Review Article

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

ABSTRACT

In article, we have reported the thermodynamic Van’t Hoff equation in study of dissociation process of solute benzoic acid into water solvent at ordinary temperature between of 288 K to 318 K. At this temperature range, the value of dissociation constant (*Kc*) of that acid is being to found as -4.169, -4.045, -3.993, -3.885, -3.848 and -3.788, for given concentrations of NaCl (sodium chloride) volume with its six ionic strength as of 0.00, 0.05, 0.10, 0.30, 0.40 and 0.50 M, respectively, which are titrimetrically analyzed with 0.05 M basic NaOH (sodium hydroxide) solution. The pH value of each solution is measured by using of digital pH-meter as well. Here, observation reported that the pH value of benzoic acid into water at that range of temperature is being inversely related to concentrations of NaCl. In graph, a value of benzoic acid with there ionic strength (I) is plotted versus equilibrium dissociation constant (*Kc*) at specific 298 K, have shown the dissociation of acid into water is increases as increase the 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 partition of solute into solvent have earlier reported [1], but, in 1891 Nernst proved it well with given partition law, $K = C_A/C_B$ [2]. In a given solvent the each solute substances having the specific solubility and there dissociation depends on various factors like as solute-solvent interaction, intermolecular forces, temperature and its dissociation into ionic form etc. Knowing, NaCl salt is an electrolytic in nature and well soluble into polar solvent like in water while its insolubilty in the non-polar solvents as in C_6H_6, $CHCl_3$ and CCl_4 etc. The electrically oppositely charge attraction in between of the solute and the solvent resulting formation a solution. On placing these ionic solute substances in solvent (polar) it ionized with furnishing of ions (cation and anions). Here, the literature survey reveals about the NaCl and benzoic acid (C_6H_5COOH) which is an ionic solid compounds and hydrated or solvated into water solvent [3], with industrial and medicinal applications about 20th century [4-5]. Although, a slightly changing appears due to solute-solvent interactions as by addition of small amount of solute into solvent [6]. Putting on the solute (C_6H_5COOH or NaCl) into water like solvents then it trying to dissolve in it and get ionizes with their strength of ions in respect of temperature [7].

In described two salts, the electrolytic action of NaCl for to increase the value of ionic strength into water of benzoic (aromatic) acid specially with molar concentrations of sodium chloride [8]. In aqueous solution (*aq*), a weak electrolyte behavior with little molar solubility of benzoic acid [9]. On dissociation into water the carboxylic (COOH) group of benzoic acid is being polarizes and producing benzoate anion ($C_6H_5COO^-$) and hydronium cation (H_3O^+) with indication H-bonding. The reaction of equilibrium dissociation of benzoic acid in its ionic form is given below -

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

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

In this work, thermodynamically, an ordinary range of temperature in between of 288 K to 318 K 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-

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

[2]. EXPERIMENTAL :

[A]- Materials: In experimental procedure, all the required reagents and chemicals are being analytical graded which have been used further as without purification for study. In solvent the distilled water is using throughout the complete work. Typically, by adopting of Vogel procedure the basic NaOH solution is prepared well which are being carbonated free [10]. This reagent graded solutions which are made of as NaCl stock solutions with ionic strength, NaOH, C_6H_5COOH (benzoic acid) and purified distilled water. By using of titration against standard NaOH basic solution the protolytic purity of benzoic acid have checked. All the calibrated as well as volumetric glassware which of A class are used.

[B]- Methods: In all solution preparation, we taking a dry cleaned six 250 ml stopper bottles and salt of benzoic acid. Firstly, weigh the benzoic acid as 1.0 gram and it placed in each of six dry cleaned bottles. Now, a 100 ml of sodium chloride (NaCl) solution we prepared in each bottle by using of volumetric flask (100 ml) of different as 0.00, 0.05, 0.10, 0.30, 0.40 and 0.50 M concentrations. Poured this prepared molar solutions in each benzoic acid containing bottles and vigorously shaking it and for 2 hours it put in a thermostat, at about 298 K. Now then with filtering to prevention of withdrawing small solids in pipette we are pipette out a 20 ml of solutions from each bottles. Then it discharged into another conical flask (250 ml) after removing the filtering. The NaCl concentrations in each of solutions with benzoic acid by applying titration method is determined against basic 0.05 M NaOH solution. The pH value of each solution we are measured well by using the digital pH meter at described ordinary temperature in between that of 288 K to 318 K ranges.

