Temperature Behaviour on Solubility and Equilibrium Dissociation Constant of Benzoic Acid in NaCl Media against NaOH Solution: A Titrimetric Study

Shiv Prakash Mishra
Assistant Professor in Chemistry (Guest), Faculty of Science
Dr. Rammanohar Lohia Avadh University, Ayodhya-224001, (U.P.), India
E-mail address: drspm9000@gmail.com

DOI: 10.29322/IJSRP.12.01.2022.p12139
http://dx.doi.org/10.29322/IJSRP.12.01.2022.p12139

Abstract: Titrimetric based study of two salts such as benzoic acid in sodium chloride (NaCl) media against sodium hydroxide (NaOH) basic solution have been reported here. Where, the aqueous solubility and equilibrium dissociation constant (Kc) of benzoic acid salt is showing at 25°C temperature in respect of thermodynamic dissociation constant (Ka). At this temperature the benzoic acid’s solubility into water and its dissociation value in six range of 0.00, 0.05, 0.10, 0.30, 0.40 and 0.50 M as for each different ionic strength (concentration) of NaCl salt, which is analyzed by titrimetrically against to 0.05 M of NaOH solution. The pH of each solutions are measured well by using of pH-meter. Here, observation reveals that, the value of pH for benzoic acid into water at applying temperature is may inversely related with strength of NaCl. In graphically, the value of ionic strength (I) of that benzoic acid is plotted against with Kc (dissociation constant) of acid in water at specific 25°C temperature. The value of Kc of benzoic acid for given each six concentration of NaCl is being -4.169, -4.045, -3.993, -3.885, -3.848 and -3.788, respectively.

Keywords: Benzoic acid, Sodium chloride, Solubility, Dissociation constant, Ionic strength.

[1]. INTRODUCTION:

Knowing, the each substance has a characteristic solubility in a given solvent because solubility depends on various factors such as temperature, intermolecular forces, solute-solvent interaction with its dissociation into ionic form and polar behaviour of substance etc [1]. The solubility and distribution or partition of solute in solvent have earlier performed [2], but in year 1891 it proved well by Nernst [3]. The solubility is defined as the concentration of the solute in solution when it is in equilibrium with the solid substance at a particular temperature and often expressed in terms of number of grams of it that can be dissolved in 100 grams of solvent. The solubility of substance is determined by preparing its saturated solution and then finding the concentration by evaporation or a suitable chemical method. An increase in temperature generally causes a rise in the solubility, but not always rise for all substances due to continuous and discontinuous solubility terms. Sodium chloride (NaCl) salt is an electrolyte and fairly soluble in water which is highly polar solvent, while it is insoluble in a non-polar solvent like benzene (C6H6), carbon tetrachloride (CCl4) or chloroform (CHCl3) etc. Here 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 (−). For example, NaCl dissolves in water to give solvated or hydrated Na⁺ and Cl⁻ ions [4].

Here, we have been reported the two salts behaviour as sodium chloride (brine) concentration on solubility of benzoic acid and its equilibrium dissociation constant (Kc) in water at 25°C (298 K) temperature. Although, literature survey have revealed about solubility and dissociation ratio of benzoic acid in aqueous NaCl medium at specific temperature [5]. Knowing. Sodium chloride (NaCl) salt is an ionic solid compound which having a 1:1 ratio of sodium and chloride ions. The pH of sodium chloride is 7.0 (neutral) and molecular weight as 58.44 g/mol. The density of it is 2.165 g/cm³ with 801°C and 1413°C its m.p. and b.p., respectively. Salt of NaCl is formed by the reaction of strong (HCl) acid and strong (NaOH) base and thus it ionize easily in aqueous solvent with highly solubility. In series of aromatic acids the benzoic acid (C6H5COOH) is a colorless crystalline solid substance having m.p. 121-122°C with pleasant smell and poor solubility in cold water [6]. In early of 20th century its salt has been used in industrial and medicinal purposes as well [7]. In chemical science the ionization of benzoic acid having a great interest with respect to temperature.

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http://dx.doi.org/10.29322/IJSRP.12.01.2022.p12139
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The carboxylic group of acid is polarize during on dissociation partially in water by forming H-bonding, and to produce benzoate anion ($\text{C}_6\text{H}_5\text{COO}^-$) and hydronium cation ($\text{H}_3\text{O}^+$).

$$\text{C}_6\text{H}_5\text{COOH} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{COO}^- + \text{H}_3\text{O}^+$$

Accordingly, the expression of Nernst distribution law which is given as- $K = \frac{C_\text{A}}{C_\text{B}}$. Here, the $C$ is as equilibrium concentration of using substances for solvent (A & B) and, the $K$ is a constant known as distribution coefficient. And the value of $K$ is independent of actual concentration of the solutions. Actually, the addition of small amount of benzoic acid (solute) salt into water as solvent gives rise a slightly changing due to water-water as well as solute-solvent interactions [8]. When salts as (NaCl or/and $\text{C}_6\text{H}_5\text{COOH}$) is put into solvents then it try to get dissolve and ionize with its ionic strength [9]. The sodium chloride (NaCl) is act as an electrolyte for to increase the ionic strength and its value in aqueous solutions of benzoic acid particularly with molar concentration of NaCl [5]. Although, in aqueous solution (aq), a little molar solubility of benzoic acid with weak electrolyte behavior [10]. In this work, at given temperature the molar solubility of benzoic acid in water (aqueous) is determined by titrimetrically against basic NaOH solution as standard strong base with study of equilibrium dissociation constant ($K_c$) and different concentration value or ionic strengths for acid.

