Solvolysis Thermodynamic Parameters of Phenyl Hydrazine Hydrochloride

Noreldin S.Y. Abdalla[1] and Farid I. El-Dossoki[2]*

[1]Chemistry Department, Faculty of Science, Tobrouk University, Libya/Tobrouk and **the current address:** Chemistry Department, University of Leicester, UK. University Road, Leicester LE1 7RH
[2]Chemistry Department, Faculty of Science, Port-Said University, Port-Said, Egypt.

***Corresponding author: feldossoki64@sci.psu.edu.eg**

ABSTRACT

The present work deals with studying the effect of solvent and temperature on the solvolysis process using both the pH-metric and the conductometric measurements. The pH and the conductivity of different concentrations of the phenyl hydrazine hydrochloride in water (H_2O), ethanol (EtOH) and in (EtOH-H_2O) mixtures with different percentages of EtOH; 30%, 50%, 70%, 100% (v/v) and at different temperatures from 293.15 to 308.15 K with a step of 5 K were measured experimentally. The conductivity of different concentrations of the phenyl hydrazine hydrochloride in aniline at the same temperatures was also measured. Depending on the measured pH and conductivity data, the solvolysis constant of phenyl hydrazine chloride was estimated. The thermodynamic parameters (free energy change, ΔG_h°, enthalpy change, ΔH_h°, entropy change, ΔS_h°, and activation energy, E_a) of the solvolysis process were evaluated from the temperature dependence of solvolysis constant. Positive values of the standard enthalpy change (ΔH_h°), indicate that the solvolysis process is endothermic process. The solvolysis constant is increase as the alcohol percentage increase from 30% - 100%, which attributed to the higher solute-solvent interaction.

Keywords:

Conductivity; pH-metric; Phenyl hydrazine hydrochloride**;** Solvolysis;

1. INTRODUCTION

Hydrolysis literally means reaction with water. It is a type of decomposition chemical reaction in which a molecule is used to break down the bonds of a particular substance. For all solvents; water and other solvents, it is preferred to use the expression; solvolysis. The first fragment of the parent molecule gains H^+ ion from the additional H_2O molecule while the rest group collects the remaining OH group. In biotechnology and as far as living organisms are suffered about these types of substances which are often polymers [1, 2]. Chemically, solvolysis is classified, into three main types which are salt, acid, and base hydrolysis. Hydrolysis occurs when a salt of a weak acid or weak base (or both) is dissolved in H_2O.

Water auto ionizes into negative hydroxyl ions and hydrogen ions and the salt breaks down into (+) and (-) ions. This is the most common solvolysis process that can be occurred. In addition, solvolysis could also be thought of as the exact opposite reaction to condensation, which is the process by which two molecules combine to form one larger molecule. The end result of this reaction is that the larger molecule ejects a H_2O molecule. Nonetheless, only a few reactions between H_2O and organic compounds that can be occurred under normal conditions.[2, 3] In general, strong acids or bases should be added in order to achieve solvolysis in which the water has no effect. The acid or base is considered a catalyst which making the reaction move faster, thereby increasing the reaction rate, but are recovered at the end of it.[3] Acid–base-catalyzed solvolysis are also common, one instance is the solvolysis of amides or esters. Their solvolysis happens when the nucleophile attacks the carbon of the carbonyl group of the amide or ester. In acid, the carbonyl group becomes protonated, and this leads to a much easier nucleophilic attack. Whilst, in an aqueous base, hydroxyl ions are better nucleophiles than dipoles such as water. In both hydrolyses processes (in acid and in aqueous base), the products are compounds with carboxylic acid groups. Salt solvolysis in water takes place by dissociation to form ions, either completely or incompletely this is depending on the respective solubility constant (Ksp). Perhaps one of the oldest examples: $NH_4Br_{(s)} \rightarrow NH_4 + Br$ the salt NH_4Br in water dissociates into NH_4^+ and Br^-[4]. There are likely four mechanisms which can be forming the salts. In the first mechanism, salt is formed from a strong acid and weak base. In the second mechanism, salt is formed from a strong base and strong acid. In the third mechanism, salt is formed from a strong base and weak acid. In the last mechanism, salt can be formed from weak acid and a weak base. In all cases the solvolysis will take place and the acidity or basicity depends on the equilibrium constants K_a and K_b. If the K_a value is greater than the K_b value, the resulting solution will be acidic and vice versa.[2, 3, 5] There are different factors can affect hydrolysis, include pH, salt concentration, temperatures and solvolysis time which have been reported in detail.[4, 6-12] Several methods, including conductometric, pH titration,[5, 13, 14] spectrophotometry,[15-17] and ion-exclusion based chromatographic[9, 18] have been used to determine the hydrolytic rate of several compounds.[12, 17, 19-21] As far as we know, the solvolysis rate of hydrazine and its derivatives have not been studied, especially for hydrazine hydrochloride salts.
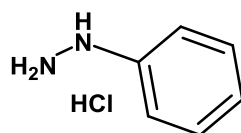
Structure 1: The Structure of Phenyl Hydrazine Hydrochloride

The objective for this paper was therefore to study the solvolysis of phenyl hydrazine hydrochloride (**Structure 1**), as an example of the salts of a weak base and strong acid, in water and alcoholic-water solvents at different temperatures (293.15, 298.15, 303.15, and 308.15 K) by using two different techniques, including pH-metric and conductometric measurements.

