Review Article

Introducing of Thermodynamic Van’t Hoff Equation in Aqueous Solubility and Dissociation Process of Benzoic Acid at Ordinary Temperature Range

ABSTRACT

In article, we have reported the introducing of thermodynamic Van’t Hoff equation in study of solubility and dissociation process of benzoic acid into water at ordinary temperature between of 16˚C to 41˚C. At this temperature range, the solubility of benzoic acid and the equilibrium dissociation constant (*Kc*) of acid into water having six different ionic strength as 0.00, 0.05, 0.10, 0.30, 0.40 and 0.50 M, for volume of sodium chloride (NaCl) is analyzed by titrimetrically with 0.05 M basic sodium hydroxide (NaOH) solution. The value of benzoic acid dissociation constant for given each six concentration of NaCl is found to being -4.169, -4.045, -3.993, -3.885, -3.848 and -3.788, respectively. The pH of each solution is measured by using of calibrated pH-meter as well. The observation reveals that the value of pH of benzoic acid into water at that temperature range is may inversely related with concentration of NaCl. In graphically, the value of benzoic acid with that of ionic strength (I) is plotted versus equilibrium dissociation constant (Kc) at specific 25˚C (298 K) temperature have shown the dissociation of acid into water is increases as increase ionic strength. But, comparatively, the graph for increasing temperature range to thermodynamic dissociation constant (*Ka*) have shown that the dissociation is not always increases as if increases temperature.

Keywords: Benzoic acid, Solubility, Ionic strength, Dissociation constant, Van’t Hoff Equation.

[1]. INTRODUCTION :

Indeed, the solubility and distribution of solute in solvent have reported earlier [1], but it proved well by Nernst (1891) with given of partition law, $K = C_A/C_B$ [2]. Each of substance has a specific solubility in a given solvent because solubility depends on various factors like as solute-solvent interaction, intermolecular forces, temperature and its dissociation into ionic form etc. Knowing, solute sodium chloride (NaCl) is an electrolytic in nature and fairly soluble in water because it polar solvent, while it is insoluble in a non-polar solvent like benzene (C_6H_6), carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$) etc. Here, the electrical attraction between the oppositely charged end of the solute and the solvent molecules results to form a solution.

When ionic substance is placed in polar solvent which ionized to solute with furnishes of cation (+) and anions (-). Hence, the NaCl dissolves in water to give solvated or hydrated Na^+ and Cl^- ions [3]. Salt NaCl is an ionic solid compound having a 1:1 ratio of (Na and Cl) ions. The pH of NaCl is neutral (7.0) with m.w. as 58.44 g/mol. The density of it is 2.165 g/cm^3 with m.p. (801°C) and b.p. (1413°C). NaCl is formed by the reaction of strong (HCl) acid and strong (NaOH) base so it ionize easily in aqueous solvent with highly solubility. In series of aromatic acids the benzoic acid (C_6H_5COOH) is a colorless crystalline solid substance (m.p. 121-122°C) with pleasant smell and poor solubility in cold water, having industrial and medicinal applications about 20th century [4, 5].

Literature survey reveals, the addition of small amount of salt of benzoic acid (solute) into water (solvent) gives rise a slightly changing due to solute-solvent interactions [6]. When solute (C_6H_5COOH) is put into solvents then it try to get dissolve and ionize with its ionic strength in respect of temperature [7]. In described two salts, the sodium chloride is act as an electrolyte for to increase the value of ionic strength in aqueous solution (*aq*) of benzoic acid particularly with molar concentration of NaCl [8]. Although, in aqueous solution, a little molar solubility of benzoic acid with weak electrolyte behavior [9]. The carboxylic group (COOH) of benzoic acid is polarize during on dissociation partially into water with forming of H-bonding and to produce benzoate anion ($C_6H_5COO^-$) and hydronium cation (H_3O^+). The dissociation equilibrium of benzoic acid in basic or anionic form is follow to these reaction-

$$C_6H_5COOH + H_2O \rightarrow C_6H_5COO^- + H_3O^+$$

$$\text{Or,} \quad C_6H_5COOH(aq) \rightarrow H^+(aq) + C_6H_5COO^-(aq)$$

In this work, thermodynamically, an ordinary temperature range in between of 16˚C to 41˚C have been reported for study of the molar solubility and dissociation constant (*Kc*) process with value of ionic strength of benzoic acid into water. It is determined by using titration method against NaOH solution as standard strong base. The equilibrium is expressed as-

$$Kc = [H^+][C_6H_5COO^-] / [C_6H_5COOH(aq)] \quad \text{.........(1)}$$

[2]. EXPERIMENTAL :

