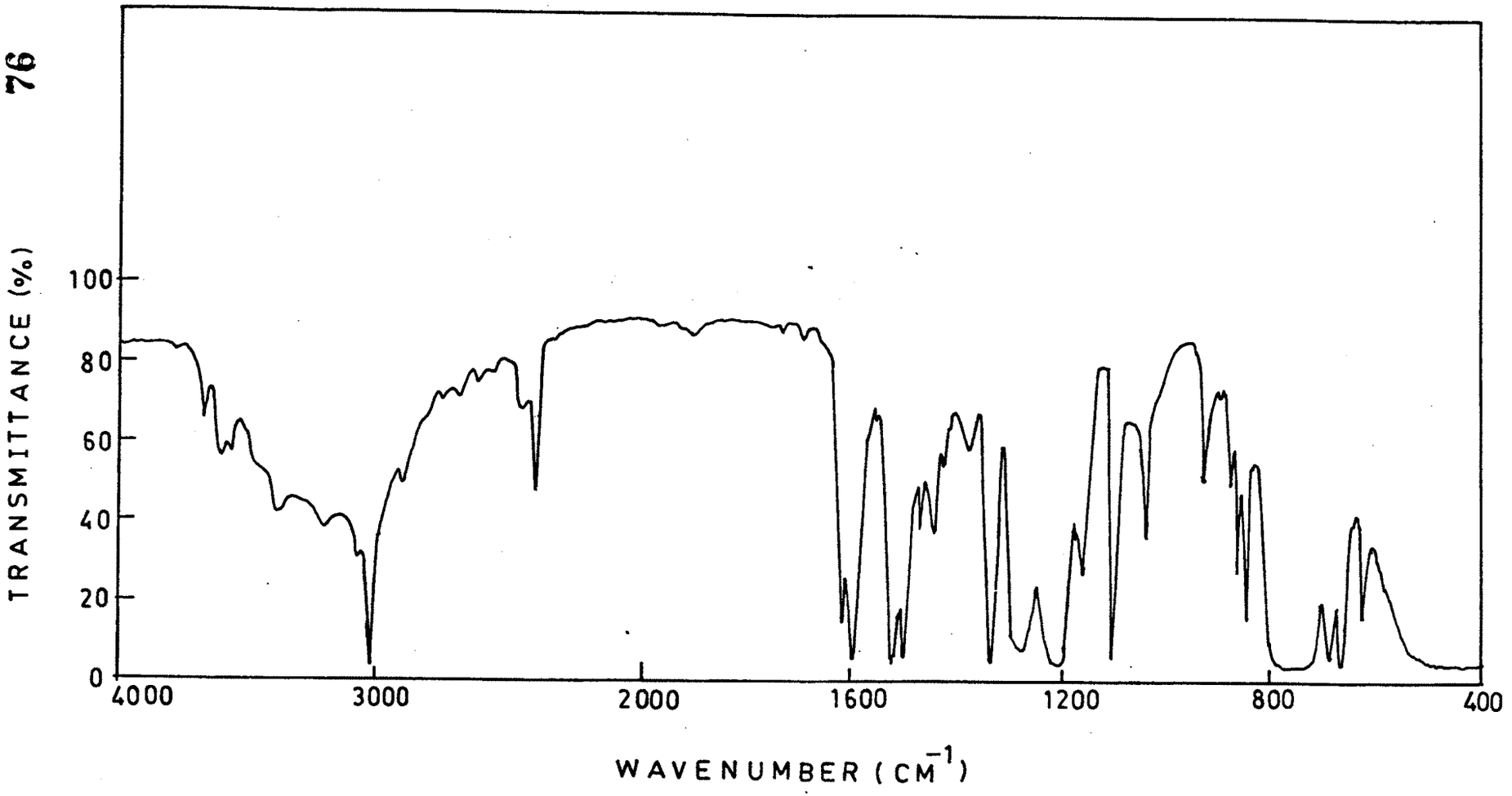

Fig. 20 — IR absorption spectrum of the (1:1) adduct [p-Nitrophenol (0·4 M) + Aniline (0·4M)] in Chloroform.

