Synthesis, Characterization and Chromatographic Study of Naphthol Derivatives

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الخلاصة:

تم تحضير سلسلة من مشتقات النفثول من مركب الآزو (A) ومركبات قواعد شيف (B_1-B_6). شخصت تراكيب المركبات المحضرة من خلال درجة الانصهار ، كروماتوغرافيا الطبقة الرقيقة ، تحليل العناصر CHN ، تقنية FTIR ، أطياف ^{1}HNMR و ^{13}CNMR.

بصورة عامة تم دراسة تسلسل خروج المركبات والفصل والخواص الثرموديناميكية للمركبات (A) و (B_1-B_6) على بعض الأطوار السائلة الثابتة (DN-1, FS-Bp10, DP5-S25, and OV-17)

حيث وجد الباحث بوجود تصرف كروماتوغرافي أعتيادي بسبب نقص حجوم الآحتجاز النوعية V_g° لمشتقات النفثول بزيادة درجة الحرارة للاطوار السائلة الثابتة المستخدمة.

Abstract:

A series of naphthol derivatives were synthesized from azo compound (A) and schiff bases compounds (B_1-B_6). The synthesized compounds structures are characterized by melting point, thin layer chromatography, CHN- analysis, FTIR, ^{1}HNMR spectra, and ^{13}CNMR.

In general, the order of elution, resolution and thermodynamic parameters of (A) and (B_1-B_6) on various liquid stationary phases (DN-1, FS-Bp10, DP5-S25, and OV-17) were discussed. The researcher found that the normal chromatographic behavior of specific retention volume V_g° of naphthol derivatives decreases by the increase of temperature of liquid stationary phases.

Keywords: *naphthol derivatives, synthesis, gas chromatography, liquid stationary phase, Temperature.*

Introduction:

Azo compounds are composed of two neighborhood nitrogen atoms connected with double-bond (N=N) [1]. Azo compounds are the important class in organic chemistry as a starting materials for most compounds. It's widely used in areas such as cosmetic, plastic, and analytical chemistry [2-6]. Anils compounds are characterized by the (N=CH) imine group which is important in most biochemical systems, inorganic, and analytical chemistry [7]. Azo-Schiff bases derivative are very important in organic, analytical, and medicinal chemistry [8].

The popularity of gas chromatography method is due to the ability to separate and quantitatively determine mixture of chemically similar substances[9].Gas chromatography was used for the separation and determination of some p-cresol derivatives by using variation polarity of liquid stationary phases (ZB-FFAP, FS-Bp10 and OV-5) [10]. Methods of synthesis and study of chromatographic application of heterocyclic compounds from imine have already been reported [11].

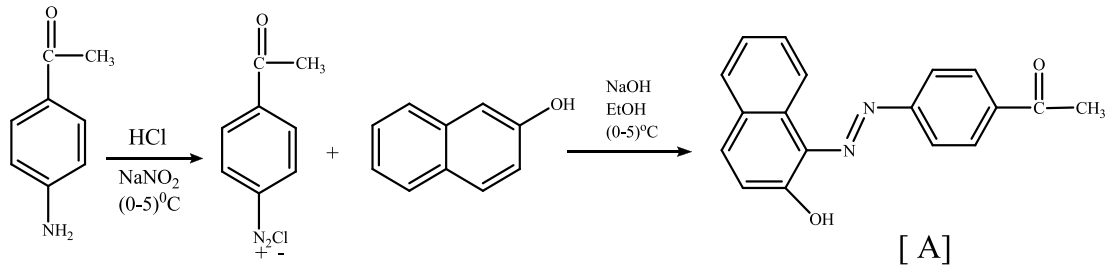
Experimental Procedure:

All chemical compounds were supplied from (Fluka, BDH, and Merck) companies in high purity. FTIR spectra (4000-400) cm^{-1} in KBr were recorded on Shimadzu FTIR-8400S, Japan. Melting point was measured using Stuart, UK. ^{1}HNMR and^{13}CNMR were recorded on Fourier transformation braker spectrometer operating at (400)µHz with (DMSO-d6) measurements made at Kashan University, Iran. Elemental analysis was measured by Euvovector, EA3000A, Italy. Thin layer chromatography (TLC) was performed in silica gel and spots were visualized by iodine.

Synthesis Methods:

A- Synthesis of Azo Compound (A).

