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Article

Conductivity Measurements of Schiff Base Nanoparticle Solutions Prepared in Water

Jassim Mohammed Thahir[1]

1. Ministry of Education – Salah al-Din Education Directorate
*Correspondence: Jasimaljanaby@gmail.com

Abstract: Graphene nanoparticles were prepared in two steps. Step 1: Preparation of graphene oxide (GO) by reacting the active groups in the graphene structures with oxidizing and acidic agents to prepare graphene oxide. Step 2: Preparation of graphene nanoparticles (NRGO) (reduction of graphene oxide GO). Reduced graphene oxide was prepared by subliming a mixture of graphene oxide with hydrated hydrazine (NH2NH2.H2O) at 100°C for 2 hours. Preparation of Schiff Nanoparticles (ArNRGOTZS): Schiff nanoparticles (ArNRGOTZS) were prepared by thermally melting ArNRGOTZ with the aldehydes used. The conductivity of the Schiff nanoparticles was studied by measuring the specific conductivity and equivalent conductivity. It was found that the specific conductivity increases with increasing concentration, while the equivalent conductivity decreases with increasing concentration.

Keywords: Conductivity, Schiff nanobases, Graphene oxide.

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Introduction

Electrical Conductivity

The electrical conductivity of any material is a measurement of how the electric charge is transferred through the material. In other words, it can be defined as a phenomenon of any material containing parts with an electric charge, which is either in the form of electrons, as in metals, or in the form of ions (positive or negative), as happens in electrolytic solutions whose conductivity results from the dissolution of salts, acids, and bases in water or another solvent. The conductivity of any medium is the inverse of the resistance and is measured as the ratio of the current flowing through a conductor to the potential difference between its ends [1]. In principle, the measurement of the electrical conductivity of electrolytic solutions is done by measuring the electrical resistance (R) that these solutions exhibit when an electric current passes through them [2]. Regarding the equivalent conductivity, the conductivity of any electrolyte solution depends on the number of ions present in the solution, their charge, and their rate of movement under the influence of the electromotive force. The equivalent conductivity expresses the electrical conductivity of a solute and is denoted by (Δ), which is defined as the conductivity of one gram equivalent of any solute between two electrodes separated by a distance of 1 cm. The equivalent conductivity can be obtained from measurements of the specific conductivity of solutions of known concentrations. Therefore, the definition of the equivalent conductivity Δ will be equal to the conductivity of one gram equivalent of a solute between two electrodes exactly one centimeter apart. The value of Δ cannot be calculated directly but is determined from the specific conductivity. If the concentration of the solution is in grams equivalents per liter, then the concentration per cm^3 is $\frac{1000}{C}$, and the volume containing one equivalent of the solute is $\frac{1000}{C}$.

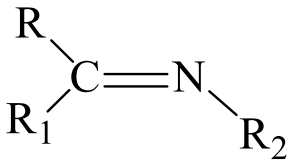
Since (L) is the conductivity of cm^3 of solution, then the conductivity of $\frac{1000}{C}$ cm^3 will be equal to:

$$\Lambda = \frac{1000\ L}{C}$$

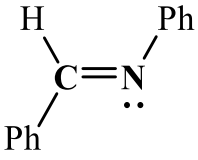
The conductivity of electrolyte solutions increases by (2%) for each degree Celsius, as ions move more freely with increasing temperature due to the decrease in viscosity of the liquid and the weakening of the bond between ions and solvent molecules at higher temperatures. Therefore, the conductivity cell must be immersed in a thermostatic bath or a temperature-controlled water bath [3]. Both specific conductivity and equivalent conductivity change with concentration. Strong electrolytes begin to experience a significant increase in specific conductivity when the concentration reaches several equivalents per liter, and this increase continues with further increases in concentration. In contrast, the increase in specific conductivity of weak electrolytes begins at low solution concentrations and then increases more gradually. In both cases, the increase in conductivity with concentration is attributed to the increase in the number of ions per unit volume of the solution. Unlike specific conductivity, equivalent conductivity (Δ) For both strong and weak electrolytes, the value increases with dilution of the solution. This is explained by the fact that the decrease in specific conductivity is too great to be compensated for by the increase in value upon dilution, and therefore the value of (Δ) increases. To determine the equivalent conductance, Kohlrausch and a number of his assistants made precise measurements. When plotting the equivalent conductance of an electrolyte at constant temperatures against the square root of the concentration of the electrolyte solutions, it mostly gives curves that turn into straight lines at low concentrations. It was found that there are two types of electrolytes. Electrolytes that give straight lines are called strong electrolytes. An important relationship can be deduced when extending the straight lines of strong electrolytes to infinite dilution to give what is called the limiting equivalent conductance, symbolized by (Δ_o), which represents the basis of Kohlrausch's Law of Independent Migration of Ions [4].