[A]- Materials: In experimental procedure, all the required chemicals and reagents have been used for study with analytical grade as of without further purification. The water which used as solvent throughout the work is distilled well about three times. Typically, the basic solution of NaOH which are carbonated free have prepared well as suggested by adopting Vogel procedure [10]. These test solutions is made of reagent grade as benzoic acid, NaOH and NaCl stock solutions with ionic strength and purified distilled water. The protolytic purity of benzoic acid have checked by using titration with standard basic solution of NaOH. In this work those calibrated volumetric glassware used which is of class 'A' as well.

[B]- Methods: In preparation of solution, we take a cleaned and dry six stoppered bottles of 250 ml and crystalline solid benzoic acid. Weigh the 1.00 g of benzoic acid and it is placed in each of six dry bottles. Now, in each bottles we are prepared a 100 ml of sodium chloride (NaCl) solution by using volumetric flask (100 ml) of different concentrations as of 0.00, 0.05, 0.10, 0.30, 0.40 and 0.50 M. These prepared different molar solutions is then poured in each benzoic acid containing bottles and shaking it vigorously and also then put in a thermostat for 2 hours, at 298 K as room temperature. Here, now we are pipette out a 20.0 ml of solutions from each bottles with filtering to prevention of withdrawing small solids in pipette. After removing the filtering, then it discharged into another conical flask of 250 ml. In each of solutions the NaCl concentration with benzoic acid is determined by applying titration method against basic NaOH solution of 0.050 M. By using 3 decimal digits calibrated pH meter we are measured the pH of each solution at described ordinary temperature in between of 16˚C to 41˚C ranges.

[3]. RESULTS AND DISCUSSION :

In study of solubility and dissociation process of benzoic acid into water at about 16˚C to 30˚C temperatures have been reported for six ionic strength of 0.00, 0.05, 0.10, 0.30, 0.40, and 0.50 M of sodium chloride (NaCl) solution. At this concentration range, the benzoic acid solubility into water is analyze by followed to applying titration method as described by Khouri [11]. Notable, we measured the pH of each solution also. Here, in table-1 we have shown the experimental data of finding average results with their measurements. Where, from the volume of 0.05 mol/litre of standard alkali sodium hydroxide (NaOH) solution, the benzoic acid solubility and pH value into aqueous (water) is inversely related with concentrations of NaCl. At six ionic strength, the table-1 show the equal volume (20.0ml) benzoic acid solution is used for each, where the value of molar solubility (α) and apparent dissociation constant (*Kc*) of acid has been found to being from 0.0215 to 0.0265, and -3.788 to -4.169, respectively. In graphically, this estimated value for equilibrium dissociation constant (*Kc*) in terms of logarithm as log *Kc* is plotted against ionic strength (I) as volume of NaCl in different range has used for benzoic acid solution at 25˚C (298 K) temperature (in figure-1). These reported value is compared with literature value of thermodynamic dissociation constant (*Ka*) as in figure-2, which may obtaining from the extrapolation to zero ionic strength by using calorimetry [12], or, other methods [13-15] as well.

Table-1. The ionic strength of NaCl on solubility and equilibrium dissociation constant of benzoic acid into water (at 25˚C).