The azo compound (A) was synthesized from 4-amino acetophenone with 2-naphthol according to Shibata method [12]. 4-amino acetophenone (1.35g,0.01mol) was dissolved in 5ml of concentrated HCl and 10 ml of distilled water. The mixture was cooled to (0) °C and (0.77g, 0.01mol) of sodium nitrite was added drop-wise with continuous stirring. The solution was left for (20)min. to be stable after completing the (1.44g,0.01mol)) of 2-naphthol dissolved in (1gm NaOH in 50ml H_2O) was added.

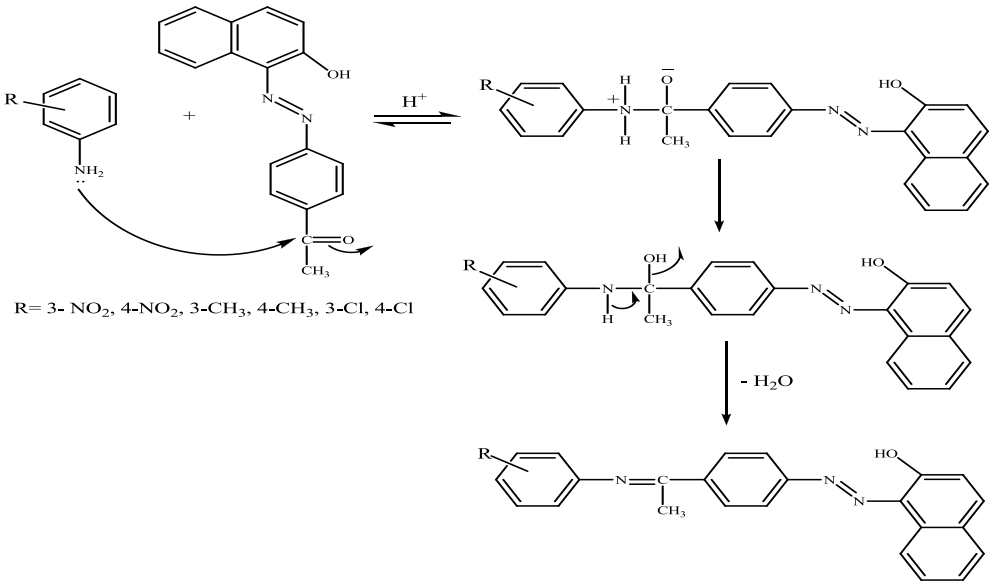


Scheme 1: Synthesis of azo compound (A)

B- General Method Synthesis of Schiff Bases Compounds (B_1-B_6).

Compound (A) (0.01mole) was dissolved in 30ml of absolute ethanol containing two drops of glacial acetic acid, then aniline derivative (3-NO_2, 4-NO_2, 3-CH_3, 4-CH_3, 3-Cl, and 4-Cl)

respectively. (0.01mole) was dissolved in 20ml of absolute ethanol and added drop-wise. The reaction mixture was refluxed with stirring in a water bath at (10) °C for (5-9)hrs. and monitored by TLC. The mixture was allowed to cool down to room temperature, the colored precipitate was filtered and recrystlized by ethanol. The physical properties and other characteristics for the synthesized Schiff bases derivatives (B1-B6) were shown in **Tables 2,3**.



Scheme 2: Mechanism of synthesis general Schiff base

Chromatographic Measurements:

GC-2014 gas chromatography, Shimadzu-Japan and DANI instruments Solution GC, 2007I- Italian are equipped with flame ionization detector (FID). The optimum carrier gas (nitrogen) flow rate was 28 cm^3 min^{-1} for capillary columns and 40 cm^3 min^{-1} for packing column at isothermal and programming columns temperature depending on column maximum operation temperature (M.O.T). The sample injection and detector temperature were higher than the separation columns 25,40 °C respectively. Samples were prepared individually by dissolving 10mg of each compound in 1 ml ethanol. The mixture was prepared by mixing 100µL from each of prepared solution. Sample sizes ranged (0.2-1.0)µL, the injection were made with a (1,2)µL by Hamilton syringe. The characteristics details of liquid stationary phases are listed in **Table 1**.

Table 1: characteristics of the used liquid stationary phases (LSP).

LSP	composition	I.D(mm)	F.T(µm)	M.O.T (C^0)	Polarity
DN-1(capillary)	10%dimethyl polysiloxane	0.53	0.25	380	non-polar
FS-Bp10(capillary)	14%cyanopropyl phenyl polysiloxane	0.25	0.25	360	moderately polar
DP5-S25(capillary)	2,3 di-o-propinoyl -6-t-butylsilyl derivative of 6-cyclodextrine	0.25	0.12	350	Polar
OV-17(packing)	50%methyl 50% phenyl polysiloxane	0.32	1.5	520	moderately polar

Results and Discussion:

The azo compound (A) was prepared from reaction of p-amino acetophenon with 2-naphthol in the presence of conc. Hydrochloric acid, sodium nitrate and sodium hydroxide at (0-5)°C. The azo compound (A) was characterized by melting point, thin layer chromatography, CHN- analysis, FTIR spectra and ^{1}HNMR spectra.

