

# A pH EFFECT ON BENZOIC ACID SOLUBILIZATION AND THEIR PARTITIONING (K) IN WATER- BENZENE SOLVENTS

Shiv Prakash Mishra

Department of Physics and Electronics  
Dr. Ram Manohar Lohia Avadh University, Ayodhya-224001, (U.P.), India  
E-mail: drspm9000@gmail.com

DOI: 10.29322/IJSRP.11.04.2021.p11233  
<http://dx.doi.org/10.29322/IJSRP.11.04.2021.p11233>

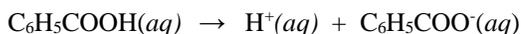
**Abstract:** The solubility of substance is depends on temperature and interaction of solute-solvent with its dissociation in ionic form as ionic strength of acid at different pH, where their partitioning ( $K$ ) are observed between two immiscible liquid-liquid solvents system. Presently, we have been reported to benzoic acid for these solubility as well as its partitioning study at different pH between in hydrophilic aqueous water and hydrophobic organic benzene layers at room temperature (25°C). Here, the benzoic acid are distributed between such solvent by applying shake-flask method and by titrimetrically, there equilibrium concentration in both solvents are analyzed. The solubility of benzoic acid and it partitioning between water and benzene buffer solution at different pH range as 4.0, 7.0 and 9.0 have been studied well.

**Keywords:** Benzoic acid, Solubility, Partitioning, pH effect, Nernst distribution coefficient.

## [1]. INTRODUCTION:

Knowing, the solubility is the property of matter referring to the ability for the solute substances in maximum amount to dissolve in solvents as given amount at a respective temperature in equilibrium under saturated solution. It expressed as in which one gram of solute is dissolving in number of milliliters of solvents. The partition coefficients provide a way to test in various solvent environments the accuracy of atomistic force fields with describing of concentration ratio of the neutral solute where the distribution of a solute as how between the two immiscible solvents system. They are used in drug design as a measure of a solute's hydrophobicity and a proxy for its membrane permeability. Although, literature reveals about the partition coefficients and their uses as well <sup>1</sup>, with partition coefficient for both solid-solid phase <sup>2</sup>, as well as where, one molten and second as solid phase <sup>3</sup>, but the liquid-liquid partition coefficients determination by methods of chromatographic separation with it separation for solute partitioning between the mobile and stationary phase <sup>4</sup>. The titrimetric study of the solubility and dissociation of benzoic acid in water <sup>5</sup>, as well as the octanol-water partition coefficient <sup>6</sup>, and salvation thermodynamics in different solvents as water-chloroform system have also been well reported <sup>7</sup>.

Concerning, the present studies of solubility and the dissociation process of many well known weak acids such as benzoic acid in water and benzene solutions have been reported over the years by following many physical and analytical methods<sup>8,9</sup>. As a temperature increases the capability of benzoic acid to dissociate decreases which that leads to reduce the value of  $K$  and process in this range is certainly exothermic as compatibility with Le Chatelier's principle <sup>10</sup>. Benzoic acid ( $C_6H_5COOH$ ) is one of the simplest organic acids of aromatic series with low solubility in water. Where the benzoic acid dissolves only slightly in cold water through the polarization of carboxylic acid group during on dissociation partially in water by forming hydrogen bonding attachment to produce benzoate anion ( $C_6H_5COO^-$ ) and hydronium cation ( $H_3O^+$ ). In saturated aqueous solution (*aq*), the benzoic acid has little molar solubility with the following equilibrium-



The molar solubility of benzoic acid in water is determined titrimetrically against a standardized strong base solution, then equilibrium can be expressed as-

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

Where,  $K_c$  is the apparent dissociation constant of benzoic acid, which is affected by several factors including temperature, pH and ionic strength *etc.*

In present work, we have been reported the pH effect on maximum solubilization and distribution or partitioning of benzoic acid in water and benzene. The hydrophilic aqueous such as water as well as in hydrophobic organic benzene phase which are determined titrimetrically, by using equation derived from Nernst distribution coefficient law, which is improved and used in this work to obtain more accurate finding results as compared to the reported its  $K$  value in the literature study<sup>11</sup>. Mathematically, the expression of Nernst distribution equation which is given as- ' $K$ ' =  $C_1/C_2$ . Where, the  $C_1$  and  $C_2$  equilibrium concentration of reporting substances for solvent-1 and -2, and  $K$  is a constant known as partition or distribution coefficient and its value is independent of actual concentration of the solutions. In case when solute undergoing partition has molecular weight in one solvent say (organic solution)  $n$  times higher than water at equilibrium, distribution ratio  $K$  becomes-  $K = C(aq)/C(org)^{1/n}$ . Here,  $C(aq)$  = equilibrium concentration of solute in aqueous solution (water) and  $C(org)$  = equilibrium concentration of solute in organic solvent (benzene). Since, benzoic acid exists as dimer in aprotic solvents like in benzene (i.e.,  $n=2,3$ ), hence the modified distribution law is valid i.e.,  $K = C(aq)/n\sqrt{C(org)}$ , where,  $C(aq)$  and  $C(org)$  are concentration of benzoic acid in aqueous and in benzene layer with partition coefficient ' $K$ ' of benzoic acid. The study of this relationship is important because it provides a means for determining the association of a substance in specific solution. Here,  $n$  is known as degree of association.