S. N.	*V* of NaCl (in mol/l)	*V* of benzoic acid solution (in /ml)	*V* of 0.05 (mol/l) NaOH (in /ml)	pH	α	*Kc*
1.	0.00	20.00ml	10.61 ± 0.014	2.884 ± 0.005	0.0265	-4.169
2.	0.05	20.00ml	10.19 ± 0.010	2.832 ± 0.005	0.0255	-4.045
3.	0.10	20.00ml	9.92 ± 0.009	2.813 ± 0.003	0.0248	-3.993
4.	0.30	20.00ml	9.51 ± 0.012	2.789 ± 0.005	0.0238	-3.885
5.	0.40	20.00ml	9.09 ± 0.011	2.763 ± 0.003	0.0227	-3.848
6.	0.50	20.00ml	8.58 ± 0.011	2.747 ± 0.007	0.0215	-3.788

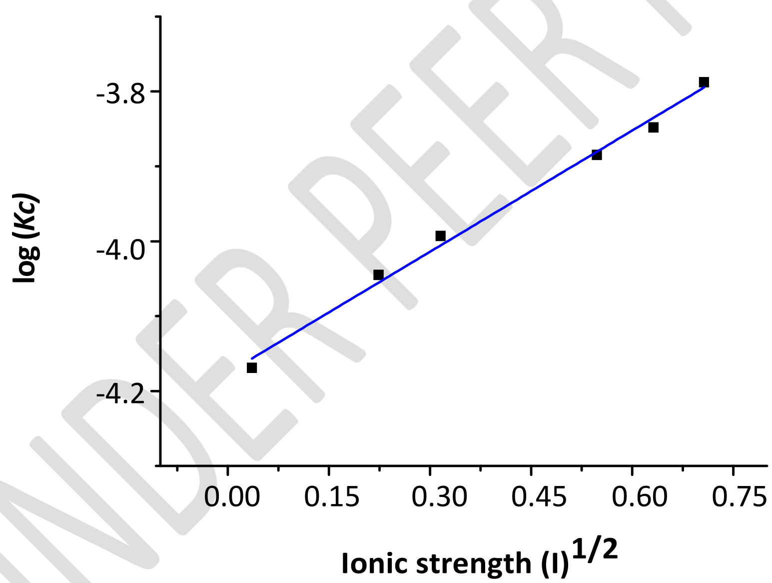

Figure-1. The plot of equilibrium dissociation constant (*Kc*) against ionic strength (I) of benzoic acid into water (at 25˚C).

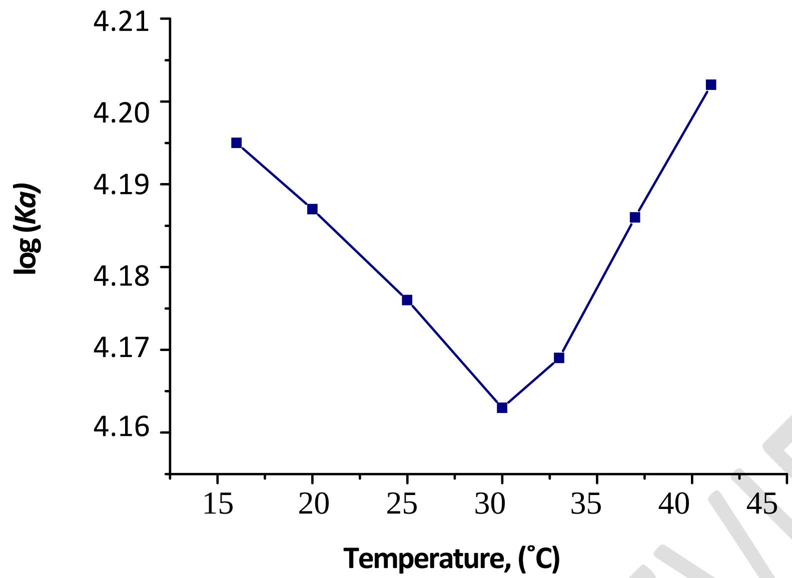

Figure-2. The plot of thermodynamic dissociation constant (*Ka*) against temperature range of benzoic acid into water.