2.   EXPERIMENTAL

2.1 Materials and apparatus

The chemicals utilized in this study are listed in **Table 1**. Bidistilled water with conductivity equal to (2 µS/cm) is used to prepare the solutions under study. The conductivity of the solutions under study was measured using the conductivity meter of type Jenway (4310) with measuring accuracy (±0.1 µS/cm). The pH of the solutions was measured using the pH-meter of type HI9813-6, with measuring accuracy

(±0.1 pH unit) at different concentrations of Phenyl hydrazine hydrochloride with temperatures. The temperature of the solutions was adjusted to the selected temperature degree (±0.1 ˚C) using ultrathermostate water bath of type JSR JSWB-11T.

Table 1. List of chemicals used in this study

| chemical	CAS No.	suppliers	Mass fraction purity, (%)	purification method	boiling Point, ° C	MW, g mol^{-1}
Phenyl hydrazine hydrochloride, $C_6H_9ClN_2$.	59-88-1	Santa Cruz Biotechnology	≥99.0%	none	250-254	44.60
Ethanol, (EtOH) C_2H_5OH	64-17-5	Sigma-Aldrich Company Ltd	anhydrous, ≥99.5	none	78	46.07
Aniline, $C_6H_5NH_2$	62-53-3	Loba Chemie Pvt Ltd	≥99.0	none	184	93.13

2.2 Procedure

0.002, 0.005, 0.01, 0.015, 0.02, 0.025 molar solutions of phenyl hydrazine hydrochloride were prepared in bidistilled water and aniline solvents. The pH of each solution in water at the selected temperature degree was measured. Also measure the conductivity of each solution in water and in aniline (κ_w and κ_a respectively) at selected temperature degree.

3.   RESULTS AND DISSECTION

3.1. Estimating the solvolysis constant of phenyl hydrazine hydrochloride by using pH measurements

The solvolysis of phenyl hydrazine hydrochloride as a salt of weak base and strong acid can be analyzed as follow: $C_6H_5NHNH_3Cl$ is made from acid HCl and base $C_6H_5NHNH_3OH$. In water $C_6H_5NHNH_3Cl$ dissociates completely in $C_6H_5NHNH_3^+$ and Cl^- ions. $C_6H_5NHNH_3^+$ ions successfully polarize as follow:

$$C_6H_5NHNH_3Cl + H_2O \longrightarrow C_6H_5NHNH_3OH + HCl$$

$$C_6H_5NHNH_3{}^+{}_{(aq)} + H_2O \longrightarrow C_6H_5NHNH_3OH + H^+$$
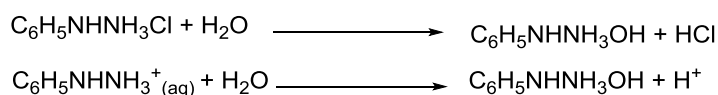
$C_6H_5NHNH_3OH$ is a weak base which dissociates a little. Thus OH^- ions of water are consumed by $C_6H_5NHNH_3^+$ and H^+ reacts with Cl^- ions. $Cl^- + H^+ \leftrightarrow HCl$; HCl is a strong acid and it dissociates completely. That means H^+ ions produced by solvolysis of $C_6H_5NHNH_3Cl$ salt remain in solution while OH^- ions get trapped by $C_6H_5NHNH_3^+$. This higher concentration of H^+ ions makes the solution acidic.

3.1.1   Quantitative Aspect of Hydrolysis.

Solvolysis is a reversible reaction. The equilibrium constant derived by application of Law of mass action to a solvolysis (or hydrolytic) reaction is called the solvolysis constant or hydrolytic constant which is represented as K_h. Now, we proceed to discuss the mathematics of solvolysis of the various types of salts, according to pH measurements. The solvolysis of a salt of a weak base BOH and a strong acid may be represented by the equation: $B^+ + H_2O \leftrightarrow BOH + H^+$
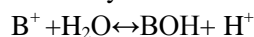
3.1.2 Solvolysis constant and the relation between K_h, K_w and K_b

Applying the Law of mass action to the above solvolysis reaction, the solvolysis constant, K_h, is given by: K_h = [H$^+$] [BOH]/ [B$^+$][H$_2$O]. Since [H$_2$O] is very large, it is taken to be constant and the solvolysis constant expression is reduced to:

$$K_h = [H^+] [BOH]/ [B^+] \tag{1}$$

$$K_h = [K_w]/[K_b] \tag{2}$$

Thus the solvolysis constant K_h varies inversely with the dissociation constant, K_b, of the base. Therefore, the weaker the base, the greater will be the solvolysis constant of the salt.