[3]. RESULTS AND DISCUSSION :

In study of process of dissociation of solute benzoic acid into water at about 288 K to 318 K temperatures have been reported for six ionic strength of 0.00, 0.05, 0.10, 0.30, 0.40, and 0.50 molar of NaCl (sodium chloride) solution. At this concentrations range, by followed to applying titration method, the solubility of benzoic acid into water is well analyze [11]. Notable, by using temperature probe we see saw that about reported range of temperatures and the pH of each solution measured also. We have shown in table- 1, the experimental data for the results finding to average measurements. As 0.05 mol/litre from volume of standard alkali solution of NaOH (sodium hydroxide), the value of pH of benzoic acid and solubility into water is inversely related to NaCl concentrations. For each six ionic strength, the table-1 show the same a 20 ml volume of solution of benzoic acid is used, where the value of apparent or equilibrium dissociation constant (*Kc*) and molar solubility (α) of benzoic acid have found being 0.0215 to 0.0265, and -3.788 to -4.169, respectively. By graph, the equilibrium dissociation constant (*Kc*) value in logarithm terms as log *Kc* is plotted versus the concentration or ionic strength (I) in different range to NaCl volume are used for solute benzoic acid solution at temperature 298 K, (figure-1). On comparison of that literature value with this observed value of thermodynamic dissociation constant (*Ka*) as in figure-2, which to be obtained from to zero ionic strength extrapolation by calorimetry using [12], and others [13-15] as well.

Table-1. At 298 K, the ionic strength (I) of NaCl on dissociation constant (*Kc*) of benzoic acid into water.

S. N.	*V* of Benzoic Acid Soln. (in /ml)	*V* of 0.05 (mol/l) NaOH (in /ml)	*V* of NaCl (in mol/l)	*Kc*	pH	α
1.	20ml	10.61 ± 0.014	0.00	-4.169	2.884 ± 0.005	0.0265
2.	20ml	10.19 ± 0.010	0.05	-4.045	2.832 ± 0.005	0.0255
3.	20ml	9.92 ± 0.009	0.10	-3.993	2.813 ± 0.003	0.0248
4.	20ml	9.51 ± 0.012	0.30	-3.885	2.789 ± 0.005	0.0238
5.	20ml	9.09 ± 0.011	0.40	-3.848	2.763 ± 0.003	0.0227
6.	20ml	8.58 ± 0.011	0.50	-3.788	2.747 ± 0.007	0.0215

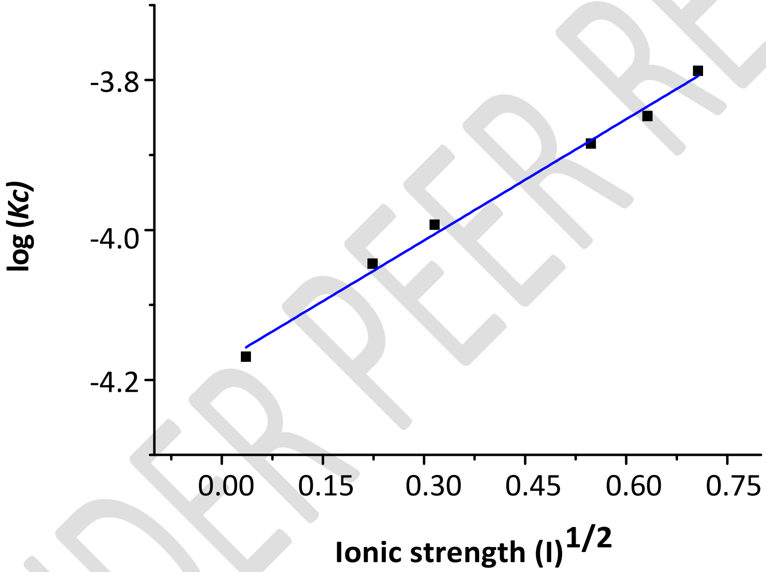

Figure-1. At 298 K, the plot of *Kc* (equilibrium dissociation constant) against I (ionic strength) of benzoic acid into water.