Thermodynamically, at ordinary temperature (16˚C to 25˚C) range, the benzoic acid dissociation constant or apparent or equilibrium dissociation constant (*Kc*) is correlated to thermodynamic dissociation constant *Ka* [16], which have compared with data of Strong *et al* [17]. Where, the *Ka* is a thermodynamic dissociation constant at infinite dilution of solution with mean activity coefficient (γ±) of the dissociated and un-dissociated ions of benzoic acid as expression, $Ka = Kc.\gamma^2\pm$ [11]. From this relation, mathematically, the mean activity coefficient of dissociated ions for solution is calculated by using of following equation-

$$\log(\gamma\pm) = 1/2\,(\log Ka - \log Kc) \text{ ....(2)}$$

or, $$\log Ka + 2B\sqrt{I} = \log K \text{ ....(3)}$$

here, the B, and, I is a quantity and ionic strength respectively, which is effected or depend upon various physical property of solutions such as including temperature [18], pressure (as Read's data) [19], and chemically electrolytic properties [20]. At room temperature (25˚C or 298 K), for aqueous solutions, the equation (3) may becomes-

$$\log Ka + 1.02\sqrt{I} = \log Kc \text{ ....(4)}$$

The dissociation constant (*Kc*) and to finding the pH value for each solution is determined by using the following given modified equation (5), which are derived from equation (1)-

$$Kc = (10^{-pH})^2 / \alpha - 10^{-pH}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

Here, the α is a total molar solubility of benzoic acid and their benzoate or hydrogen ions in the aqueous solution, as [($C_6H_5COOH_{(aq)}$) to ($C_6H_5COO^-$) = (H^+) = 10^{-pH}], which can be determined from given such following equation-

$$\alpha = (V_{NaOH} \times M_{NaOH}) / V_{(Benzoic\ Acid)} \ldots\ldots.(6)$$

Where, the V_{NaOH}, M_{NaOH} and $V_{(Benzoic\ Acid)}$ are the volume of NaOH (litre^{-1}), molarity of NaOH (per mol /l), and volume of benzoic acid (litre^{-1}) respectively.

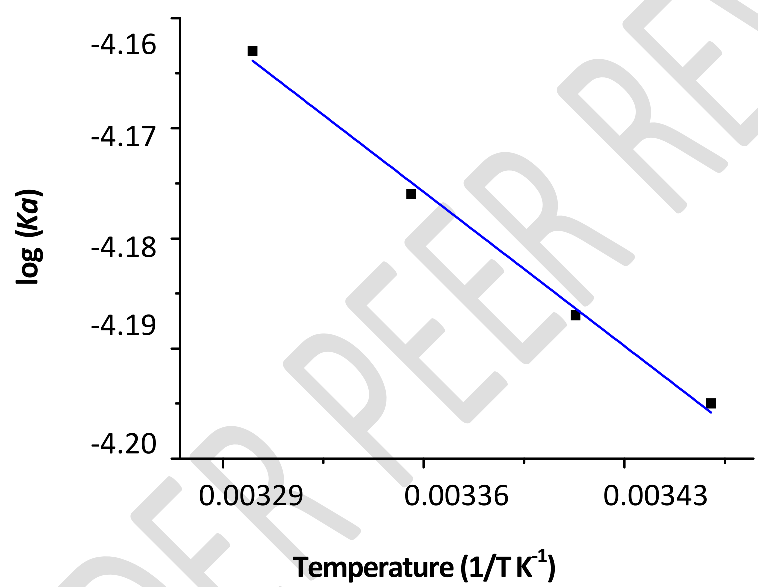

Figure-3. The plot of thermodynamic dissociation constant (*Ka*) versus temperature (T) of benzoic acid into water.

The solubility and dissociation process of benzoic acid is being temperature dependent because, if temperature increases in range between of 16 to 30˚C, the value of *Ka* is may inversely proportional. But it may contrast, because as temperature further increases in range of between 30 to 41˚C, then the *Ka* value is may directly proportional with temperature. Actually, from this observation we can say that, there are no regular correlation between thermodynamic dissociation constant (*Ka*) of benzoic acid and the temperatures range which is used. Thus from experimental data, in titration with used NaOH amount (20.ml) and the pH value for each temperature, the benzoic acid solubility into water is directly proportional with temperature. And, the benzoic acid molecules capability which to dissociate is not increases always as increases of temperature. Although, by thermodynamic study there are no revealing of dissociation process well, but, at ordinary temperature (16˚C to 30˚C upto 41˚C) range the changing value of both entropy (ΔS) and enthalpy (ΔH) is obtained by applying Van't Hoff equation during benzoic acid dissociation process. This equation (7) can be expressed as-

$$\log Ka = \frac{-\Delta H}{2.303\ R} 1/T + \frac{\Delta S}{R} \text{..................} (7)$$