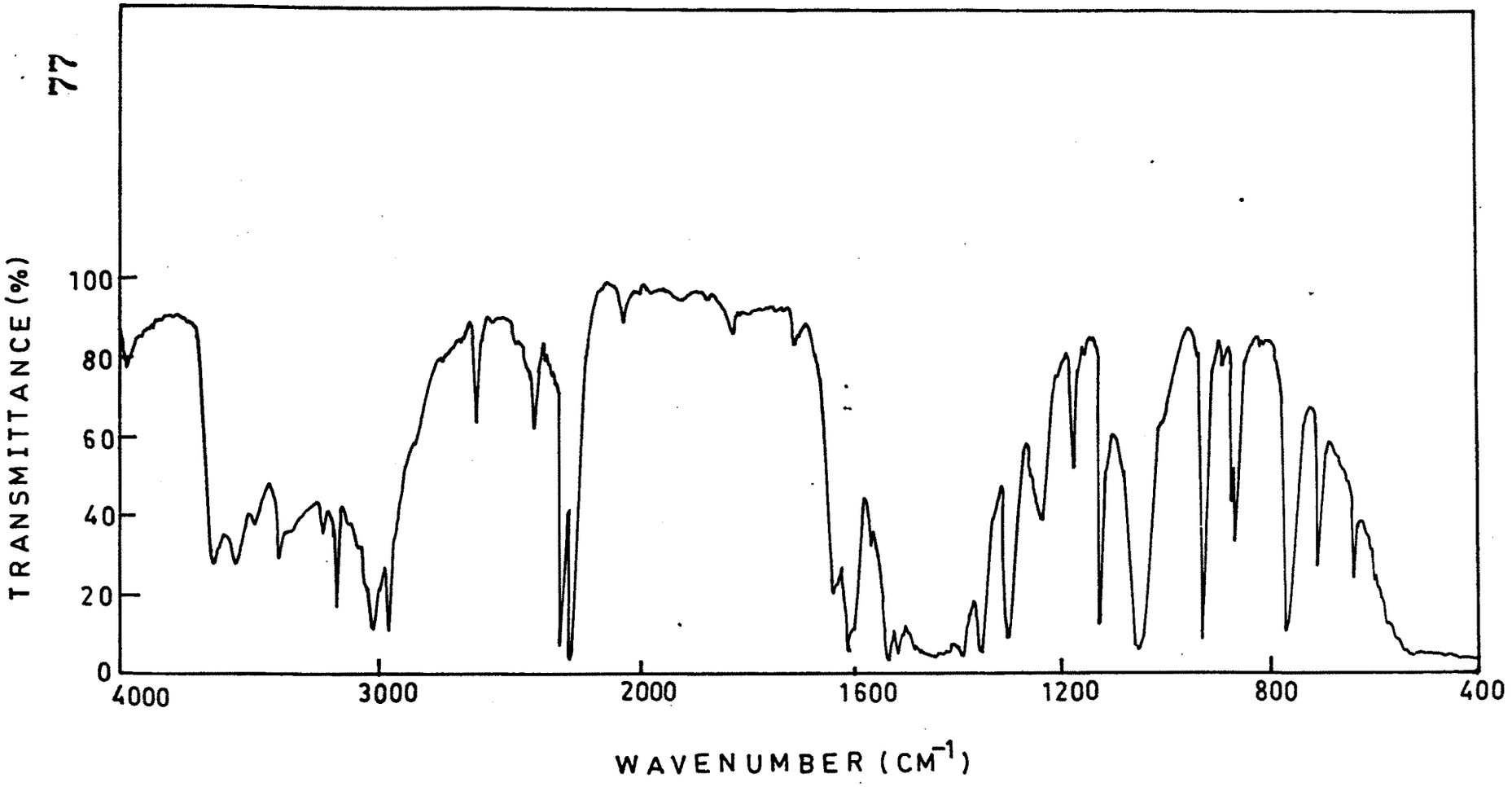

Fig . 21 — IR absorption spectrum of the(1:1) adduct [p-Nitrophenol(0·4M) + Aniline(0·4 M)] in Acetonitrile .