Schiff bases

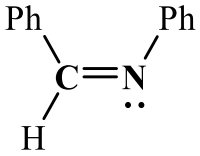
Schiff bases are defined as compounds containing the azomethine group. They are named after Schiff [5], who first synthesized these compounds in 1864 by condensing aldehydes or ketones with aromatic primary amines [6]. Millions of these compounds and their derivatives have been prepared. They are characterized by carrying a pair of electrons on the nitrogen atom of the double bond, enabling them to react with many electron-seeking reagents that catalyze substitution, cyclization, and coordination reactions. The structural formula for Schiff bases is:



Their naming depends on the nature of the groups R1, R2, and R3 [7]. Schiff bases have two geometric forms: E and Z [8]. One can be transformed into the other [9].



(*E*)-*N*-benzylideneaniline



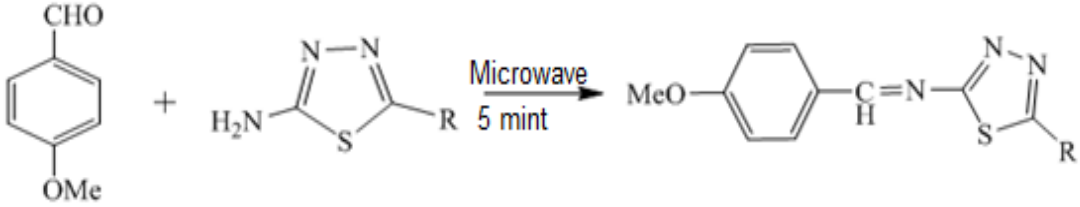
(*Z*)-*N*-benzylideneaniline

Studies have shown that Schiff bases form charge-transfer complexes as electron donors (n) through the azomethine group with a number of electron acceptors such as iodine [10, 8], forming 1:1 σ*-n molecular complexes. They also form 1:1 π*-n molecular complexes with dicyanodichloro-1,4-benzoquinone [11] (DDQ), chloranyl [12], 2,3,5,6-tetrachloro-1,4-benzoquinone (P-CA), and pentafluorobenzaldehyde. These studies also calculated the ionization potentials of the molecules involved in forming the complexes, as well as the equilibrium constants (bonding constants) and molar absorption coefficients for these complexes.

These studies also determined the ionization potentials of the molecules involved in forming the complexes.

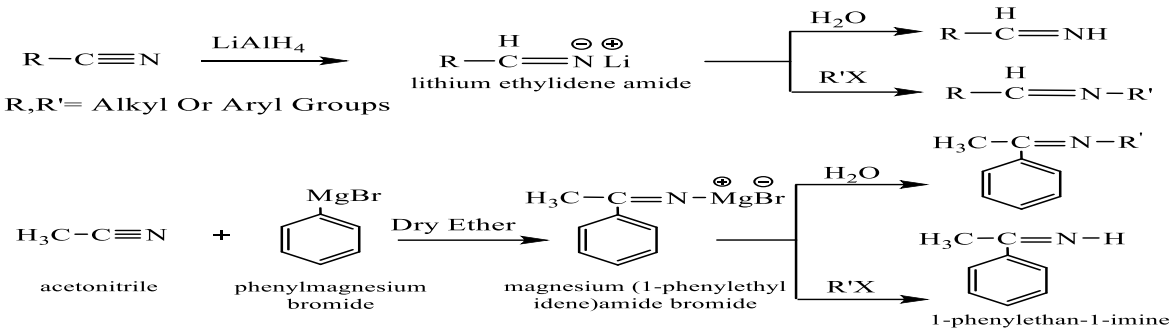
Preparation of Schiff Bases

The preparation of Schiff bases has garnered significant attention from researchers, leading to the preparation of numerous Schiff bases using various methods, including the reaction of cyclic amine derivatives with aromatic aldehydes, as shown below [13, 14].



R=Alkyl group

Schiff bases have also been prepared by the reduction of nitriles with certain organonuclear reagents. This is achieved through reduction with reducing agents such as LiAlH4 or hydrogen, in the presence of metals acting as catalysts (Ni, Pd, Pt). The reaction is then carried out with water or alkyl halides, or by adding them to organometallic reagents such as Grignard's reagent in the presence of dry ether [15]. Further details are provided below:



Materials and methods

Equipment used: Electronic balance, conductivity meter, thermostatic water bath, magnetic stirrer, conductivity cell. Centrifuge, oil bath, oven