Although, the salt of aromatic benzoic acid (benzenecarboxylic acid) have been used in early 20<sup>th</sup> century as in industrial purposes, therapeutically and medicinal respective way<sup>12,13</sup>. The benzoic acid (M.F.C<sub>6</sub>H<sub>5</sub>COOH) is a colourless crystalline organic solid substance having m.p. 121°C with faint pleasant odour. Here, in present study we have been selected a benzoic acid because its suite solubility in variety of polar and nonpolar solvents such as benzene (C<sub>6</sub>H<sub>6</sub>), carbon tetra chloride (CCl<sub>4</sub>), chloroform (CHCl<sub>3</sub>), alcohol (C<sub>2</sub>H<sub>5</sub>OH), acetone (CH<sub>3</sub>COCH<sub>3</sub>) and in liquor ammonia (liq.NH<sub>3</sub>), etc. The solubility of benzoic acid at different pH range in acidic, neutral and basic buffer solutions and there partitioning is studied well at room temperature about 25°C. By using titrimetric method, where, the two immiscible solvent as hydrophilic aqueous water and hydrophobic organic benzene has been selected for study of partitioning or distribution or partition coefficient. The crystalline benzoic acid is partitioning between the liquid water and liquid benzene system by applying of shake-flask method. The concentration of acid in both solvents is analyzed by acid-base titration method.

## [2]. EXPERIMENTAL:

In experimental procedure, all required chemicals and solvents which are used in this study as an analytical reagent grade on laboratory based as well as the solvent distilled water is also freshly prepared which is used during throughout the work. The carbonate free sodium hydroxide (NaOH) solutions are prepared as work suggested by Vogel<sup>14</sup>. The provided benzoic acid, (C<sub>6</sub>H<sub>5</sub>COOH) is of Research Lab Fine Chemicals Industries, Mumbai, and using buffer solutions as range pH 4.0, 7.0 and 9.0 of Merck Specialties Private Limited, Mumbai, India.

Applying of acid-base titrimetric method we are estimated the benzoic acid solubility( $S$ ) at varies pH buffer solution at 25°C maintaining room temperature. Now, in different beakers take 100ml buffer solution of various ranges pH as 4.0, 7.0 and 9.0, and then in every beaker is added about 200mg of solid benzoic acid and it well stirred with glass rod for producing saturated solution. Notably, some solid undissolved and must be left. If required these solution is heated. Cooling these prepared solution at room temperature and withdrawn a 5.0ml of these solution into dry conical flask ( $W_1$ ) as previously weight. Again weight ( $W_2$ ) of 5.0ml contains conical flask and titrate against of these solution with 0.05N NaOH solution, which are freshly prepared by using an indicator as phenolphthalein. The appearing pink colour show it end point and recorded these reading. In g/100g of solvent the solubility of benzoic acid is determined by described formula as given below with comparing solubility against prepared distilled water as blank. Between the solubility of benzoic acid in g/100g in using solvent and buffer solution of different pH is plotted in

graph. In graph method, the effect of pH effect on benzoic acid solubility has been studied.

Here,

The empty conical flask weight =  $W_1$

The 5.0 ml solution containing conical flask weight =  $W_2$

The weight of solution,  $(W_2 - W_1)$  gram =  $W_3$

The solute weight ( $C_6H_5COOH$ ) =  $0.122 \times 0.05 \times$  burette reading ( $V$ ) =  $W_4$

The weight of solvent,  $(W_3 - W_4)$  =  $W_5$

In g/100 g of solvent the solubility( $S$ ) of benzoic acid =  
solute weight ( $W_4$ )  $\times$  100/ solvent weight ( $W_5$ ).