3.1.3 The relation between pH, concentration (C) and K_h

$$pH = -(1/2)\log K_h - (1/2)\log C \tag{3}$$

The value of K_h was estimated by plotting pH vs. logC which give a straight line with slope = -(1/2) and intercept = -(1/2)logK_h. The pH of different concentrations (0.002, 0.005, 0.010, 0.015, 0.02, 0.025M) of Phenyl hydrazine hydrochloride in water at different temperature (293.15, 298.15, 303.15, and 308.15 K) was measured and recorded in **Table 2**.

The pH values are increased with increasing of ethanol percentage in the mixture. This may be due to lower acidity of ethanol. Also, the pH values are decreased with rising of the T and concentration, which may be due to increase in the ionization process and libration of H$^+$.

The solvolysis constant K_h of phenyl hydrazine hydrochloride in H$_2$O over the temperature range of (293.15 - 308.15 K) was estimated according to equation **11** by plotting of pH versus log C (**Figure 1** as example), where the intercept equal (- 1/2 log K_h). The values of the solvolysis constants (K_h) were presented in **Table 3**.
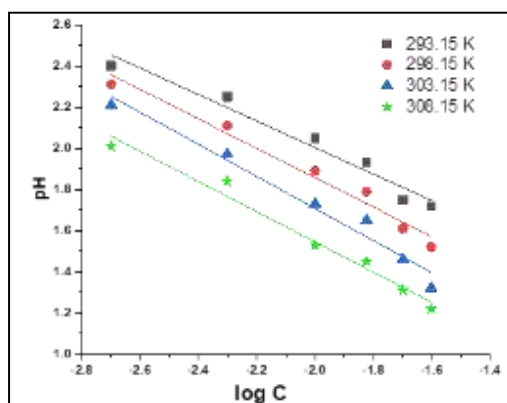

Figure 1. pH versus log C for Phenyl hydrazine hydrochloride at different temperatures in H$_2$O

The free energy change of solvolysis (ΔG_h°) was calculated at different temperatures by applying the following equation:

$$\Delta G_h^\circ = \text{-2.303RT log } K_h \tag{4}$$

Table 2. The pH of different concentrations of phenyl hydrazine hydrochloride in H_2O, EtOH and EtOH-H_2O mixed solvents at different temperatures

Conc.	pH in 0.0% EtOH				pH in 30% EtOH			
$mol.l^{-1}$	293.15 K	298.15 K	303.15 K	308.15 K	293.15 K	298.15 K	303.15 K	308.15 K
0.002	2.40	2.31	2.21	2.01	3.60	3.50	3.40	3.30
0.005	2.25	2.11	1.97	1.84	3.05	3.00	2.95	2.90
0.010	2.05	1.89	1.73	1.53	2.85	2.80	2.75	2.70
0.015	1.93	1.79	1.65	1.45	2.77	2.70	2.62	2.40
0.020	1.75	1.61	1.46	1.31	2.55	2.50	2.45	2.30
0.025	1.72	1.52	1.32	1.22	2.50	2.40	2.30	2.20
$mol.l^{-1}$	pH in 50% EtOH				pH in 70% EtOH			
0.002	3.90	3.80	3.70	3.60	4.15	4.0	3.85	3.70
0.005	3.10	3.15	3.20	3.25	4.00	3.90	3.80	3.85
0.010	2.60	2.65	2.70	2.75	3.80	3.75	3.70	3.50
0.015	2.50	2.55	2.60	2.65	3.50	3.30	3.10	2.90
0.020	2.30	2.35	2.40	2.45	3.10	2.95	2.89	2.50
0.025	2.20	2.25	2.30	2.35	2.80	2.70	2.60	2.40
$mol.l^{-1}$	pH in 100% EtOH							
	293.15 K		298.15 K		303.15 K		308.15 K	
0.002	3.20		3.10		3.00		2.90	
0.005	2.90		2.80		2.70		2.60	
0.010	2.65		2.50		2.40		2.30	
0.015	2.40		2.30		2.20		2.10	
0.020	2.20		2.10		2.00		1.90	
0.025	2.10		2.00		1.90		1.80	

The enthalpy change (ΔH_h°) and the entropy change (ΔS_h°) of solvolysis applying the following equation by plotting (ΔG_h°), versus (T) (**Figure 2a**, as example) where the intercept is (ΔH_h°) and the slope is ($-\Delta S_h^\circ$),

The activation energy of
$$\Delta G_h^\circ = \Delta H_h^\circ \text{ -T}(\Delta S_h^\circ) \tag{5}$$
the solvolysis process (K_h) was calculated by applying Arrhenius equation where the solvolysis process depending on temperature degree as follow:

$$K_h = \text{A e}^{(-Ea/RT)} \tag{6}$$

Plotting of (ln K_h) versus (1/T), gives straight line with slope equal (-Ea/R), where R is the universal gas constant (8.314 J/K *mol*) (**Figure 2b**, as an example). The values of the solvolysis constant K_h, the free energy change (ΔG_h°), enthalpy change (ΔH_h°), the entropy change (ΔS_h°) and the activation energy (E_a) of the solvolysis process are summarized in **Tables 3**. According to the results obtained, the K_h is greatly