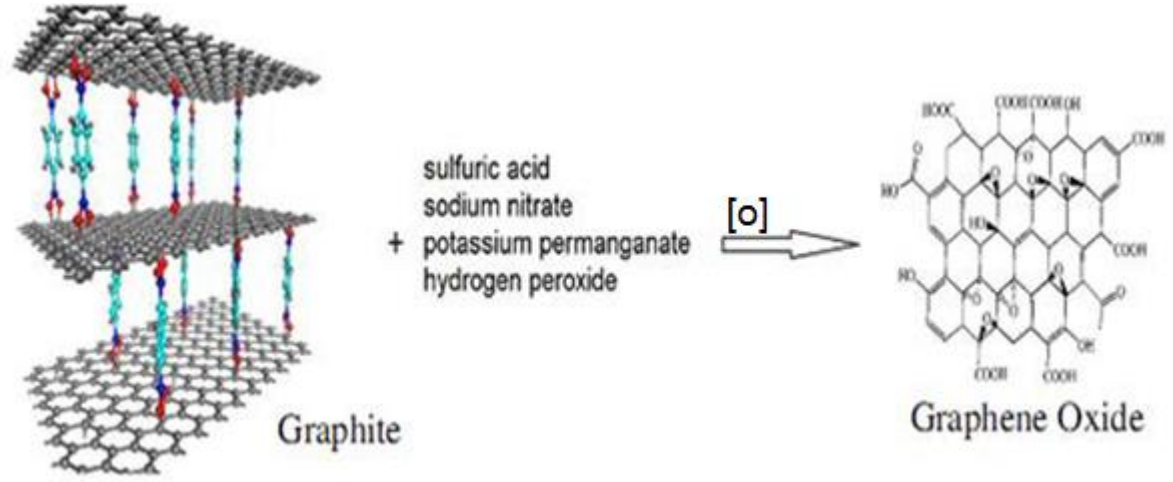
Practical Part

Preparation of Graphene Nanoparticles

The preparation was carried out in two steps:

Step 1: Preparation of Graphene Oxide (GO) (Hammer Method)

Place 46 ml of concentrated sulfuric acid in an ice bath in a suitable flask until the temperature is homogeneous. Then, gradually add 0.0176 mol (1.5 g) of sodium nitrate over 15 minutes, stirring at 0°C. Gradually add 1 g of graphite dust to the mixture over 10 minutes. Finally, gradually add 0.042 mol (6 g) of potassium permanganate over 15 minutes, carefully maintaining a temperature below 20°C. The mixture was left in an ice bath for 5 minutes. It was then removed from the ice bath and left to be magnetically stirred for 2 hours. Next, 46 ml of distilled water was added very slowly over 20 minutes using a dropper. The temperature was then raised to 98°C for 20 minutes. Afterward, 140 ml of warm distilled water (50°C) was added and stirred for 10 minutes at room temperature. Then, 15 ml of 30% hydrogen peroxide was added and stirred for 30 minutes. Finally, 300 ml of distilled water was added and the mixture was left to stand for 24 hours. The mixture was collected by centrifugation at 6000 rpm. The precipitate was washed once with a 10% hydrochloric acid solution and then five times (45 ml x 5) with deionized water until the pH reached 7. Finally, it was dried at 60-70°C until a constant weight was achieved [16].



Step Two: Preparation of Graphene Nanoparticles (NRGO) (Reduced Graphene Oxide GO)

Place 0.1 g of graphene oxide in a suitable round-bottom flask and add 1 mL of hydrochloric acid. Continue stirring until the solution is homogeneous (becomes a clear solution without suspended particles). Add 1 mL of aqueous hydrazine. Incubate the mixture at 100°C for 2 hours. Collect the black precipitate by centrifugation at 6000 rpm and wash it several times with deionized water to remove excess hydrazine. Dry at 70°C [17].

Preparation of Schiff Nanobases (ArNRGOTZS) by Thermal Melting

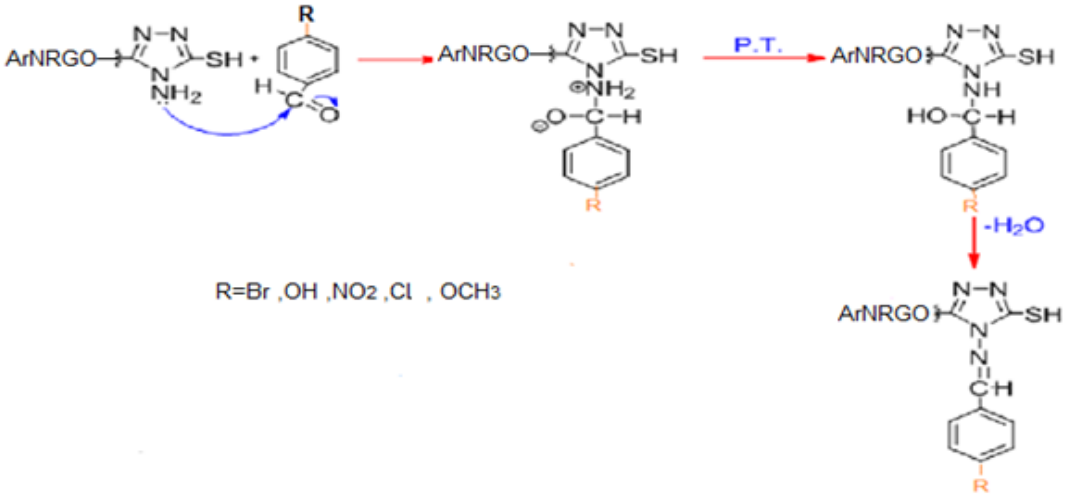
Mix 0.1 g of ArNRGOTZ with 0.3 g of 4-Bromobenzaldehyde, 0.0024 mol of 0.3 g of 4-Hydroxybenzaldehyde, 0.3 g of 4-Nitrobenzaldehyde, 0.3 g of 4-Chlorobenzaldehyde, or 0.3 g of 4-Methoxybenzaldehyde in a heat-resistant flask. Heat the mixture in an oil bath with stirring using a glass motor for 5-10 minutes at a specific temperature (see Table 1) until the molten changes color and consistency. Cool the product to room temperature [18].