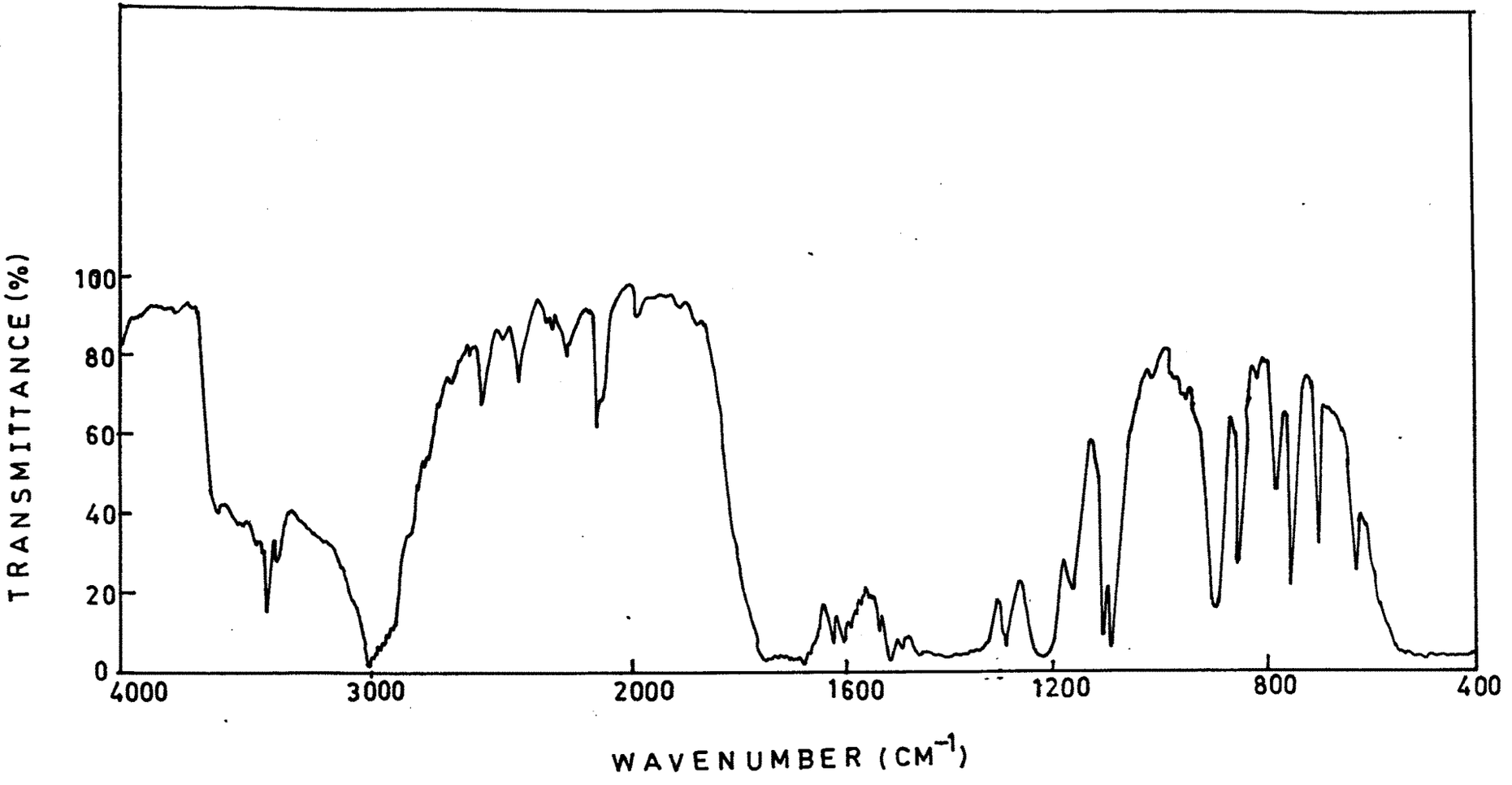

Fig. 22 – IR absorption spectrum of (1:1) adduct [p–Nitrophenol (0·4 M) + Aniline (0·4 M)] in Acetone.