influenced by both temperature and solvent compositions. Increasing the temperature degree, lead to significant increases in the solvolysis reaction rate of phenyl hydrazine hydrochloride. This can be related to increase in the ionization process and libration of hydrogen ion as the temperature degree increase. This was subsequently confirmed by the positive values of the free energy change and the activation energy of the solvolysis process.[12, 17, 19-22] The positive values of the free energy change (ΔG_h°) and the standard enthalpy change (ΔH_h°), indicate that the solvolysis process is non spontaneous endothermic process.[12, 17, 19-21]. The solvolysis constant is increase as the alcohol percentage increase from 30-100%. This may be due to the higher solute-solvent interaction.[12, 17, 19-21]
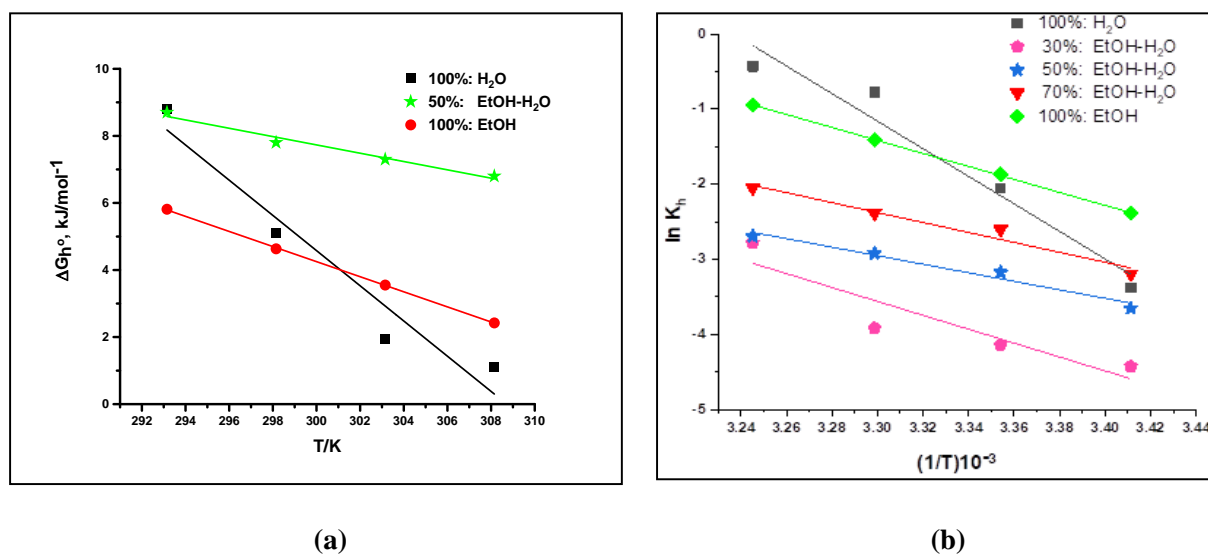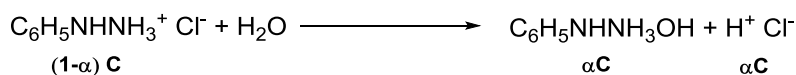

(a)   **(b)**

Figure 2. (**a**). The temperature dependence of (ΔG_h°), for phenyl hydrazine hydrochloride in different solvents; (**b**). Relation of ln lnK_h *vs*. (1/T) for phenyl hydrazine hydrochloride in different solvents.

3.2. Estimation of solvolysis constant of phenyl hydrazine hydrochloride using conductometric measurements.

According to the conductometric measurements, the solvolysis constant of the salt can be determined as in the following manner: The Phenyl hydrazine hydrochloride solvolysis in the following manner liberating free acid:

$$C_6H_5NHNH_3^+ \ Cl^- + H_2O \longrightarrow C_6H_5NHNH_3OH + H^+ \ Cl^-$$
$$(1-\alpha) \ C \qquad\qquad\qquad\qquad \alpha C \qquad\qquad \alpha C$$

The solvolysis constant K_h is given by:

$$K_h = \alpha \ C \ \alpha \ C/(1-\alpha)C = \alpha^2 \ C \qquad\qquad (7)$$

Where α is the degree of solvolysis and C is the concentration of Phenyl hydrazine hydrochloride salt in *mol*/L. The molar conductance of a solution of phenyl hydrazine hydrochloride is related to the concentration and the K_h, as follow:

From equation **15**, $K_h = \alpha^2 \ C$; $\alpha = (\Lambda_w - \Lambda_a) / (\Lambda_o - \Lambda_a)$ (8)

Where; Λ_o is the limiting molar conductance of HCl in an aqueous solution at 25°C = 426.16 S cm^2 mol^{-1}.