The FTIR spectrum as shown in **Figure 1** showed appearance absorption band at (3343)cm^{-1} due to stretching vibration of the hydroxyl group [13]. Absorption band at(1653)cm^{-1} due to carbonyl group of ketone, absorption band at (1502)cm^{-1} due to stretching vibration of the (N=N) for azo group, beside the disappearance of the absorption band in the region (3290 and 3180)cm^{-1} due to the symmetric and a symmetric stretching vibration of the (NH_2) group.

The^{1}HNMR spectra of compound (A) **Figure 2**. Shows the following characteristic chemical shift, (DMSO-d_6)ppm, proton of methyl group for acetyl appeared at the 3.38ppm as singlet signal, the aromatic ring proton as multiple signal at (7.3-8.3)ppm, and signal at (∫12.1)ppm due to the (O-H) proton in naphthol ring.

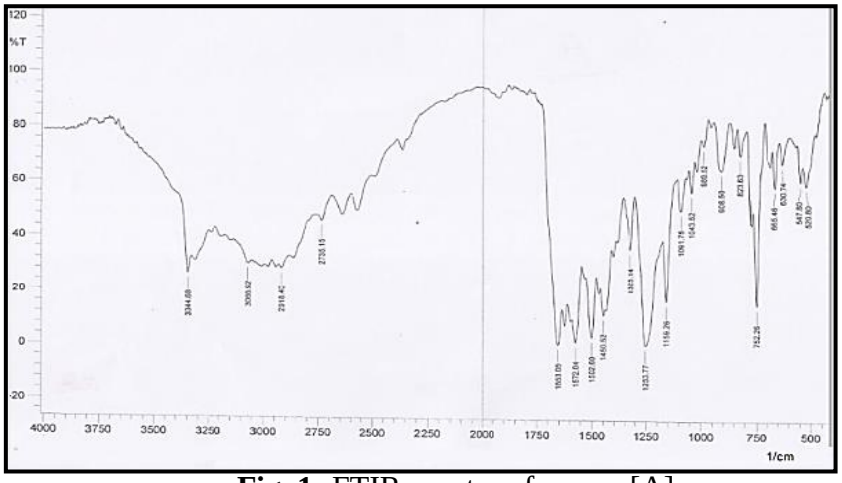


Fig. 1: FTIR spectra of comp. [A]

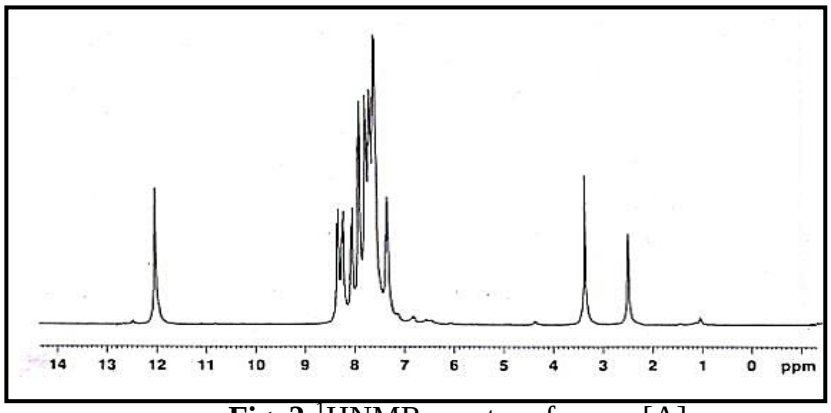


Fig. 2:[1]HNMR spectra of comp.[A]

Characterization of azo Schiff bases (B1-B6):

The reaction of azo compound (A) with different primary amines is one of the most common reaction to synthesize Schiff bases. The structure of the product is assignment on its melting point. CHN analysis, FTIR spectroscopy and some of derivatives by [1]HNMR spectra and[13]CNMR. The FTIR spectra of Schiff bases (B1 and B2) **Figures 3,4** showed the appearance of characteristic absorption bands in the region (3317-3433)cm^{-1} due to stretching vibration of hydroxyl group of naphthyl ring. Also the FTIR spectra of the compounds (B1and B2) showed the appearance absorption band in the region (1606-1616)cm^{-1} due to stretching vibration of the (C=N) for imine group and the absorption bands in the region (1354-1396)cm^{-1} due to stretching vibration of the (C-NO_2) group, beside the disappearance of the band in the region (1654)cm^{-1} due to stretching vibration of the (-$COCH_3$) group.