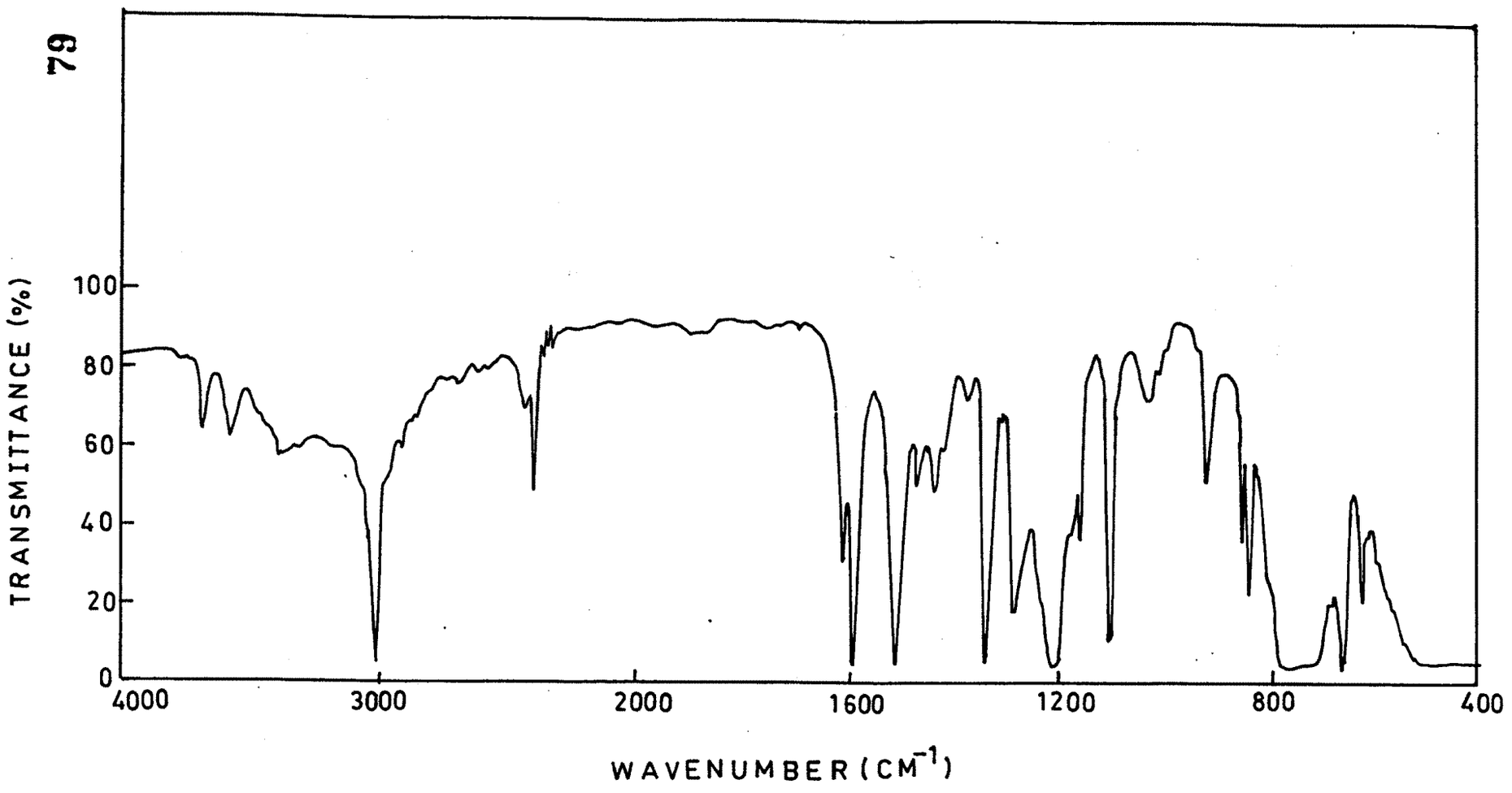

Fig. 23 — IR absorption spectrum of (1:1) adduct [p-Nitrophenol (0·4 M) + p-Toluidine (0·4 M)] in Chloroform.