Table 3. The values of the solvolysis constant (K_h), standard free energy change (ΔG_h°, kJ *mol⁻¹*), standard enthalpy change (ΔH_h°, kJ *mol⁻¹*), standard entropy change (ΔS_h° kJ *mol⁻¹* K) and the activation energy (E_a, kJ *mol⁻¹*) of the solvolysis process of phenyl hydrazine hydrochloride at different temperature in the solvent used, derived from pH measurements

Solvent	T/K	K_h	ΔG_h°	ΔH_h°	ΔS_h°	E_a
0.0% EtOH	293.15	0.034	8.80	162	0.525	0.155
	298.15	0.128	5.10			
	303.15	0.460	1.95			
	308.15	0.650	1.10			
30% EtOH	293.15	0.012	10.78	77.870	0.227	0.042
	298.15	0.016	10.25			
	303.15	0.020	9.86			
	308.15	0.062	7.12			
50% EtOH	293.15	0.026	8.70	44.912	0.124	0.046
	298.15	0.042	7.80			
	303.15	0.054	7.30			
	308.15	0.068	6.80			
70% EtOH	293.15	0.041	7.78	54.835	0.161	0.054
	298.15	0.074	6.45			
	303.15	0.092	6.01			
	308.15	0.129	5.24			
100% EtOH	293.15	0.092	5.81	71.767	0.225	0.071
	298.15	0.154	4.63			
	303.15	0.244	3.55			
	308.15	0.389	2.42			

Λ_w is the molar conductance of Phenyl hydrazine hydrochloride of molar concentration, C in aqueous solution at 298 K. Λ_a is the molar conductance of Phenyl hydrazine hydrochloride of molar concentration, C in aniline solution at 298 K. In aniline solution it supposes that the phenyl hydrazine hydrochloride is unhydrolysed and remain in the molecular state. It follows that the conductivity due to the resulted HCl from one g equivalent of phenyl hydrazine hydrochloride in an aqueous solution of molar concentration, C is ($\alpha \Lambda_o$) while the conductivity due to one g equivalent of the unhydrolysed phenyl hydrazine hydrochloride in aqueous solution of molar concentration, C is $\{(1-\alpha) \Lambda_a\}$, then

$$\Lambda_w = (\alpha \Lambda_o) + \{1- \alpha) \Lambda_a\} \tag{9}$$
$$= \alpha \Lambda_o + \Lambda_a - \alpha \Lambda_a$$
$$\Lambda_w - \Lambda_a = \alpha \Lambda_o - \alpha \Lambda_a$$
$$\Lambda_w - \Lambda_a = \alpha (\Lambda_o - \Lambda_a) \tag{10}$$
$$\alpha = (\Lambda_w - \Lambda_a) V / (\Lambda_o - \Lambda_a) \tag{11}$$

The value of the solvolysis constant K_h can be calculated directly from;

$$\alpha = (\Lambda_w - \Lambda_a) / (\Lambda_o - \Lambda_a) \quad K_h = \alpha^2\, C \tag{12}$$

Also, the value of the solvolysis constant K_h can be calculated applying the following equation:

$$\log K_h = 2 \log \alpha + \log C$$

$$\text{or} \qquad 2 \log \alpha = \log K_h - \log C \tag{13}$$

Draw the relation between log C and log α to obtain the value of K_h from the intercept. The value of Λ_w and Λ_a can be calculated by using the following equation:

$$\Lambda_w = 1000\, \kappa_w/C \text{ in water where}$$

$$\Lambda_a = 1000\, \kappa_a/C \text{ in aniline where}$$

Where (κ_w and κ_a) are the conductivity of Phenyl hydrazine hydrochloride in water and in aniline respectively which measured using a conductivity cell. The conductivity of different concentrations (0.002, 0.005, 0.010, 0.015, 0.02, 0.025M) of Phenyl hydrazine hydrochloride in water and in aniline at different temperature (293.15, 298.15, 303.15, and 308.15 K) was measured and recorded in **Table 4.**

According to the results listed in **Table 4** the value of the conductivity of phenyl hydrazine hydrochloride in aniline is very lower than that in either H_2O or the EtOH-H_2O mixture over the all temperatures range used. This can be mainly attributed to no solvolysis of phenyl hydrazine hydrochloride in aniline. κ_a values are almost equal for each concentration of phenyl hydrazine hydrochloride at the same T, while these values are increased with increasing of the temperatures. This is as a result of in aniline solution it supposes that the phenyl hydrazine hydrochloride is unhydrolysed and remain in the molecular state. As the T increase the hydrolysis of phenyl hydrazine hydrochloride may increase and so the conductivity, κ_a increases. The solvolysis constant of Phenyl hydrazine hydrochloride was calculated according to equation **13** by plotting log α versus log C (**Figure 3**).
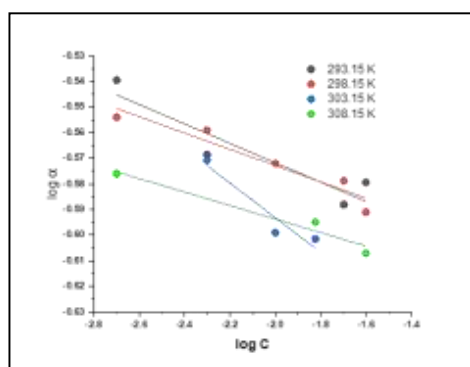

Figure 3. Log (C) *vs*. log (α) for Phenyl hydrazine hydrochloride in H_2O at different temperatures

The free energy change (ΔG_h°), the enthalpy change (ΔH_h°), the entropy change (ΔS_h°) and the activation energy (E_a) of the solvolysis process of phenyl hydrazine hydrochloride were calculated as explained in the pH measurements according to equations **13-15**. **Figure 4a**, show the relation between (ΔG_h°), and (T) for estimation of $(\Delta H_h^\circ$ and $\Delta S_h^\circ)$, **Figure 4b,** show the relation of ln K_h *vs*. (1/T) for calculation of the activation energy of the solvolysis process.