Table (1) shows the temperatures required to prepare Schiff bases.

Comp No.	ArNRGOTZ With (1-5)	Tem P.
1	4-Bromobenzaldehyde	61
2	4-Hydroxybenzaldehyde	118
3	4-Nitrobnzaldehyde	119
4	4-Chlorobenzaldehyde	52
5	4-Methoxybenzaldehyde	208

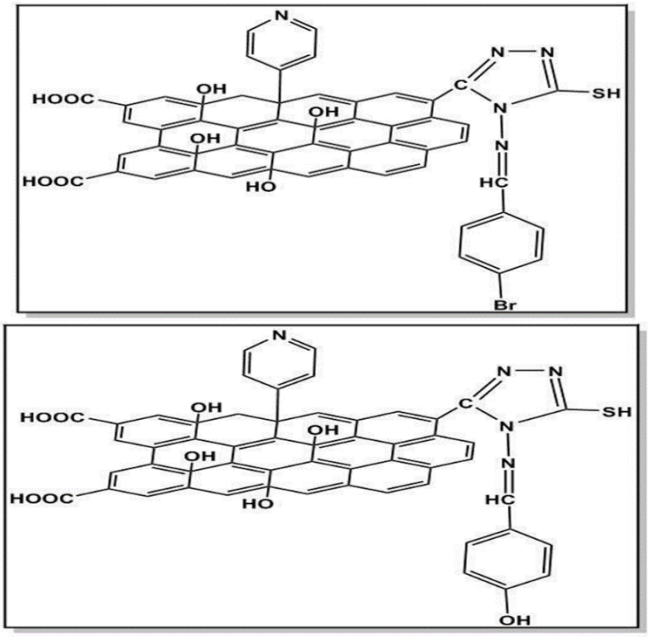
Preparation of solutions of Schiff nanobase compounds prepared in water:

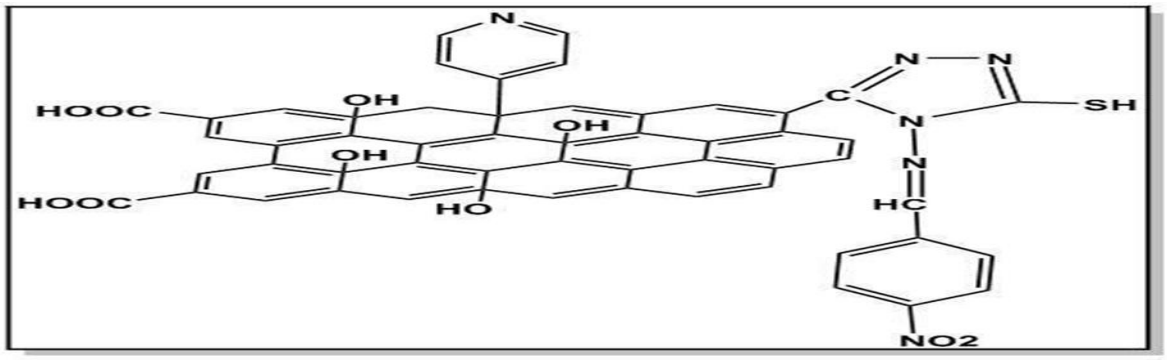
Solutions of Schiff nanobases were prepared by dissolving the required weight of them in (25) ml of conductivity measurement water. As in scheme 1



Scheme 1. illustrates the preparation of Schiff nanobases (Ar-NGTZS)

Prepared compounds





Conductivity measurements of prepared Schiff nanobase solutions in water:

Conductivity measurements of prepared Schiff nanobase solutions were performed in a thermostatic water bath conductivity measurement cell. The temperature at which the conductivity was to be measured was fixed (298.16 K). At the required temperature, the conductivity of the solution was measured, then a volume of (5 ml) of conductivity measurement water was added, and the conductivity of the solution was measured again. The process was repeated for fifteen measurements by adding a volume of (5 ml) of conductivity measurement water each time. The conductivity of all prepared Schiff nanobases was measured in the same way.