The FTIR spectra of compounds (B3 and B4) **Figures** 5,6, **Figures** 7,8 confirmed the appearance of imine group bands at (1620-1624)cm^{-1} and (OH) group bands at (3414-3271)cm^{-1} and also bands at(1506--1469)cm^{-1} belong to the (N=N) group.

The FTIR spectra of compounds (B5 and B6) were devoid of medium bands at (1622)cm^{-1} at tributed stretching frequency of the imine group. Bands at (1502-1519) cm^{-1} were due to the(N=N) azo group. The bands at (821-858)cm^{-1} were due to the stretching vibration of (C-Cl) group.

Some of the azo –schiff bases were characterized by [1]HNMR spectroscopy. The[1]HNMR spectrum shows the following characteristic chemical shift for compound (B2), the signal of (OH) proton absorbed at (11.5)ppm and signals at (7.1-803)ppm due to protons of aryl ring. The proton of methyl group absorbed at (2.8)ppm as singlet signal. The The[1]HNMR spectra of compounds (B3 and B4) shows the following characteristic chemical shifts (DMSO-d_6)

signals at (1.6-2.1)ppm due to protons of methyl group at position -3 and -4 respectively. The aromatic ring protons as multiplete at (6.9-8.3)ppm, signals at (10.8-11.8)ppm due to the (OH) proton.

Some of the azo-schiff bases were characterized by ^{13}CNMR spectroscop. ^{13}CNMR spectrum shows the following characteristic chemical shifts for compounds (B4 and B5). The signal of carbon (CH_3) absorbed at (22.4-36.5)ppm, the carbon of the carbon of the phenyl ring and naphthyl ring absorbed at (105-140.5)ppm.

Table 2: Physical properties of the azo –Schiff bases derivatives.

Sym.	**M.F**	**M.Wt.**	**m.p(C^0)**	**Rf(MeOH: Benzene)(1:4)**	**Yield%**	**Color**
A	$C_{18}H_{14}N_2O_2$	290	250-252	0.56	83%	Red
B1	$C_{24}H_{18}N_4O_3$	410	232-233	0.43	78%	Red dark
B2	$C_{24}H_{18}N_4O_3$	410	225-227	0.48	80%	Red
B3	$C_{25}H_{21}N_3O$	379	190-192	0.35	82%	Brown
B4	$C_{25}H_{21}N_3O$	379	196-198	0.38	75%	Brown dark
B5	$C_{24}H_{12}N_3OCl$	399.5	210-212	0.62	78%	Red
B6	$C_{24}H_{18}N_3OCl$	399.5	218-220	0.68	80%	Red dark

Table 3: The values of the (CHN) analysis for the azo-schiff bases derivatives.

Sym.	Str.	M.Wt.	Cal. C Found. C	H H	N N
A	$C_{18}H_{14}N_2O_2$	290	74.422 74.123	4.827 4.718	9.655 9.589
B1	$C_{24}H_{18}N_4O_3$	410	70.243 69.989	4.390 4.352	13.658 13.597
B2	$C_{24}H_{18}N_4O_3$	410	70.243 70.164	4.390 4.369	13.658 13.612
B3	$C_{25}H_{21}N_3O$	379	79.155 18.485	5.540 5.482	11.817 11.793
B4	$C_{25}H_{21}N_3O$	379	79.055 79.068	5.540 5.498	11.817 11.798
B5	$C_{24}H_{12}N_3OCl$	399.5	72.090 71.989	4.505 4.489	10.513 10.485
B6	$C_{24}H_{18}N_3OCl$	399.5	72.090 70.058	4.505 4.493	10.513 10.499

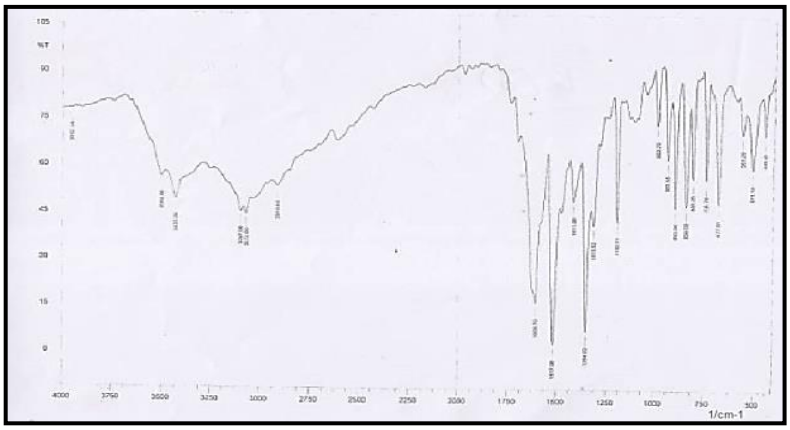


Fig.3: FTIR spectra of comp. B1.