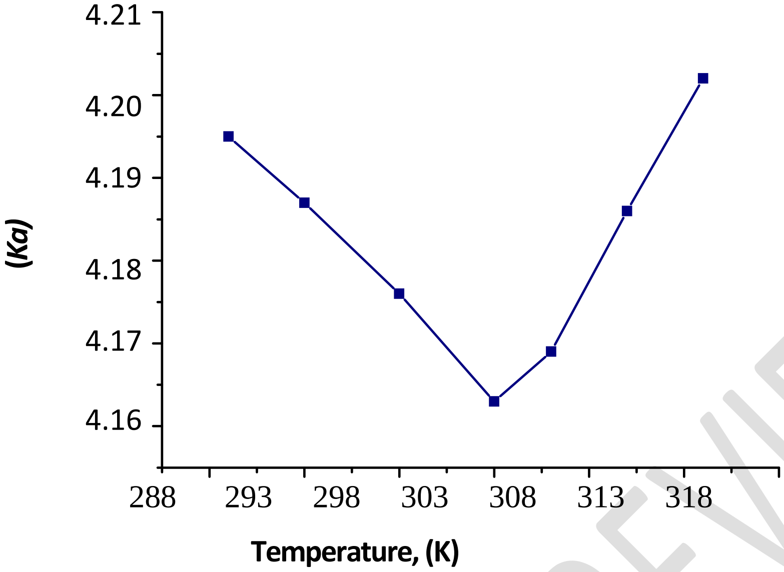

Figure-2. The plot of *Ka* (thermodynamic dissociation constant) of benzoic acid into water against temperature (T) range.

Thermodynamically, at ordinary temperature (288 K to 318 K) range, the apparent or equilibrium dissociation constant is collectively called as benzoic acid dissociation constant (*Kc*). Although, these *Kc* and thermodynamic dissociation constant (*Ka*) is correlated well [16], also, in comparison of Strong *et al* data [17]. Accordingly, this *Ka* is the un-dissociated and dissociated ions of benzoic acid at infinite dilution of solution with there mean activity coefficient (γ±) which given in expression as $Ka = Kc.\gamma^2\pm$ [11]. From these mathematically relation, for solution the mean activity coefficient of ions (dissociated) can be calculated easily by applying of following equation-

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

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

here, the I, and, B as the ionic strength and quantity, and it is dependent or effected on physical properties of solutions like the electrolytic property [18], pressure (Read's data) [19], temperature [20]. At temperature 298 K, the above given equation (3) is may be-

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

In finding of the determination of pH value for each solution and dissociation constant (*Kc*) of acid, we using the modified equation (1) to equation (5) is given bellow-

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

Where, in aqueous solution, α is a total molar solubility of solute benzoic acid ($C_6H_5COOH_{(aq)}$) and its ions to [($C_6H_5COO^-$) = (H^+) = 10^{-pH}]. And it determined to be from as equation (6)-

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

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

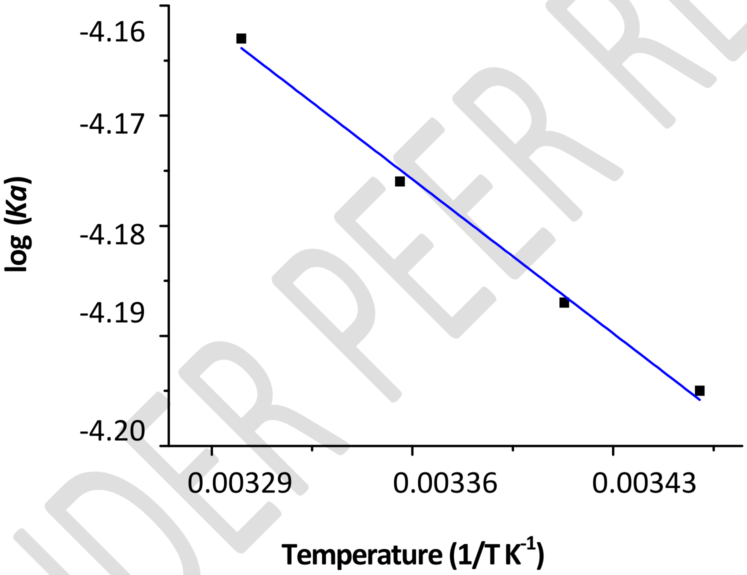

Figure-3. The plot of *Ka* (thermodynamic dissociation constant) versus T (temperature) of benzoic acid into water.