Results and Discussion

Electrical Conductivity

The electrical conductivity of Schiff nanobase solutions prepared in conductivity measurement water was studied, the conductivity of which was subtracted from the electrical conductivity values of the Schiff nanobases at an absolute temperature of (298). Tables (2) to (4) show that the value of the specific conductivity increases with increasing concentration, while the equivalent conductivity decreases with increasing concentration. This is explained by the fact that the increase in the specific conductivity is less than what is compensated for by the increase in the value of L/C. When the concentration increases, the value of Δo decreases, as shown in Figures (1) to (3). As for the values of Kb: equilibrium constant, Δo: equivalent conductivity at infinite concentration shown in Tables (2) to (4), they were calculated from the equation: /⊚⊚⊚⊚⊚⊚⊚ₒ + C⊚/K♭⊚ᵐₒ from drawing the relationship between CΔ and 1/Δo (Δo equivalent conductivity Semens.$Cm^2.eq^{-1}$), as in Figures (4) to (6). The low Kb values indicate that these bases are very poorly conductive and are closer to sparingly soluble salts. The difference in these values is attributed to the different effects of the substituent groups on these bases. As for the reason for the difference in Δo values, it is attributed to the molecular structure of these compounds (substitution), since Δo depends on the mobility of the molecule in solution (positive or negative ion). It is controlled by four forces: the electrical forces, which are equal to the potential resulting from the electrode or the charge of the molecule in the solution. The parts tend to move towards one of the electrodes. This effect is partially balanced by the frictional forces, which represent a characteristic property of each molecule. These two effects play an important role in estimating the continuity of the solution, which approaches infinite dilution (2). All of these compounds exhibited weak electrolyte behavior. This was demonstrated by plotting the relationship between the square root of different concentrations of their solutions and the equivalent conductivity (Δ). The relationship was shown as a curved line, with none of the solutions exhibiting a straight line, indicating that these solutions behave as weak electrolytes (124). Furthermore, their degree of dissociation (ά) is low, as shown in Tables (2) to (4). Consequently, their electrical conductivity L is very low, resembling that of sparingly soluble salts (which they are indeed sparingly soluble). Therefore, Δs can be considered as Δ, where Δs is the equivalent conductivity of the insoluble salt.

Table (2) shows the results obtained for the values of (**, ά b,Ķ Λₒ** specific conductivity, **Λ**) with respect to the concentration of the first compound.

NO.	$C_{mol.L^{1-}}$ ×10^{-4}	√C ×10^{-2}	Λ $S.eq^{-1}.cm^2$	s/cmμ	Λ_o	cĶ	ά
					2500	4.35×10^{-7}	
1	4.052	2.013	78.07	31.2			0.0312

2	5.871	2.423	67.7	39.74			0.0270
3	7.469	2.733	59.58	44.50			0.0238
4	8.946	2.991	55.45	49.60			0.0221
5	10.349	3.217	50.97	52.74			0.0203
6	11.655	3.414	48	55.94			0.0192
7	12.924	3.595	44.87	57.99			0.0179
8	14.137	3.76	43.26	61.15			0.0173
9	15.319	3.914	41.56	63.66			0.0166
10	16.459	4.057	40.04	65.90			0.016
11	17.572	4.192	38.96	68.46			0.0155
12	18.645	4.318	38.01	70.86			0.0152
13	19.713	4.44	37.2	73.32			0.0148
14	20.702	4.55	35.98	74.48			0.0143
15	21.715	4.66	35.4	76.87			0.0141

Table (3) shows the results obtained for the values of (, **ά b,Ķ Λ**o specific conductivity, **Λ**) with respect to the concentration of the two compound.

NO.	$C_{mol.L^{1-}}$ $\times10^{-4}$	$\sqrt{C}\times10^{-2}$	Λ $S.eq^{-1}.cm^2$	s/cmμ	Λ_o	cĶ	ά
					1666	1.55×10^{-6}	
1	4.052	2.013	97.59	39.52			0.0585
2	5.871	2.423	84.75	49.74			0.0508
3	7.469	2.733	74.48	55.56			0.0446
4	8.946	2.991	68.25	61.01			0.0409
5	10.349	3.217	63.71	65.62			0.0382
6	11.655	3.414	60	69.60			0.036
7	12.924	3.595	56.25	72.56			0.0337
8	14.137	3.76	54.08	76.25			0.0324
9	15.319	3.914	51.96	79.50			0.0311
10	16.459	4.057	50.05	82.08			0.03
11	17.572	4.192	48.70	85.22			0.0292
12	18.645	4.318	47.52	88.38			0.0285
13	19.713	4.44	45.75	90.03			0.0274
14	20.702	4.55	44.97	93.09			0.0269
15	21.715	4.66	44.25	96.02			0.0265

Table (4) shows the results obtained for the values of (, **ά b,Ķ Λ**o specific conductivity, **Λ**) with respect to the concentration of the three compound.

NO.	$C_{mol.L^{1-}}$	$\sqrt{C}$	Λ $S.eq^{-1}.cm^2$	s/cmμ	Λ_o	cĶ	ά
	$\times10^{-4}$	$\times10^{-2}$			2000	1.54×10^{-6}	
1	4.052	2.013	117.1	47.38			0.0585
2	5.871	2.423	101.7	59.28			0.0508
3	7.469	2.733	89.37	66.67			0.0446
4	8.946	2.991	81.9	73.21			0.0409

5	10.349	3.217	76.25	78.53			0.0381
6	11.655	3.414	72	83.52			0.036
7	12.924	3.595	67.5	87.07			0.0337
8	14.137	3.76	64.9	91.50			0.0324
9	15.319	3.914	62.35	95.45			0.0311
10	16.459	4.057	60.06	98.50			0.0300
11	17.572	4.192	58.44	102.27			0.0292
12	18.645	4.318	57.02	106.05			0.0285
13	19.713	4.44	55.8	109.98			0.0279
14	20.702	4.55	53.97	111.71			0.0269
15	21.715	4.66	52.2	113.27			0.0261

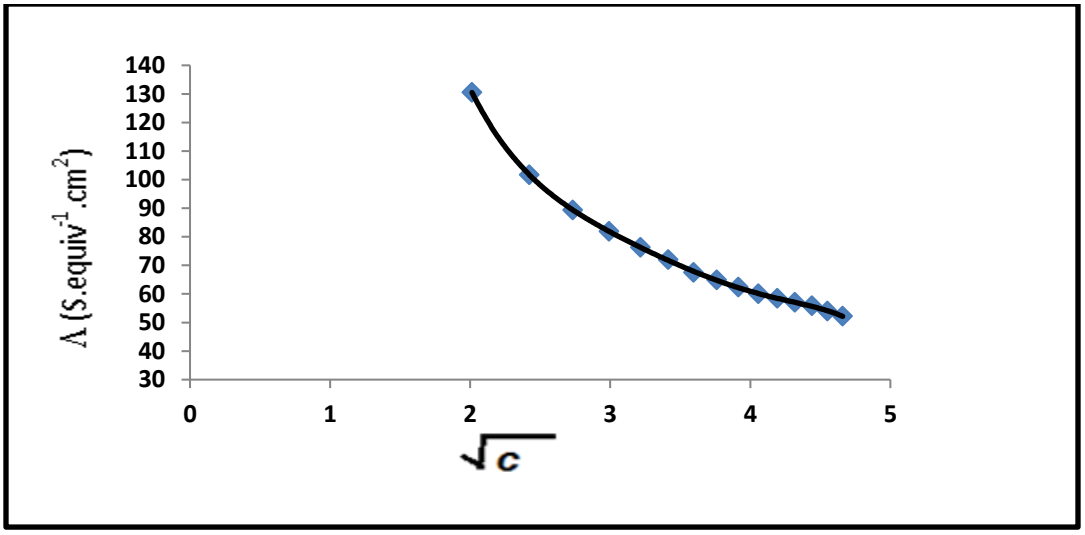


Figure (1) illustrates the relationship between the square root of the concentration versus the continuity of compound(1)

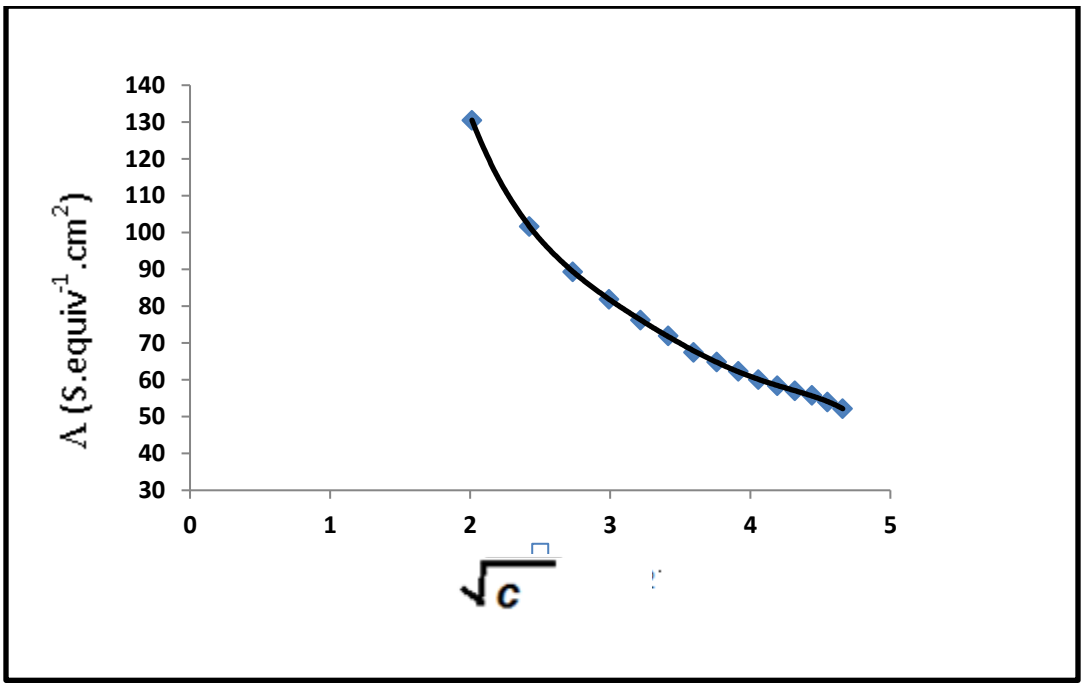


Figure (2) illustrates the relationship between the square root of the concentration versus the continuity of compound(2)