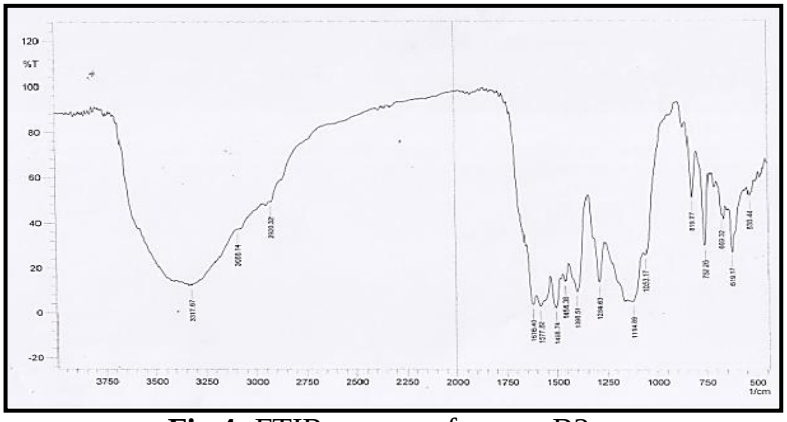


Fig.4: FTIR spectra of comp. B2.

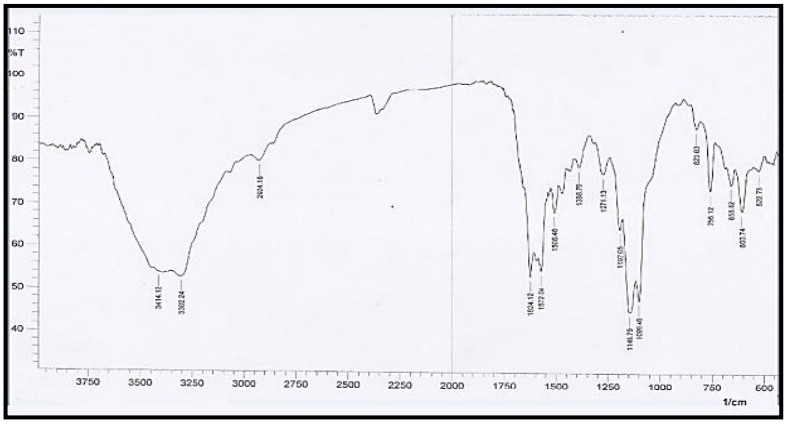


Fig.5: FTIR spectra of comp. B3.

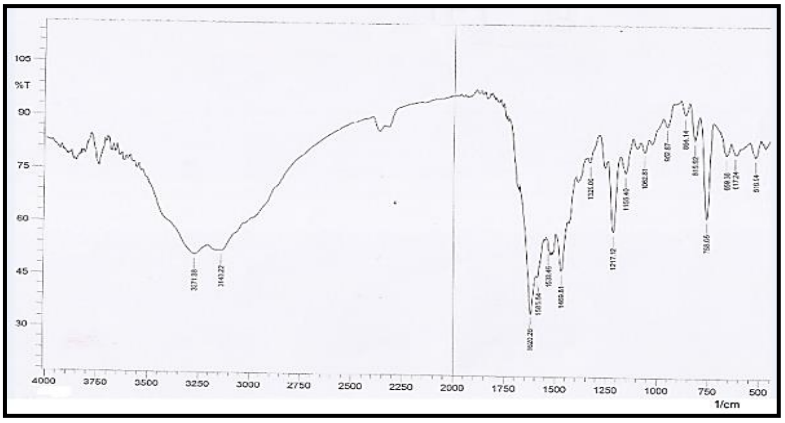


Fig.6: FTIR spectra of comp. B4.