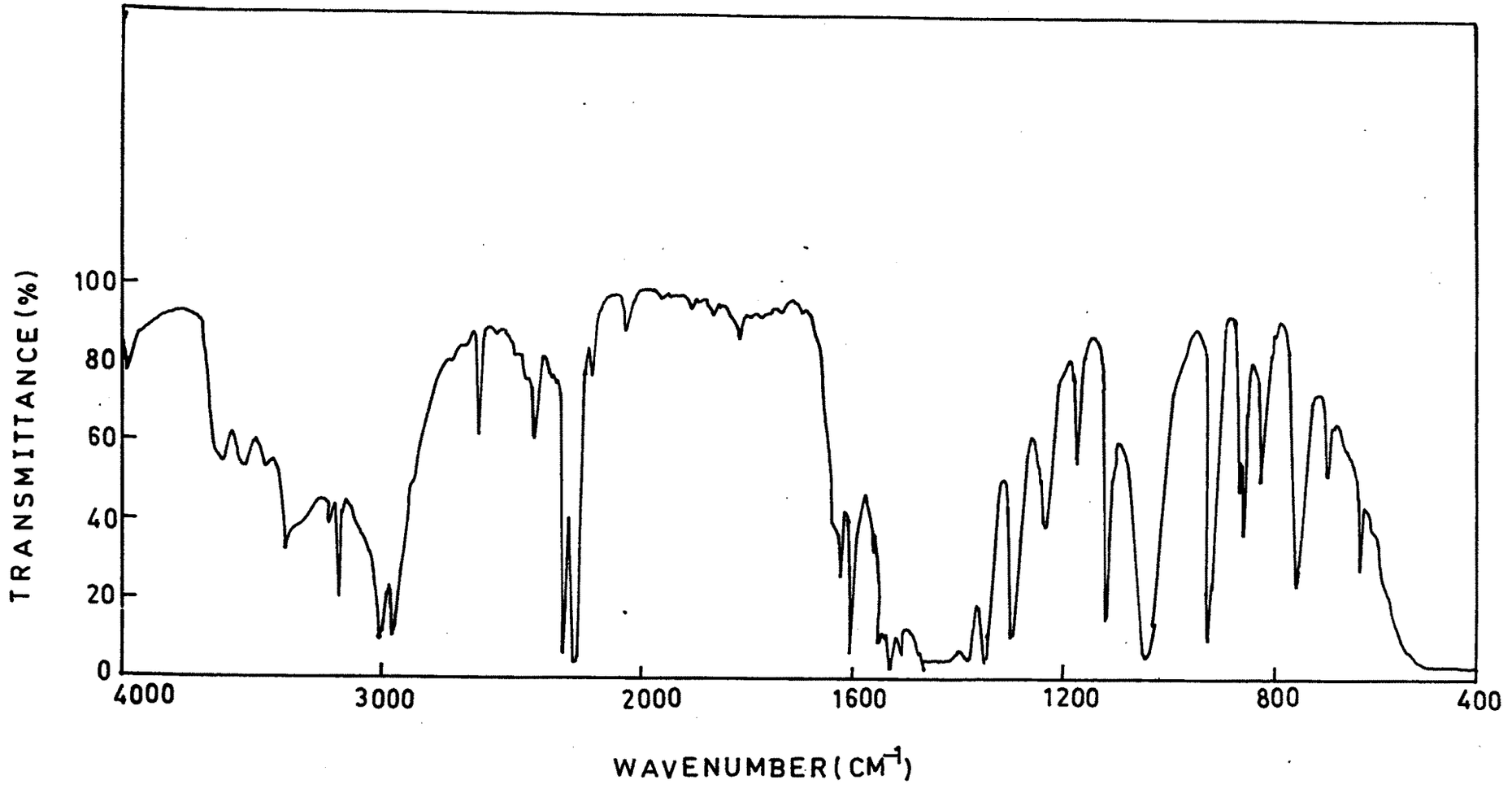

Fig. 24 – IR absorption spectrum of (1:1) adduct [p-Nitrophenol (0·4 M) + p-Toluidine (0·4 M)] in Acetonitrile .

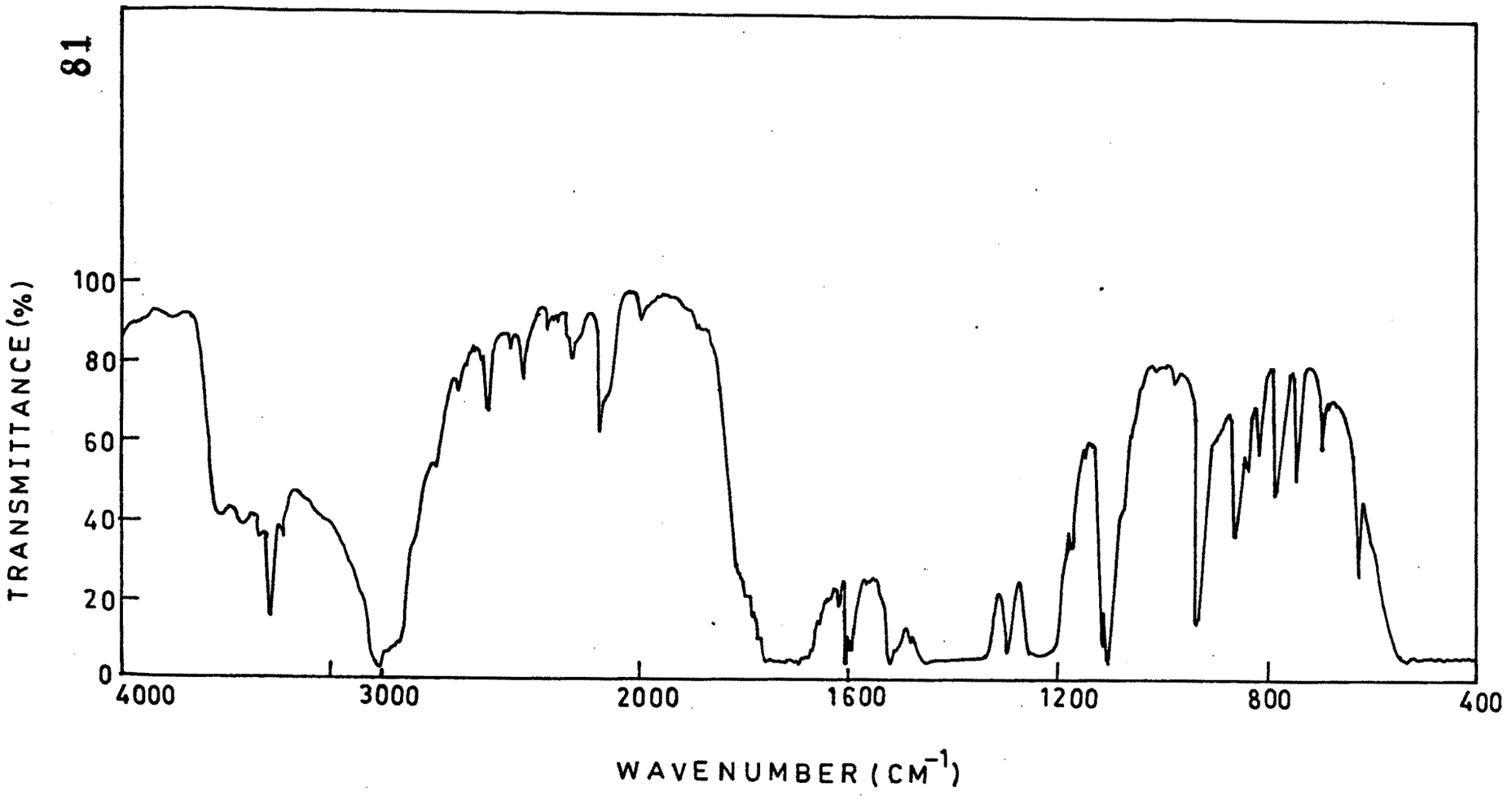

Fig. 25 — IR absorption spectrum of (1:1) adduct [p-Nitrophenol (0·4M) + p-Toluidine (0·4M)] in Acetone .