Table 4. The conductivity (μS/cm) of different concentrations of phenyl hydrazine hydrochloride in water (κ_w) and in aniline (κ_a) at different temperatures

Conc.	0.0% EtOH							
	293.15 K		298.15 K		303.15 K		308.15 K	
mol l⁻¹	κ_w	κ_a	κ_w	κ_a	κ_w	κ_a	κ_w	κ_a
mol l⁻¹	0.0% EtOH							
0.002	228.00	0.710	237	0.70	245.80	0.690	254.9	0.690
0.005	532.50	0.820	585	0.99	637.46	1.150	689.9	1.320
0.010	1135.5	1.775	1137	2.38	1138.45	2.585	1139.9	2.790
0.015	1489.5	4.175	1603	4.37	1716.50	4.565	1829.9	4.760
0.020	2038.0	4.360	2241	4.55	2443.90	4.740	2646.9	4.930
0.025	2598.0	3.580	2721	4.70	2843.90	5.820	2966.9	6.930
mol l⁻¹	30% EtOH							
0.002	220	0.710	251	0.70	280	0.690	308	0.690
0.005	550	0.820	583	0.99	610	1.150	640	1.320
0.010	960	1.775	1060	2.38	1160	2.585	1250	2.790
0.015	1270	4.175	1390	4.37	1500	4.565	1620	4.760
0.020	1507	4.360	1590	4.55	1680	4.740	1770	4.930
0.025	1750	3.580	1887	4.70	1740	5.820	2140	6.930
mol l⁻¹	50% EtOH							
0.002	266	0.002	266	0.002	266	0.002	266	0.002
0.005	420	0.820	460	0.99	510	1.150	577	1.320
0.010	695	1.775	813	2.38	898	2.585	953	2.790
0.015	953	4.175	1115	4.37	1560	4.565	1252	4.760
0.020	1109	4.360	1290	4.55	1398	4.740	1496	4.930
0.025	1200	3.580	1398	4.70	1519	5.820	1798	6.930
mol l⁻¹	70% EtOH							
0.002	48	0.710	51	0.70	55	0.690	58	0.690
0.005	103	0.820	119	0.99	135	1.150	150	1.320
0.010	204	1.775	221	2.38	243	2.585	265	2.790
0.015	336	4.175	370	4.37	404	4.565	435	4.760
0.020	421	4.360	470	4.55	519	4.740	567	4.930
0.025	496	3.580	551	4.70	606	5.820	661	6.930
mol l⁻¹	100% EtOH							
0.002	19.77	0.710	21.48	0.70	23.19	0.690	58	0.690
0.005	58.37	0.820	63.08	0.99	67.79	1.150	150	1.320
0.010	124.67	1.775	134.48	2.38	144.29	2.585	265	2.790
0.015	192.37	4.175	206.78	4.37	221.19	4.565	435	4.760
0.020	231.37	4.360	251.78	4.55	272.19	4.740	567	4.930
0.025	289.37	3.580	313.78	4.70	338.19	5.820	661	6.930

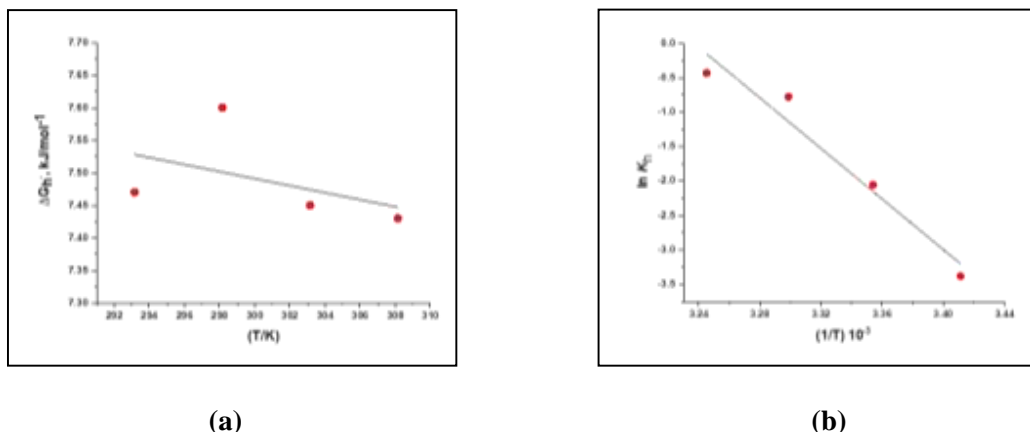**(a)**   **(b)**

Figure 4. (**a**): The temperature dependence of (ΔG_h°), for Phenyl hydrazine hydrochloride at different solvents; (**b**): Relation of ln K_h *vs*. (1/T) for Phenyl hydrazine hydrochloride in H_2O