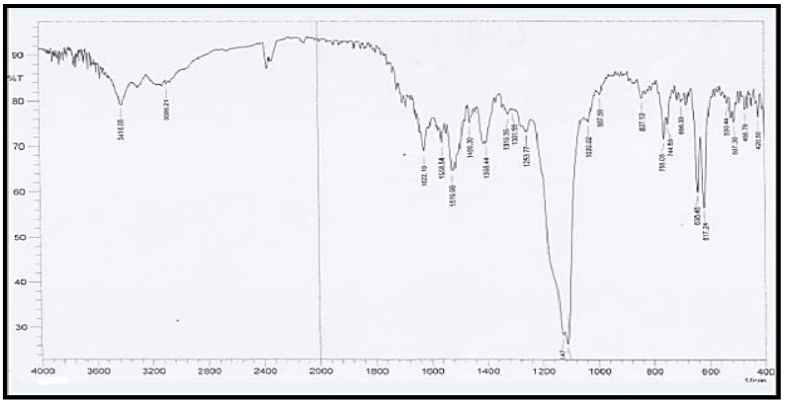


Fig.7: FTIR spectra of comp. B5.

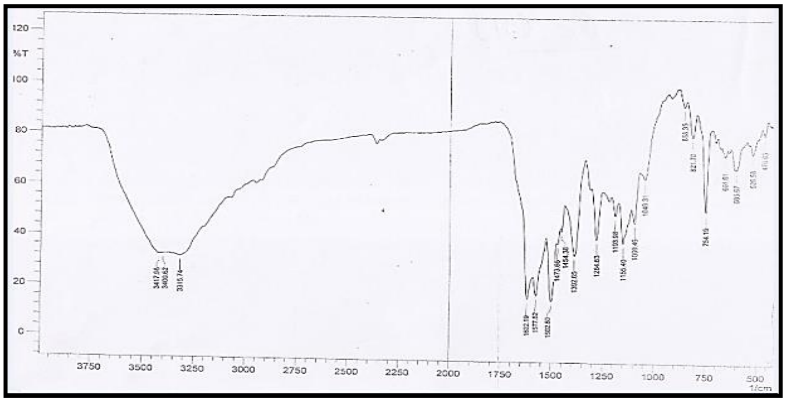


Fig.8: FTIR spectra of comp. B6.

Theory:

Retention volume V_R is often used for identification and it is normally determined by the chromatogram by using the following equation: $V_R = X/S \cdot Fc$, where X is the distance from the injection point to the peak maxima, S is the chart speed and Fc is the volume flow rate of carrier gas at the temperature of the column and its outlet pressure. The term X/S gives the retention time t_R. The retention volume measured corrected for the dead space: $V_R^- = V_R - V_m$

, where V_m is the dead volume (Interstitial volume). Due to compressibility of the carrier gas (J), the follow equation derived by Martin and James [14,15].

$J = 3 (P_i / P_o)^2\text{-}1 / 2 (P_i / P_o)^3\text{-}1.$

Which P_i and P_o are the inlet, outlet pressure respectively, so the corrected retention volume is defined as the net retention volume, $V_N = (V_R^- - V_m) . J$

The net retention volume depends upon the temperature and the amount of liquid stationary phase. Therefore in order to take into account the weight of stationary phase in column(3), specific retention volume was derived:

$V_g^\circ = 273 . V_N / Tc . W_L .$

The plots of log V_g° values of naphthol derivatives compounds against reciprocal column temperature, **Figures 9 -11** showed linear relationship indicating that the V_g° values are controlled by the type and extent of interaction occurring between these compounds and the stationary phases.

At present, gas chromatography is considered one of the most suitable techniques for the determination of thermodynamic properties, so in this investigation. Thermodynamic parameters were calculated for naphthol derivatives on some LSP . In which the partial molar enthalpy ΔHs^0 of solutions were calculated from the slope of the linear relation of log V_g° vs. 1/Tc (Clausius-Clapeyron, Henry) [16].

$\text{Log } V_g^\circ = - \Delta Hs^0 / 2.303 R Tc + \text{constant.}$

There values showed that the stationary phase DP5-S25 has the most negative values of ΔHs^0, which means the highest interaction between DP5-S25and these compounds.

The investigation attempts to find the optimum conditions (Nitrogen flow rate, applied pressure, sample injection) for the sequential separation were defined for the azo compound (A) and schiff bases compounds (B_1-B_6) on various liquid stationary phases DN-1, FS-Bp10, DP5-S25, and OV-17 are shown in **Figures** 12-14. The order of elution and resolution of studied compounds show normal chromatographic behavior decreased in specific retention volumes with the increase of column temperature through the relationship between log log V_g° vs. 1/Tc. The negative values of DP5-S25 consider the high negative value of ΔHs^0 and the reaction was exothermic, on the other hand the highest negative value of ΔS^0 means less random of solutes on LSP, so it was more selective towards to prepared compounds are listed in **Tables 4-6**. Fig. 9Graph of log V_g° versus 1/Tc for naphthol derivatives on DN-1 .