At different pH range the partitioning or partition coefficient of benzoic acid is estimated by using acid-base titrimetric and shake-flask method. Where, in beaker a 10 % benzoic acid solution in benzene (BB solution) have been prepared well. The prepared four different solution in separating funnel with same quantity and pH range of buffer solution (40ml +4.0) is given below-

1. The buffer solution, (40ml, pH 4.0) + BB solution, 40ml.
2. The buffer solution, (40ml, pH 4.0) + BB solution, 30ml + benzene, 10ml.
3. The buffer solution, (40ml, pH 4.0) + BB solution, 25 ml + benzene, 15 ml.
- 4 The buffer solution, (40 ml, pH 4.0) + BB solution, 20 ml + benzene, 20 ml, .

At room temperature ( $25^{\circ}C$ ) these containing flasks have shaken for one day (24hours) on water-bath incubator shaker. Allowing, all the solutions for  $\frac{1}{2}$  hour to stand for equilibrium obtained which is containing lower aqueous with upper as benzene layer. In dry beaker the lower aqueous layer of each flask are removed by retaining of layer of benzene in separating flask. Now, into a dry conical flask we pipette out aqueous layer of about 10ml, and against with 0.01N NaOH solution we titrated it by using indicator as phenolphthalein. The pink colour as it end point. We record this reading well. A 5.0ml of benzene layer pipette out in a another dry conical flask and adding 10ml of distilled water. From 0.1N NaOH we titrate against of these solution using indicator as phenolphthalein also. A pink colour is appearance as end point of reaction and record this observe reading also. For buffer solution of pH 7.0 and 9.0, the same procedure has been follows with blank sample as distilled water. For such system the partitioning ( $K$ ) estimation is calculated by applying giving formula-

[1]- *In moles/litre the benzoic acid for aqueous layer concentration ;*

As determination of normality it is calculated by applying following normality equation-

$$N_1V_1 = N_2V_2 \dots\dots\dots(i)$$

Where,

the  $N_1$  is normality of aqueous layer written as,  $N(aq)$  and the  $N(aq) = 0.01 V_2 / 10 \dots\dots(ii)$

and, the  $N_2$  is normality of NaOH which involve for titration as  $N(org) = 0.01 N$ , thus, the  $N(aq) = C(aq) \dots\dots\dots(iii)$

The  $V_1$  is taken volume of aqueous layer (10 ml), and  $V_2$  the consumed burette reading of volume of NaOH.

[2]- *In moles/litre the benzoic acid for organic layer concentration;*

As determination of normality it is calculated by applying following normality equation-

$$N_3V_3 = N_4V_4 \dots\dots\dots(iv)$$

Where,

the  $N_3$  is organic layer normality as  $N(org)$ , =  $0.1 V_4 / 5 \dots\dots(v)$

and the  $N_4$  is normality of NaOH which used for titration as  $N(org) = 0.1 N$ , thus the,

$$N(org) = C(org) \dots\dots\dots (vi)$$

The  $V_3$  is taken volume of organic layer (5.0ml), and  $V_4$  as the consumed burette reading of volume of NaOH.

**[3]- The partitioning (K) for water-benzene system;**

The partition coefficient of aqueous-organic system which is determined from applying equation-

Hence,  $K = C(aq) / C(org)^{1/2} \dots\dots (vii)$

Where, (at equilibrium),  $K = [Aqueous\ layer\ Concentration\ (C_w)] / [Organic\ layer\ Concentration\ (C_o)^{1/2}]$

**[3]. RESULT AND DISCUSSION:**

The benzoic acid solubility is depends on temperature, pressure, interaction of solute-solvent with solute dissociation in solvent into ionic form, hydrogen bonding formation and substances polarity-nonpolarity, etc. At 25°C the analysis of solubility(S) of benzoic acid have been shown in table-1. In observation, we have found that benzoic acid solubility at room temperature about 25°C in distilled water are being to  $0.142 \pm 0.033$  g/100g of aqueous and at different pH since 4.0, 7.0 and 9.0 it varies to  $0.153 \pm 0.012$ ,  $0.186 \pm 0.145$  and  $0.148 \pm 0.708$  g/100g with solvent for benzene-buffer solution, respectively. This observation reveals that the value is being maximum at neutral pH (7.0) buffer solution.

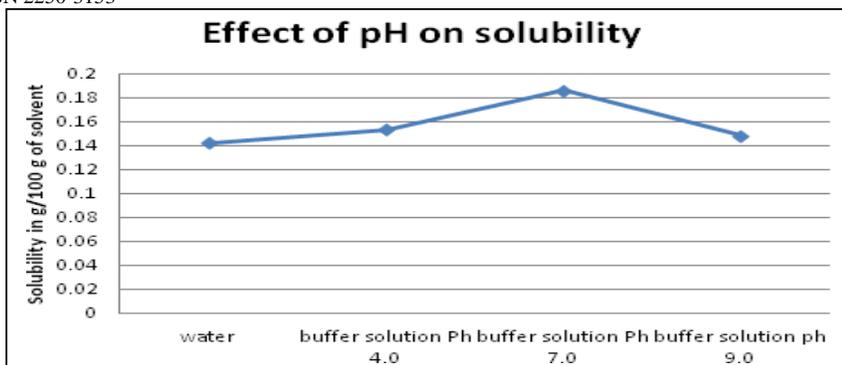
**Table-1. At 25°C Solubility analysis of Benzoic Acid**

(The result at 25°C and, Mean  $\pm$  SD )

S.N.	Using Solvents	Specific Solubility(S) (gm/100gm of solvent)
1-	Distilled water	$0.142 \pm 0.033$
2-	Benzene-buffer solution, pH 4.0	$0.153 \pm 0.012$
3-	Benzene-buffer solution, pH 7.0	$0.186 \pm 0.145$
4-	Benzene-buffer solution, pH 9.0	$0.148 \pm 0.708$

expressed as; n=3,

In graphically, the study of benzene-water system where both graphs are plotted in respect of partitioning or partition coefficient (K) and different pH containing buffer solutions as well as pH effect on partitioning of benzoic acid. The study reveals that the ratio  $C_w/C_o$  (concentration of water and organic) of layer may not remain constant but the  $C_w/C_o^{1/n}$  ratio is remain constant in partitioning of solute as benzoic acid between water-benzene system. This is indicating the association of molecule in dimer form (dimerization) due to hydrogen bonding formation between benzoic acid molecules in organic benzene layer and in aqueous water layer the remaining monomer molecules<sup>15</sup>. The figure-1 have shown benzoic acid solubility with pH effect, where graph is plotting between different pH containing buffer solution in g/100 g of solvent. It is suggested that in acidic medium the benzoic acid solubility in variety of pH buffer solution is becoming slightly higher in comparison of basic pH due to their strength of ionic dissociation<sup>16</sup>.



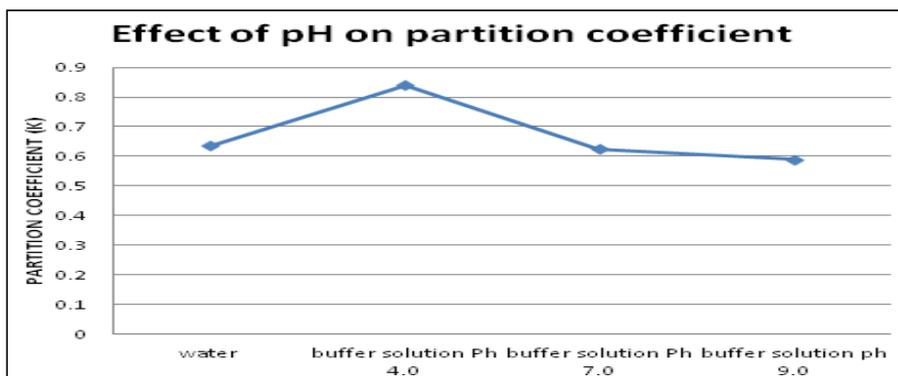
**Figure-1. The pH effect on benzoic acid solubility**

In table-2, we have reported the pH analysis on partitioning (*K*) of benzoic acid in system of water and benzene with buffer solution where the value as being 0.636 as well as the combine value as 0.841, 0.624 and 0.589 being for buffer solutions at different range pH 4.0, pH 7.0 and pH 9.0, respectively.

**Table-2. The pH analysis on partitioning 'K' of benzoic acid**

S.N.	Using Solvents	Partition coefficient ( <i>K</i> )
1-	Benzene-water system	0.636
2-	Benzene-buffer solution, pH 4.0	0.841
3-	Benzene-buffer solution, pH 7.0	0.624
4-	Benzene-buffer solution, pH 9.0	0.589

The figure-2 have been shown, where, the graph is plotted between partitioning (*K*) and the buffer solutions of different pH value. Graph observation indicate that, the benzoic acid partitioning in acidic pH medium is higher in comparison of neutral and basic medium as well.



**Figure-2. The pH effect on partition coefficient of benzoic acid**

**[4]. CONCLUSION:**

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<http://dx.doi.org/10.29322/IJSRP.11.04.2021.p11233>

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In present article, we are reported the study of solubility of benzoic acid and their partitioning or partition coefficient between particular or two different immiscible solvents with association and dissociation of solute. The benzoic acid solubility(S) at different ranges pH buffer solutions as in all acidic, neutral and basic medium have analyzed by titrimetrically and their partitioning study by using shake flask method for hydrophilic aqueous water and hydrophobic organic benzene system, at 25°C in respective of room temperature with variety range of pH as 4.0, 7.0 and 9.0, respectively.

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

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