The values of the solvolysis constant (K_h), free energy change (ΔG_h°), enthalpy change (ΔH_h°), entropy change (ΔS_h°), and the activation energy (E_a), of the solvolysis process of phenyl hydrazine hydrochloride are listed in **Table 5.** The results listed in **Table 5** indicated that the solvolysis constant increase as the temperature degree increase as subsequently confirmed by the positive values of the free energy change (ΔG_h°), and the activation energy of the solvolysis process.[12, 17, 19-21] The positive values of the free energy change (ΔG_h°) and the standard enthalpy change (ΔH_h°), indicate that the solvolysis process is non spontaneous endothermic process.[12, 17, 19-21] The solvolysis constant decrease as the ethanol added to water. This may be due to the lower dielectric constant and lower dipole moment of EtOH-H_2O mixed solvent than that of H_2O. On the other hand, the effect of ethanol percentage is not as expected. It was observed that the solvolysis constant values increase with increasing the EtOH percentage from 30 to 100%. This may be due to the higher solute-solvent interaction.[19&20]
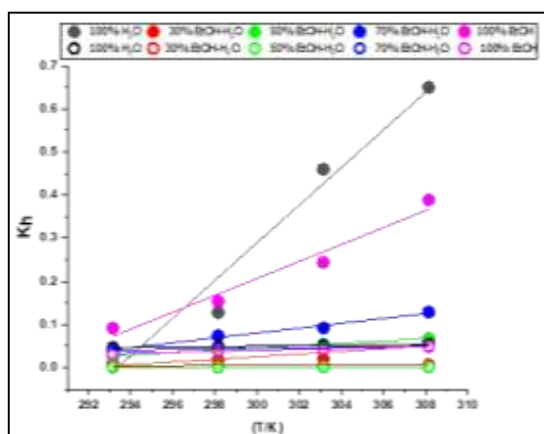

Figure 5. Comparison of the solvolysis constant Kh values for of phenyl hydrazine hydrochloride using the pH measurement (●) and the conductivity measurement (5).

Table 5. The values of the solvolysis constant (K_h), standard free energy change (ΔG_h°, kJ mol^{-1}), standard enthalpy change (ΔH_h°, kJ mol^{-1}), standard entropy change (ΔS_h° KJ mol^{-1}. K) and the activation energy (E_a, *kJ mol^{-1}*) of the solvolysis process of phenyl hydrazine hydrochloride, derived from conductometric measurements.

Solvent	T/K	K_h	ΔG_h°	ΔH_h°	ΔS_h°	E_a
0.0% EtOH	293.15	0.047	7.47	9.111	-0.005	0.028
	298.15	0.049	7.60			
	303.15	0.051	7.45			
	308.15	0.055	7.43			
30% EtOH	293.15	0.0041	13.35	26.330	-0.044	0.014
	298.15	0.0047	13.24			
	303.15	0.0050	13.00			
	308.15	0.0069	12.74			
50% EtOH	293.15	0.0010	16.74	22.916	- 0.021	0.024
	298.15	0.0012	16.54			
	303.15	0.0014	16.50			
	308.15	0.0016	16.40			
70% EtOH	293.15	0.040	7.82	11.499	-0.012	0.011
	298.15	0.043	7.79			
	303.15	0.048	7.63			
	308.15	0.050	7.62			
100% EtOH	293.15	0.031	8.43	465.21	-0.0205	0.001
	298.15	0.040	7.98			
	303.15	0.043	7.93			
	308.15	0.049	7.73			

It is worth noting that, in both techniques, (pH and conductivity measurement), the solvolysis constant values are different to each other, although both of which for the same compound as shown in **Figure 5**.

The result showed that, in all cases, the K_h values which derived from conductometric measurements are lower than the corresponding K_h values from pH measurements (see **Tables 3 and 5**). This may be attributed to the higher sensitivity of conductivity technique to the change in temperature to that of pH technique.

4. CONCLUSIONS

The solvolysis process of phenyl hydrazine hydrochloride in H_2O and in EtOH-H_2O mixtures with different percentages of ethanol; 30%, 50%, 70%, 100% at different temperature (293.15, 298.15, 303.15, and 308.15 K) were studied using the conductometric and pH metric measurements. The results show that the solvolysis constant increase as the temperature degree increase indicating that the solvolysis process is non spontaneous endothermic process. The solvolysis constant is increase as the ethanol % increase from

30%-100%. This may be due to the higher solute-solvent interaction. In comparing the obtained values of the solvolysis constant from both the pH and the conductivity measurements, it was noted that the conductivity values are lower than that of pH values. This may be due to the higher sensitivity of conductivity measurements to the change in temperature than that of pH measurements.

REFERENCES

[1]   Raymond Chang, J. T. J., *Physical chemistry for the chemical and biological sciences*. University Science Books, 2000.

[2]   Freifelder, D., *Study guide for Molecular biology,* , 2nd ed. (A series of books in biology, Series of books in biology (Jones and Bartlett)). Boston: Jones and Bartlett, 1987, p. 834.

[3]   Glasstone, S., *The electrochemistry of solutions*, 3rd ed. Ann Arbor, MI: Methuen and Co. Ltd., London, 2001.

[4]   Rúa, J., J. Soler, F. Busto, and D. De Arriaga, "The pH Dependence and Modification by Diethyl Pyrocarbonate of Isocitrate Lyase from Phycomyces blakesleeanus," *European Journal of Biochemistry*. 232, 2, 381-390, 1995.

[5]   Campbell, A. N. and E. Bock, "The Limiting Equivalent Conductances of Ammonium Chloride, Ammonium Bromide, and Ammonium Nitrate at 35 °C," *Canadian Journal of Chemistry*. 36, 2, 330-338, 1958.

[6]   Tan, Z. H. *et al.*, "Hydrogen generation via solvolysis of Mg_2Si," *Journal of Alloys and Compounds*. 770, 108-115, 2019.

[7]   Fang, F., Y. Liu, F. Meng, W. Wang, T. Xue, and T. Qi, "Influence of magnesium and aluminum salts on solvolysis of titanyl sulfate solution," *Transactions of Nonferrous Metals Society of China*. 25, 10, 3475-3483, 2015.

[8]   Barth, A. P., C. F. Tormena, and W. H. Viotto, "pH influences solvolysis of sodium polyphosphate in dairy matrices and the structure of processed cheese," *Journal of Dairy Science*. 100, 11, 8735-8743, 2017.

[9]   Terborg, L. *et al.*, "Ion chromatographic determination of solvolysis products of hexafluorophosphate salts in aqueous solution," *Analytica Chimica Acta*. 714, 121-126, 2012.

[10]   Bayissa, L. D., Y. Ohmae, and M. Hojo, "Specific influence of salts on the solvolysis reaction rate of p-nitrophenyl anthranilate in binary acetonitrile-water solvents," *Journal of Molecular Liquids*. 199, 294-300, 2014.

[11]   Li, S., D. Gan, Y. f. Zhu, Y. Liu, G. Zhang, and L. Li, "Influence of chloride salts on hydrogen generation via solvolysis of MgH_2 prepared by hydriding combustion synthesis and mechanical milling," *Transactions of Nonferrous Metals Society of China*. 27, 3, 562-568, 2017.

[12]   Safraoui, A., M. Calmon, and J.-P. Calmon, "Kinetics of the alkaline solvolysis of several alkyl phenylcarbazates," *Journal of the Chemical Society, Perkin Transactions 2,* 9, 1349-1352, 1991.

[13]   Dong, S., M. J. Bortner, and M. Roman, "Analysis of the sulfuric acid solvolysis of wood pulp for cellulose nanocrystal production: A central composite design study," *Industrial Crops and Products*. 93, 76-87, 2016.

[14]   Licht, S., K. Longo, D. Peramunage, and F. Forouzan, "Conductometric analysis of the second acid dissociation constant of H_2S in highly concentrated aqueous media," *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*. 318, 1, 111-129, 1991.

[15]   Buss, J. L. and P. Ponka, "Solvolysis of pyridoxal isonicotinoyl hydrazone and its analogs," *Biochimica et Biophysica Acta (BBA)-General Subjects*. 1619, 2, 177-186, 2003.

[16]   Kundu, A., S. Dasmandal, T. Majumdar, and A. Mahapatra, "Effect of cosolvents in the presence

of sodium dodecyl sulfate micelles on the rate of alkaline solvolysis of tris (2,2′-bipyridine) iron(II) complex," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 452, 148-153, 2014.

[17]   Ballance, S., K. A. Kristiansen, J. Holt, and B. E. Christensen, "Interactions of polysaccharides extracted by mild acid solvolysis from the leaves of Sphagnum papillosum with either phenylhydrazine, o-phenylenediamine and its oxidation products or collagen," *Carbohydrate Polymers*. 71, 4, 550-558, 2008.

[18]   Karlsson, A. and S. K. Singh, "Acid solvolysis of sulphated polysaccharides. Desulphation and the effect on molecular mass," *Carbohydrate Polymers*. 38, 1, 7-15, 1999.

[19]   El-Dossoki, F. I., N. S. Y. Abdolla, E. A. Gomaa, and O. K. Hamza, "An insight into thermodynamic and association behaviours of cocamidopropyl betaine (CAPB) surfactant in water and water–alcohol mixed media," *SN Applied Sciences*. 2, 4, 690, 2020.

[20]   El-Dossoki, F. I., N. S. Y. Abdolla, and S. E. T. Elmasly, "The transport properties and the association behavior of some 1:1 and 2:1 electrolytes in some binary alcoholic–aqueous mixtures," *Journal of Molecular Liquids*. 163, 3, 135-140, 2011.