The dissociation equilibrium of benzoic acid in basic or anionic form is follow these reaction- 

$$\text{C}_6\text{H}_5\text{COOH}^{\text{aq}} \rightarrow \text{H}^+(\text{aq}) + \text{C}_6\text{H}_5\text{COO}^-\text{(aq)}$$

Where, the equilibrium dissociation constant ($K_c$) can expressed as-

$$K_c = \frac{[\text{H}^+][\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}^{\text{aq}}]} \ldots \ldots (1)$$

[2]. EXPERIMENTAL :

Herein, all the required chemicals have been used as of analytical reagent grade with without further purification. The water have used as solvent throughout the experimental, which is distilled well three times. Typically, the basic solution of NaOH which are carbonated free have prepared well as suggested by adopting Vogel procedure [11]. 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 against a standard solution of NaOH. In this work those calibrated volumetric glassware used which is of class ‘A’ as well. In preparation of solution, we take a cleaned and dry six stopper 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 with NaOH solution of 0.050 M. Using of a 3 decimal digits calibrated pH meter we are measured the pH of each solutions at noticed temperature.

[3]. RESULTS AND DISCUSSION :

The solubility and equilibrium dissociation constant ($K_c$) of benzoic acid into water at room temperature (25°C) have been reported for six different samples in range of 0.00, 0.05, 0.10, 0.30, 0.40, and 0.50 M by adding sodium chloride (NaCl) salts. For six different concentration of NaCl, the benzoic acid solubility in water is analyze by followed to applying titration method as described by Khouri.
[12], and also measured the pH of each solutions. Here, the 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 sodium hydroxide (NaOH) solution, the benzoic acid solubility and pH value in aqueous water inversely related with concentrations of NaCl. Table-1 show at six different molar concentration of NaCl, the equal volume (20.0ml) benzoic acid solution is used for each, where the value of molar solubility ($\alpha$) and dissociation constant ($K_c$) of acid has been found to be from 0.0215 to 0.0265, and -3.788 to -4.169 respectively. Graphically, this estimated value of dissociation constant in terms of logarithm as log $K_c$ is ploted against ionic strength (I) as volume of NaCl in different range has used for benzoic acid solution at 25˚C temperature (as in figure-1). On comparing these reported value with literature value for $K_a$ which may obtaining from the extrapolation to zero ionic strength by using calorimetry [13], or other methods[14-16].

Table-1. At 25˚C, the effect of concentration of sodium chloride salt on solubility and dissociation constant of benzoic acid into water.

<table>
<thead>
<tr>
<th>S. N.</th>
<th>V of NaCl (in mol/l)</th>
<th>V of benzoic acid solution (in /ml)</th>
<th>V of 0.05 (mol/l) NaOH (in /ml)</th>
<th>pH</th>
<th>$\alpha$</th>
<th>$K_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.00</td>
<td>20.0ml</td>
<td>10.61 ± 0.014</td>
<td>2.884 ± 0.005</td>
<td>0.0265</td>
<td>-4.169</td>
</tr>
<tr>
<td>2.</td>
<td>0.05</td>
<td>20.0ml</td>
<td>10.19 ± 0.010</td>
<td>2.832 ± 0.005</td>
<td>0.0255</td>
<td>-4.045</td>
</tr>
<tr>
<td>3.</td>
<td>0.10</td>
<td>20.0ml</td>
<td>9.92 ± 0.009</td>
<td>2.813 ± 0.003</td>
<td>0.0248</td>
<td>-3.993</td>
</tr>
<tr>
<td>4.</td>
<td>0.30</td>
<td>20.0ml</td>
<td>9.51 ± 0.012</td>
<td>2.789 ± 0.005</td>
<td>0.0238</td>
<td>-3.885</td>
</tr>
<tr>
<td>5.</td>
<td>0.40</td>
<td>20.0ml</td>
<td>9.09 ± 0.011</td>
<td>2.763 ± 0.003</td>
<td>0.0227</td>
<td>-3.848</td>
</tr>
<tr>
<td>6.</td>
<td>0.50</td>
<td>20.0ml</td>
<td>8.58 ± 0.011</td>
<td>2.747 ± 0.007</td>
<td>0.0215</td>
<td>-3.788</td>
</tr>
</tbody>
</table>

Figure-1. At 25˚C, the plot value of equilibrium dissociation constant ($K_c$) versus ionic strength (I) of benzoic acid into water.
Figure-2. The temperature behaviour on thermodynamic dissociation constant (Ka) of benzoic acid into water.