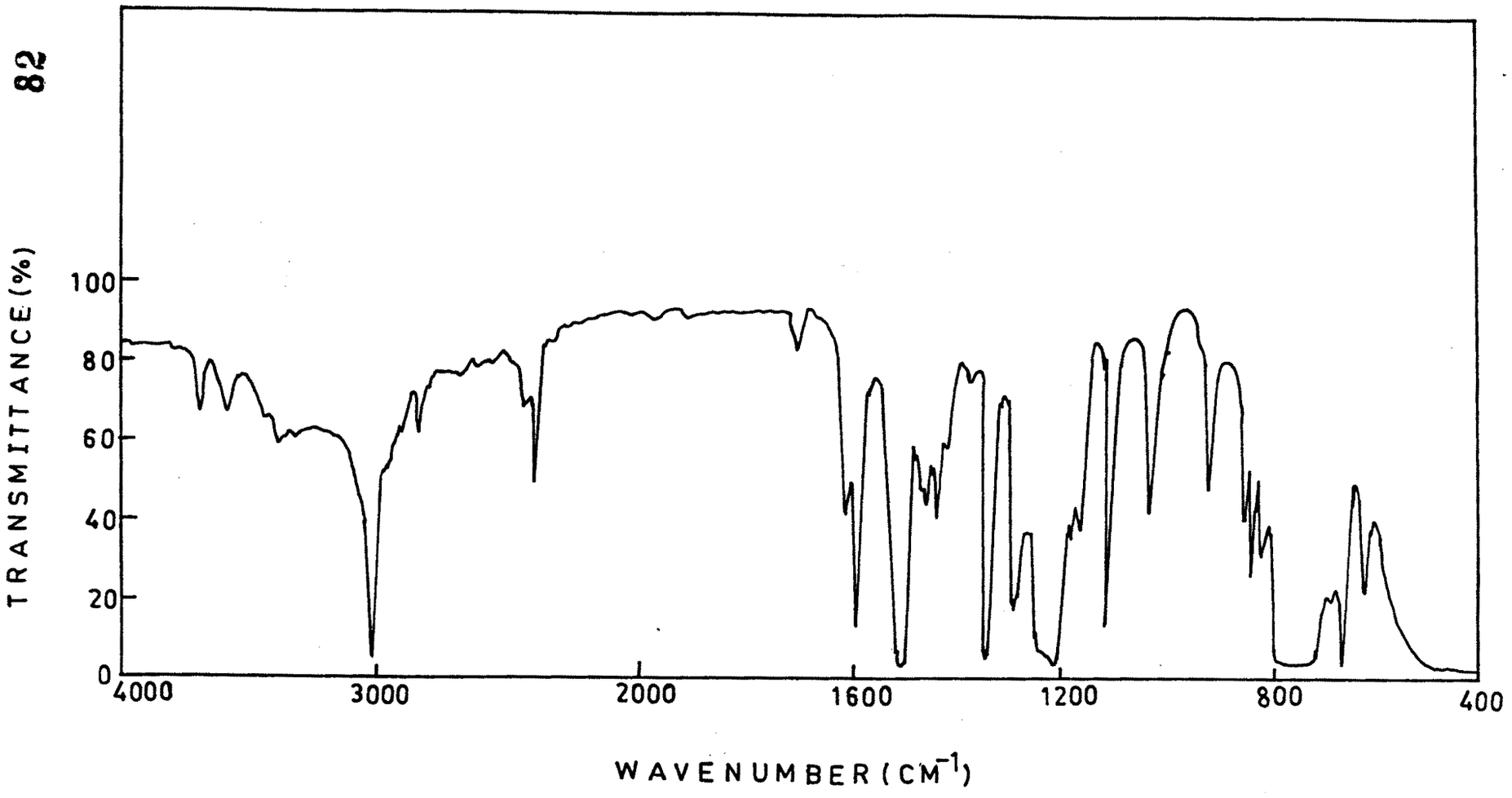

Fig.26 – I R absorption spectrum of (1:1) adduct [p-Nitrophenol (0·4M) + p- Anisidine (0·4 M) in Chloroform .

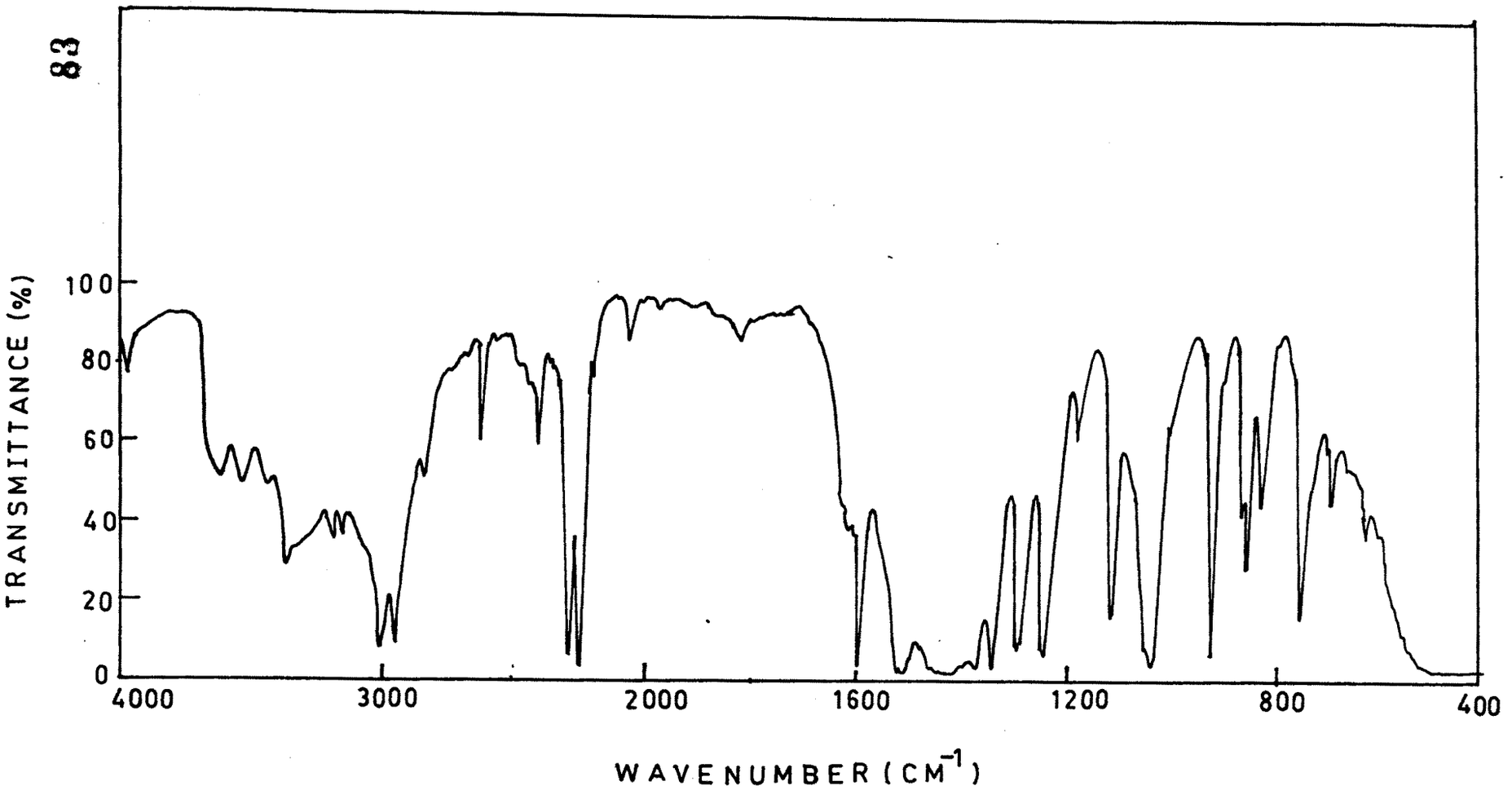

Fig. 27 — I R absorption spectrum of (1:1) adduct [p-Nitrophenol (0·4M) + p-Anisidine (0·4M)] in Acetonitrile .