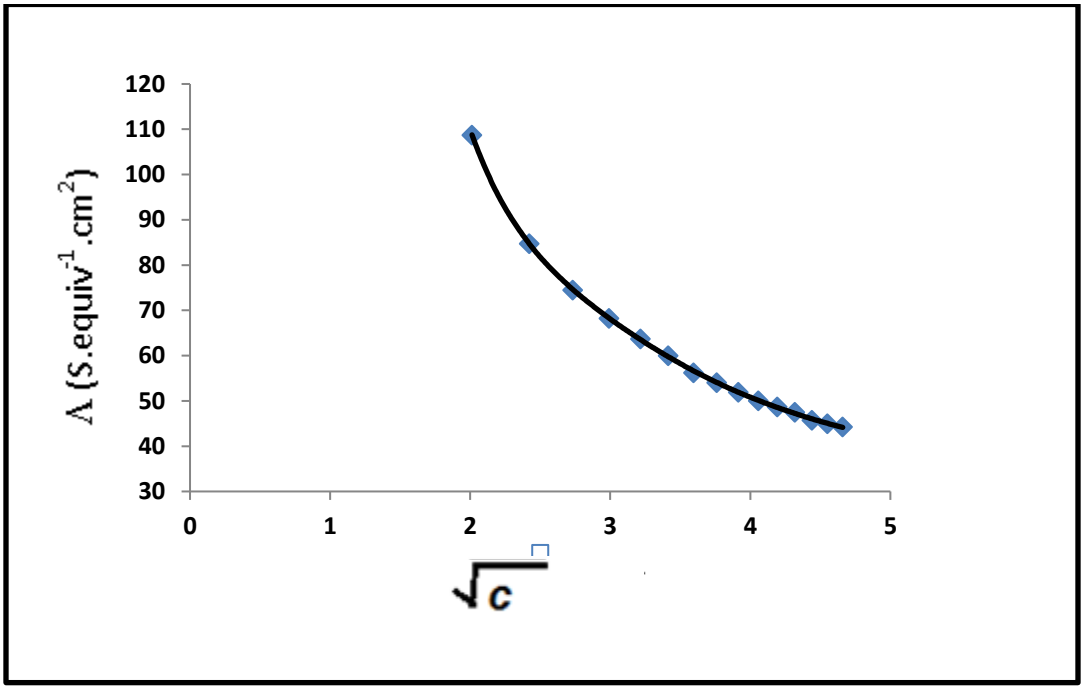


Figure (3) illustrates the relationship between the square root of the concentration versus the continuity of compound(3)

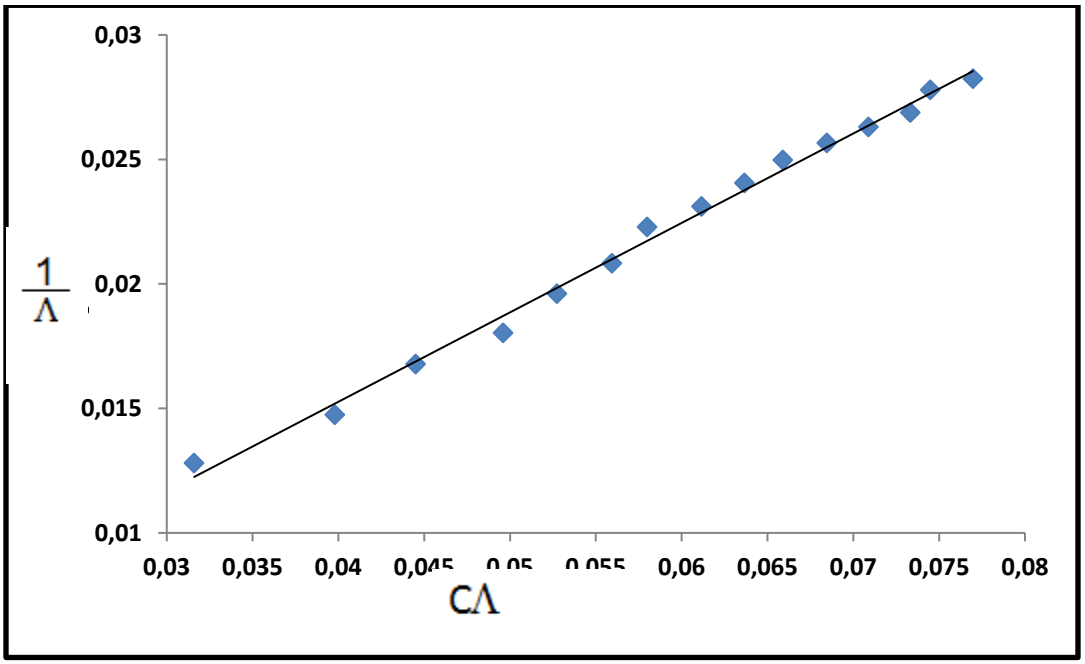


Figure (4) illustrates the relationship between ⊚⊚⊚₀ and C⊚ compound(1)