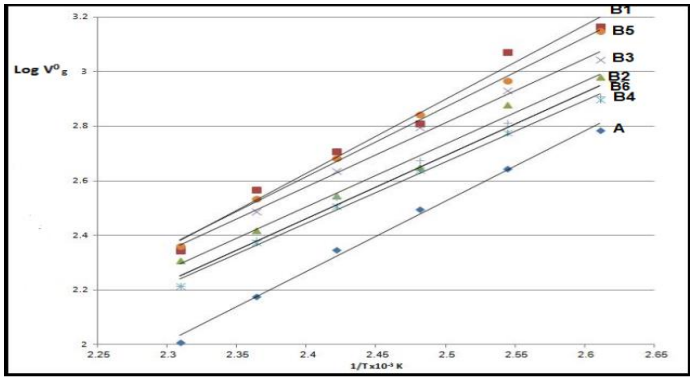


Figure 9: Graph of log V_g ° versus 1/Tc for naphthol derivatives on DN-1.

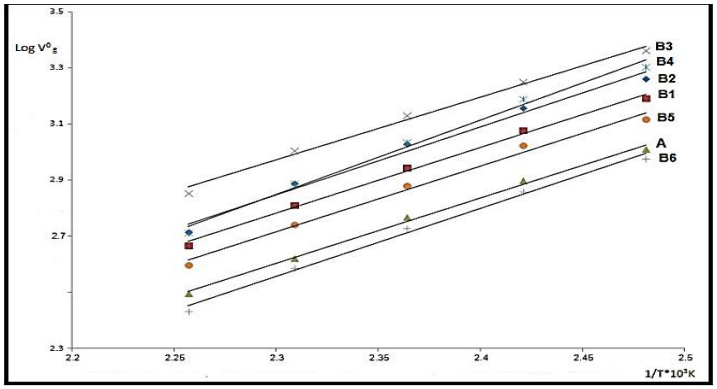


Figure 10: Graph of log V_g° versus 1/Tc for naphthol derivatives on. FS-Bp10.

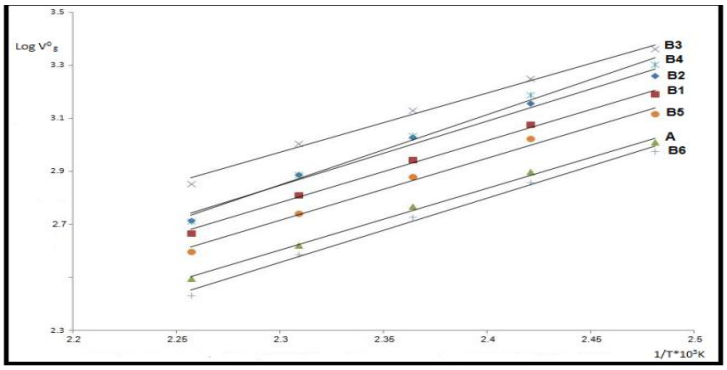


Figure 11: Graph of log V_g ° versus 1/Tc for naphthol derivatives on DP5-S25.

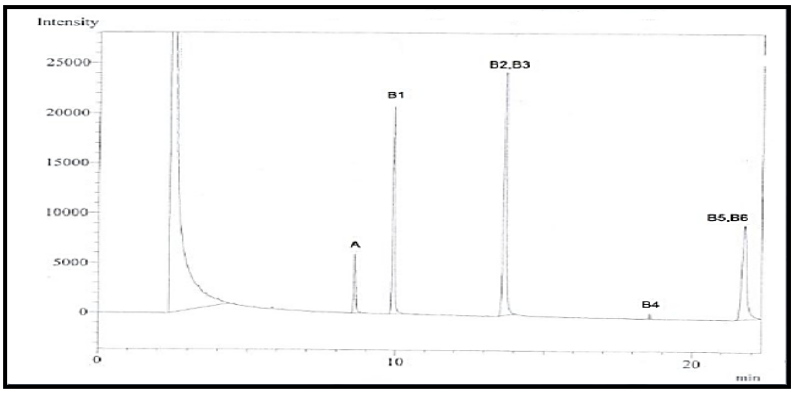


Figure 12: Chromatogram of naphthol derivatives on DN-1 Chromatographic conditions: oven 100 C^0-2 C^0/min – 180C^0, Inj. split- 240C^0 -1:50,carrier gas N_2 28ml/min., Det FID.