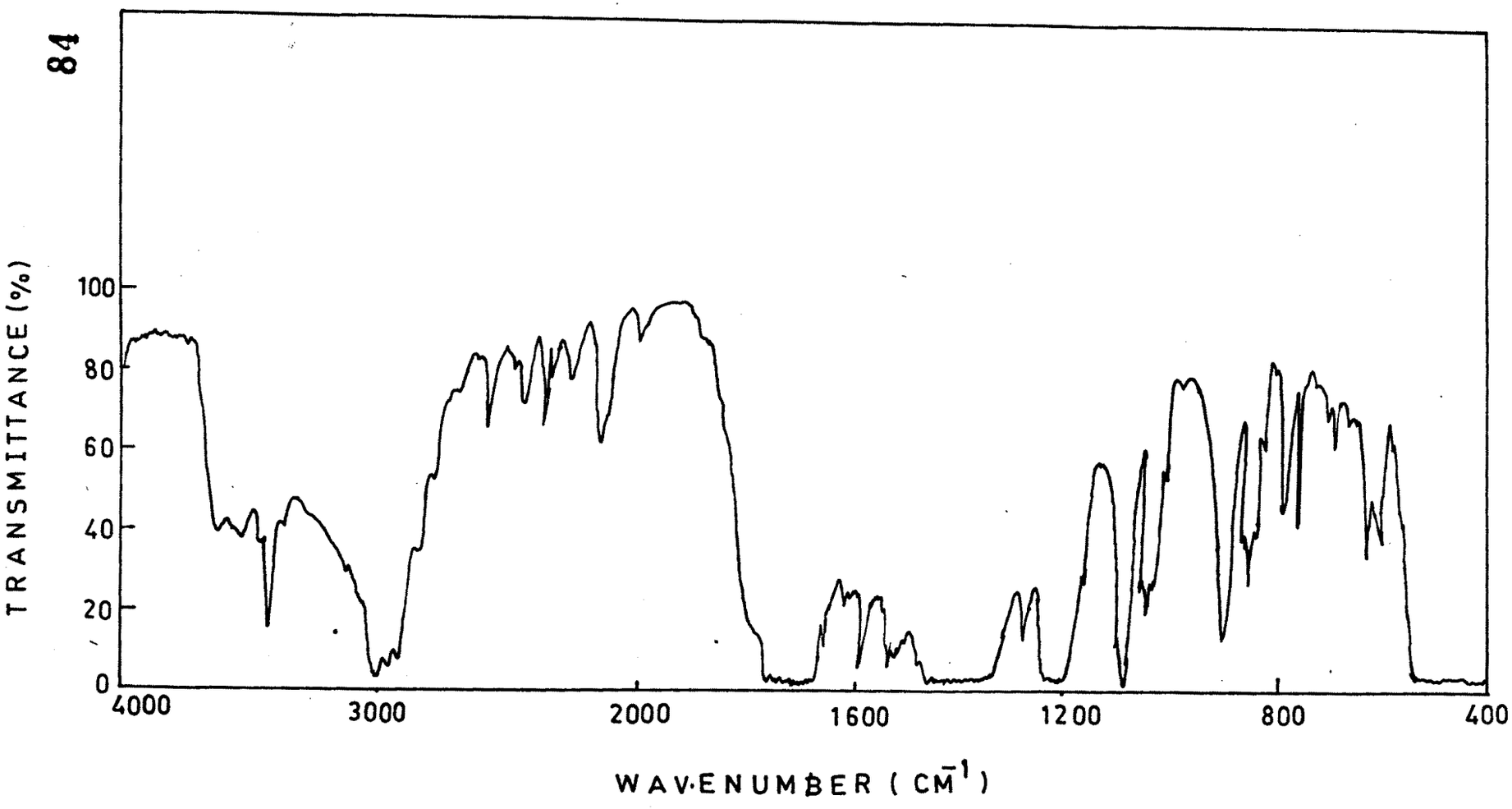

Fig. 28 — IR absorption spectrum of (1:1) adduct [p-Nitrophenol (0.4 M) + p-Anisidine(0.4M)] in Acetone.

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