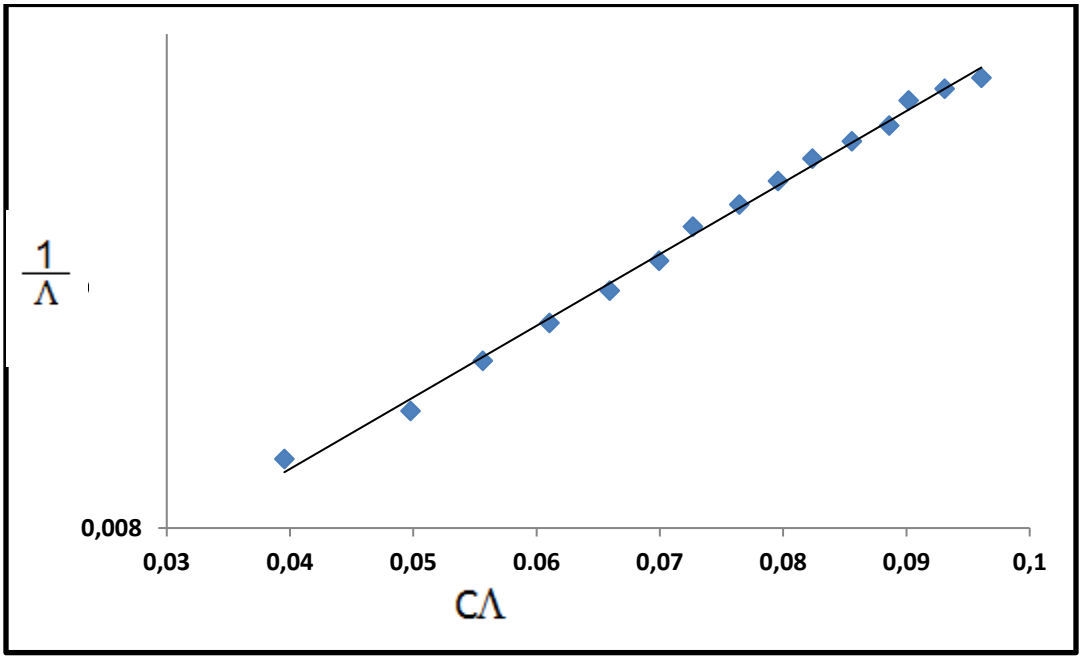


Figure (5) illustrates the relationship between ⊚⊚⊚₀ and C⊚ compound(3)

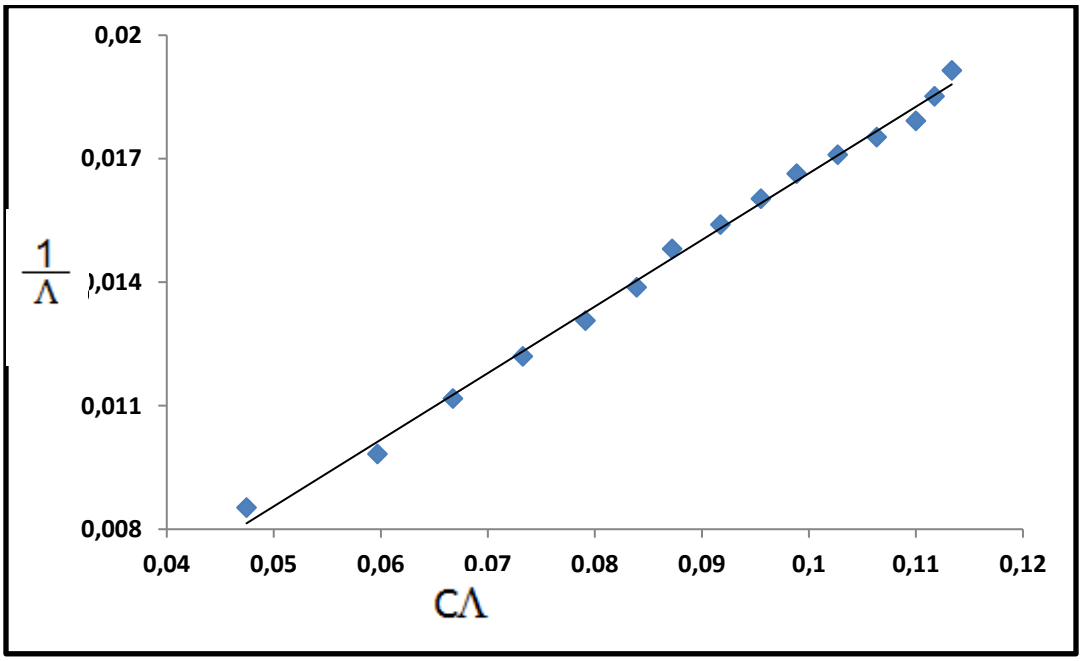


Figure (6) illustrates the relationship between ⊚⊚⊚₀ and C⊚ compound(3)

Conclusions

The specific conductivity increases with increasing concentration, while the equivalent conductivity decreases with increasing concentration. The low Kb values indicate that these bases are very poorly conductive and are closer to sparingly soluble salts. Their degree of dissociation (ά) is low, as shown in Tables (2) to (4), and therefore their electrical conductivity L is very low. The thermal stability of the decorative compounds and the corresponding Schiff base derivatives is good.

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