Here, in Van't Hoff equation, the R is a molar gas constant having value to 8.314 $J.K^{-1}.mol^{-1}$ with account of ΔH and ΔS, which are on temperature independent because of the small change in values of temperature in relatively. A data analysis of log *Ka* to 1/T between 16˚C- 41˚C range of temperature is illustrated well in figure-3. The finding results for benzoic acid dissociation into water for thermodynamic parameters values in standard way are being as ΔH = 3.823 $kJ.mol^{-1}$ and ΔS = -29.14 $kJ.mol^{-1}$.

Notable, the dissociation of benzoic acid into water is as endothermic and reports to energy change to be positive (+ve) which lead to dissociation process of acid molecule is non-spontaneous. If value of energy change becomes negative (-ve) it means that into water the acid is attain a highly ordered state during after its process of dissociation. The dissociation of acid in water having different behaviour at higher temperature than above 30˚C. As increases the temperature the benzoic acid capability to dissociation is decreases with reducing value of *Ka*. In this range of temperature the process is being exothermic with the compatibility to principle of Le Chatelier [11, 21]. The acidic strength of benzoic acid is effected by temperature change which lead to inductive effect inside the acid molecule and can reveals the charge movement through atoms in molecule of acid resulting the polarization of bond in continual state [22]. Benzoic acid molecules show less acidic behavior at over 30˚C temperature because effect of electron releasing group is decreases inside the molecule of acid on acidic hydrogen [17].

As in repeating of same adapted titration method at 25˚C as room temperature for about six more time where the benzoic acid solubility is same for ionic strength of NaCl into water with pH measurement of each solution. But at range of temperatures between 16˚C to 41˚C, the results average is show a high precision for volume (V) of NaOH and pH value. At these temperature the value of dissociation constant for used each concentration of NaCl solution is determined by applying of same methodology as used in case of 25˚C for each temperature. Notably, the volume of each solution is temperature dependent due to there thermal expansion, thus thermodynamically, the molarity which used is may not convenient. These problem can be resolve with maintaining equal concentration of sodium chloride for reported all temperatures. For this work, we are testing that the decrease or increase in volume of NaCl solution inside the volumetric flask (100ml) at selected each temperature which relative to standard flask's volume at 20˚C. Then NaCl solution is prepared with the volume of starting less or more than 100 ml as to be 100 ml exactly with selected temperature when thermal equilibrium attained inside the thermostat. In dissociation process of benzoic acid a Debye-Huckel limiting law can apply for improve to finding more accurate results, although, at higher temperature and pressure (in bar) the dissociation of acid or any solute with infinity dilution the thermodynamic parameters is retrieved [17, 19, 23], with conductance of ions like Na^+, Cl^-, H^+ and OH^- [24]. Although, dissociation process of NaCl salt is may verify by change of enthalpy (ΔH) with Born-Haber based [25].

[4]. CONCLUSION:

In conclusion, we have reported the introducing of thermodynamic based Van't Hoff equation for in study of solubility and dissociation process of benzoic acid into water at ordinary temperature between 16˚C to 41˚C. At this temperature range, the aqueous solubility and the equilibrium dissociation constant (*Kc*) of benzoic acid with six ionic strength of 0.00, 0.05, 0.10, 0.30, 0.40 and 0.50 M, for volume of sodium chloride (NaCl) is analyzed by titrimetrically against a 0.05 M alkali sodium hydroxide (NaOH) solution. The value of benzoic acid dissociation constant for given each six concentration of NaCl is found to being -4.169, -4.045, -3.993, -3.885, -3.848 and -3.788, respectively. The pH of each solution is measured by using of pH-meter. Observation reveals that, the pH value of benzoic acid into water at that temperature range is may inversely related with concentration NaCl. Graphically, the value of benzoic acid with ionic strength (I) is plotted against equilibrium dissociation constant (Kc) at specific 25˚C or 298 K temperature have shown the dissociation of acid into water is increases as increase ionic strength. But, in comparative, the graph for at temperature range to thermodynamic dissociation constant (*Ka*) have shown that the dissociation is not always increases as if increases temperature.

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