The solubility and process of dissociation of benzoic acid is being temperature dependent, because, if temperature is increases in between of 289 K to 298 K upto 303 K, the *Ka* value is being proportional inversely. Although, this may in contrast, because as further increasing of temperature from 303 K upto 318 K, then the value of *Ka* may proportional directly in respect to temperature. In fact, from this observation we can say that, here, no regular correlation in between of applied range temperature and in benzoic acid thermodynamic dissociation constant (*Ka*). Hence, in titration from the experimental data against using 20ml NaOH and the value of pH for temperatures, the solubility of benzoic acid into water is proportional directly to temperature. Indeed, the capability of benzoic acid molecules to dissociate into solvent is always not increases as the temperature increases. Actually, there are no well revealing about process of dissociation from thermodynamic study, but, at ordinary temperature (288 K to 303 K upto 318 K) 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-

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

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 289 K to 314 K (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}.

Attentionally, the benzoic acid dissociation into water solvent is a process of endothermic with positive (+ve) energy changes which has lead to non-spontaneous process of dissociation for that acid. And, if the value is becoming a negative (-ve) for energy changing, then it means, the benzoic acid having a highly ordered state (entropy) attain into water after during its dissociation process. Notably, at above or higher 303 K temperature, the benzoic acid dissociation into aqueous solvents showing a different behavior. Over at temperature 303 K, the molecules of acid show less acidic nature because of electron releasing group effect which decreases inside the acid molecules on acidic hydrogen [17]. As increases temperature, the dissociation capability of benzoic acid is be found to decreases with reducing of that *Ka* value. In these temperature range the process of dissociation is may be an exothermic with principle of Le Chatelier, in compatibility [11, 21]. The temperature changing is effected to the acidic strength of benzoic acid which lead to inductive effect inside the benzoic acid molecules with movement of charge in continual state through acid atoms resulting the bond polarization [22].

In dissociation process of benzoic acid by applying the titration methodology which are adapted at 298 K as about room temperature well. But, in study, at about 288 K to 318 K temperature ranges, the average of results has shown a high precision for value of pH and NaOH volume (V) with concentrations of NaCl. Notable, the solutions volume has been dependent on temperature because there is thermal expansion. Hence, in thermodynamic way, the used molarity which is being not convenient. In testing of NaCl concentrations, we have reported that, the increase or decrease of NaCl volume inside in a 100 ml of volumetric flask as standard volume of flask at selected or particular temperature about 293 K. Here, the preparation of solution of NaCl as about 100 ml to starting volume where the attain of thermal equilibrium inside to thermostat for selected temperature. In process of benzoic acid dissociation we can apply a limiting law of Debye-Huckel in finding or improving of results with more accuracy. Although, at higher pressure (in bar) and temperature (K) the thermodynamic parameters are retrieved for dissociation of any solute or acid with infinity dilution [17, 19, 23], with conductance of ions like Na^+, Cl^-, H^+ and OH^- [24,25]. Yet, the dissociation process of NaCl salt is to be verify by changing of enthalpy (ΔH) on the based of Born-Haber [26].

[4]. CONCLUSION:

In conclusion, we have reported a introducing of thermodynamic based Van’t Hoff equation in study of process of dissociation of solute (benzoic acid) into solvent (water) in between of 288 K to 318 K temperature. At this temperature range, the benzoic acid dissociation constant (*Kc*) value are being to found as -4.169, -4.045, -3.993, -3.885, -3.848 and -3.788, for given six concentrations of sodium chloride (NaCl) to 0.00, 0.05, 0.10, 0.30, 0.40 and 0.50 M, respectively, which are analyzed by titration method versus a 0.05 M alkali solution of NaOH (sodium hydroxide). By using of a digital pH-meter we measured the pH value of prepared each solution. The observation has estimated that, the value of pH for benzoic acid at reported temperature range into water is being related inversely with concentrations of NaCl. In graph, the benzoic acid value with their ionic strength (I) is plotted against dissociation constant (Kc) at particular temperature (298 K) are shown the acid dissociation 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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