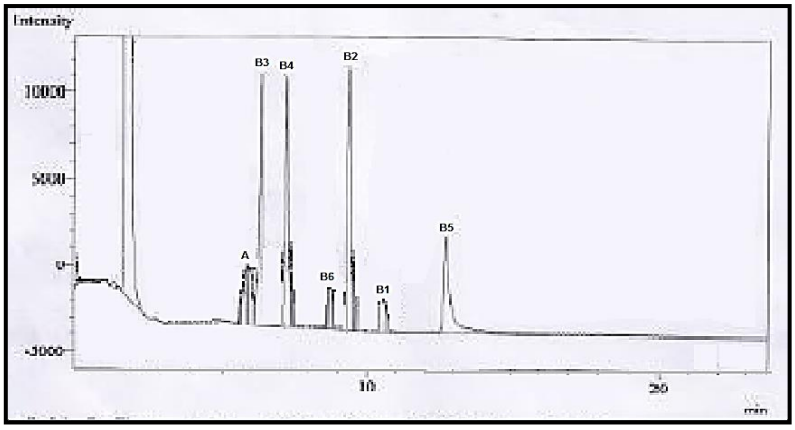


Figure 13: Chromatogram of naphthol derivatives on FS-Bp10 Chromatographic conditions: oven 100 C^0-2.5 C^0/min – 200C^0,Inj. Split-240C^0 -1:50,carrier gas N_2 28ml/min, Det FID

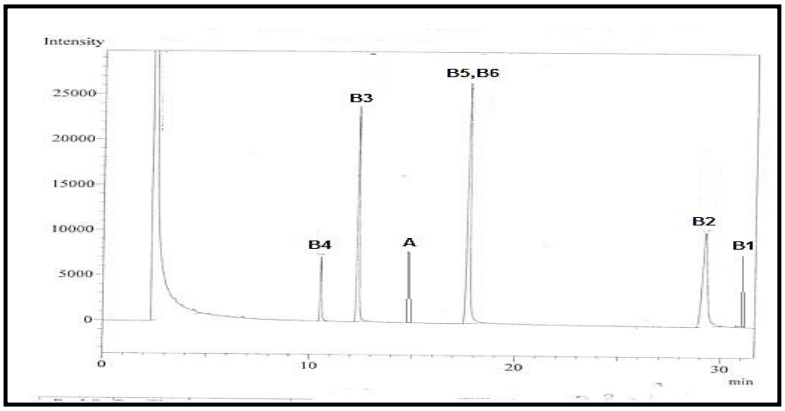


Figure 14: Chromatogram of naphthol derivatives on Dp5-S25 Chromatographic conditions: oven 130 C^0-2.5 C^0/min – 210C^0, Inj. split- 250C^0 -1:50,carrier gas N_2 28ml/min., Det FID.

.**Table 4:** Thermodynamic data of naphthol derivatives on DN-1.

Compound	ΔHs^0 KJ.mol^{-1}	ΔS^0 KJ.mol^{-1}	ΔG KJ.mol^{-1}
A	-13.24	-3.45	1014.86
B1	-13.25	-4.00	1178.75
B2	-11.59	-3.63	1070.15
B3	-12.69	-4.95	1462.41
B4	-13.04	-4.12	1214.72
B5	-11.91	-3.79	1117.51
B6	-12.87	-4.41	1301.31

Table 5: Thermodynamic data of naphthol derivatives on FS-Bp10.

Compound	ΔHs^0 KJ.mol^{-1}	ΔS^0 KJ.mol^{-1}	ΔG KJ.mol^{-1}
A	-14.96	-4.35	1281.34
B1	-15.06	-4.20	1236.54
B2	-14.55	-3.97	1168.51
B3	-13.69	-3.65	1074.01
B4	-14.34	-4.09	1204.48
B5	-15.81	-3.62	1062.95
B6	-13.87	-3.81	1121.51

Table 6: Thermodynamic data of naphthol derivatives on DP5-S25.

Compound	ΔHs^0 KJ.mol^{-1}	ΔS^0 KJ.mol^{-1}	ΔG KJ.mol^{-1}
A	-16.02	-5.14	1515.70
B1	-14.76	-4.66	1373.92
B2	-16.10	-5.07	1494.76
B3	-14.78	-5.65	1668.92
B4	-14.94	-4.79	1412.48
B5	-15.31	-4.62	1361.45
B6	-15.66	-4.81	1417.72

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