As in figure-2, at a given temperature the equilibrium or apparent dissociation constant (Kc) of benzoic acid is correlated to thermodynamic dissociation constant (Ka) [17], which have compared from data of Strong et al [18]. Where, the Ka is a thermodynamic dissociation constant at infinite dilution of solution with mean activity coefficient (γ±) of the dissociated and undissociated ions of benzoic acid as expression, \( Ka = Kc \gamma^2 \) [12]. From this relation, mathematically, the mean activity coefficient of dissociated ions for solution is calculated by using of following equation-

\[
\log (\gamma^±) = 1/2 (\log Ka - \log Kc) \ldots \ldots (2)
\]

or,

\[
\log Ka + 2B \sqrt{l} = \log Kc \ldots \ldots (3)
\]

where, 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 [19], pressure (as Read’s data) [20], and chemically electrolytic properties [21]. At room temperature (25°C), for aqueous solutions, the equation (3) can becomes-

\[
\log Ka + 1.02 \sqrt{l} = \log Kc \ldots \ldots (4)
\]

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)-

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

Here, the α is a total mol solubility of benzoic acid and their benzoate or hydrogen ions in the aqueous solution, as \([\text{C}_6\text{H}_5\text{COOH}_{\text{aq}}] \) or \([\text{C}_6\text{H}_5\text{COO}^-] \) = (H+) \( = 10^{\text{pH}} \), which can be determined from given such following equation-

\[
\alpha = (V_{\text{NaOH}} x M_{\text{NaOH}}) / V_{\text{C}_6\text{H}_5\text{COOH}} \ldots \ldots (6)
\]

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

The solubility and dissociation constant (Kc) value of benzoic acid at 25°C (room temperature) in water for NaCl solution a same concentration used at same temperature, which are estimated by titrimetrically. If temperature increase in range between 25 to 30°C, the value of Kc is may inversely proportional, but it may contrast, because as temperature further increase in range of between 30 to 41°C the Kc value is directly proportional with temperature. There are no actually correlation between dissociation constant of benzoic acid and the temperatures range which is used. Thus from the data of experimental, in titration the used NaOH amount and the pH value for used each temperature, the benzoic acid solubility between water is directly proportional with temperature and benzoic acid molecule’s capability which to dissociate is not increases always as increases of temperature. Although, by thermodynamic study there are no revealing of dissociation process well. The dissociation of benzoic acid in water is as endothermic and reports to energy change to be positive which lead to dissociation process of acid molecule is nonspontaneous. If value of energy change becomes negative it means that in water the acid is attain a highly ordered state during after its process of dissociation. The solubility and dissociation of benzoic acid in water having different behaviour at higher temperature than above 30°C. As increases the temperature the benzoic acid capability to dissociate is decreases with reducing value of Kc. In this range of temperature the process is being exothermic with the compatibility to principle of Le Chatelier [12, 22]. 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 [23]. 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 [18].

By repeating of the same adapted titration procedure at 25°C temperature as six more time where the benzoic acid solubility is same for NaCl concentration in water with pH measuring of each solution. But at range of temperatures between 25°C and 41°C, the results
average is show a high precision for volume (V) of NaOH and pH values. At these temperature the value of dissociation constant (Kc) for used each concentration of NaCl is determined by applying of same methodology as used in case of 25°C for each temperature. Notably, the volume of each solutions 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 used 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 [18,20,24] with conductances for Na⁺, Cl⁻, H⁺ and OH⁻ [25]. Although, NaCl dissociation is may verify by change of enthalpy (H°) with Born-Haber based[26].

[4]. CONCLUSION:

In conclusion, we have reported the study of solubility and equilibrium dissociation constant (Kc) of benzoic acid in NaCl media against basic solution of NaOH at 25°C temperature by titrimetrically well. Knowing, the solubility of solute in given solvents is depend on various factors such as temperature, pressure, intermolecular forces, dielectric constant, pH value, solute-solvent interaction and dissociation of solute in solvent into ionic form etc. At 25°C temperature the benzoic acid solubility into water and their dissociation at six range of 0.00, 0.05, 0.10, 0.30, 0.40 and 0.50 M as for each different ionic strength or concentration of sodium chloride have been analyzed by titrimetrically against of 0.05 M sodium hydroxide (NaOH) solution. Here, the pH of each solution is measured well by using of calibrated pH-meter. The observation reveals that the pH value of benzoic acid into water at given temperature is may inversely related with concentration of NaCl. In graphically, the ionic strength (I) value of that benzoic acid is plotted against with dissociation constant (Kc) of acid into water at specific 298 K temperature. The values of acid dissociation constant for each concentration of NaCl is found to between of -3.788 to -4.169, respectively.

ACKNOWLEDGEMENTS: These work supported by various respective Journals and books. The author thanks to gratefully acknowledge support of Faculty of Science, Dr. Rammanohar Lohia Avadh University, Ayodhya-224001, (U.P.), India, for providing help in useful discussion and necessary facilities to valuable data.

REFERENCES:


