

Research Article

Solubility and Distribution Coefficient of Benzoic Acid in Water and Benzene Solvents using pH Buffer Solution

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Abstract

In article, we are reported the solubility and partition or distribution coefficient of solute benzoic acid between solvents of hydrophilic water and hydrophobic benzene in buffer solution which have been studied at room temperature (25°C). In different range of pH buffer solution the benzoic acid solubility (in g/100g of solvent) are analyzed by titration method as well as the partitioning of such acid in using these two immiscible solvents by shake-flask method. The solubility and distribution of solute benzoic acid in distilled water and in benzene-buffer solution of pH 4.0, pH 7.0 and pH 9.0 as in acidic, neutral and basic medium are well determined. The observation reveals the solubility of solute benzoic acid in buffer solutions as in acidic pH (4.0) is about slightly higher than basic (pH 9.0) medium, but in comparing of distribution coefficient of acid in acidic medium is higher than both neutral (pH 7.0) and basic pH.

Keywords: Benzoic acid, Solubility, Distribution coefficient, pH Buffer solution, Nernst partition equation

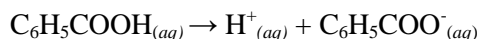
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Introduction

Although, firstly Berthelot and Jungfleisch was reported about the solubility of solute and their distribution ratio or partition between two immiscible solvents [1], later on by Nernst [2]. The distribution coefficient for both solid-solid phase [3], and where, one molten and second as solid phase [4], as well as the liquid-liquid partition coefficients now have been determined by using methods of chromatographic separation with its separation for solute partitioning between the mobile and stationary phase [5]. The titrimetric study of the solubility and dissociation of benzoic acid in water [6], the octanol-water partition coefficient [7], and salvation thermodynamics in solvents as water-chloroform system have also been well reported [8]. Present studies of solubility and the dissociation process of known weak acids such as benzoic acid in water and benzene solutions have been reported over the years by following adapted physico-analytical method [9-11]. Here we reported solubility and partition coefficient (K) study at room temperature but as the 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 [12].

The benzoic acid (C_6H_5COOH) is one of the simplest organic acids of aromatic series with less solubility in water. Where, in cold water the benzoic acid slightly dissolves 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^+) [6]. In saturated aqueous solution (aq), the benzoic acid has little molar solubility with the following equilibrium-



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

$$Kc = [H^+][C_6H_5COO^-] / [C_6H_5COOH_{(aq)}]$$

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

In this article, we have been reported the solubility and distribution coefficient of solute benzoic acid between water and benzene solvents in using buffer solutions. Solubility of acid in both solvents like hydrophilic aqueous water and hydrophobic organic benzene 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 [13]. 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. $n = 3$), hence the modified distribution law is valid as $K = C(aq)/n\sqrt{C(org)}$, 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.

Knowing, the benzoic acid having M.F. C_6H_5COOH and M.P. $121^\circ C$, is a colourless crystalline solid substance with pleasant odour and its salts have been used in early 20th century as in industrial purposes, therapeutically and medicinal respective way [14,15]. 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_6H_6), carbon tetrachloride (CCl_4), chloroform ($CHCl_3$), alcohol (C_2H_5OH), acetone (CH_3COCH_3) and in liquor ammonia (liq. NH_3), 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 $25^\circ C$. By using titration 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 as well.

Experimental

In this experimental procedure, the 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 [16]. The provided benzoic acid, (C_6H_5COOH) is of Research Lab Fine Chemicals Industries, Mumbai, and using buffer solutions of pH 4.0, pH 7.0 and pH 9.0 as of Merck Specialties Private Limited, Mumbai, India.

Applying titration method, we have estimated the benzoic acid solubility at varies pH buffer solution at $25^\circ C$ 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 un-dissolved 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 record these reading of burette (V). 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, if

The conical flask weight (empty) = W_1

The 5.0 ml solution containing conical flask weight = W_2

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

The solute weight (C_6H_5COOH) = (g/w of substance x N x ml of solution used) = ($0.120 \times 0.05 \times V$) = 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) x 100/ solvent weight = (W_5).

At different pH range the partitioning or partition coefficient of benzoic acid is estimated by using acid-base titration and shake-flask method. Where, in beaker a 10 % benzoic acid solution in benzene (2B solution) have been prepared well. The prepared four different solution in separating funnel with same quantity and pH range of buffer solution (40ml + pH 4.0) is given below

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

At 25°C these containing flasks have shaken for one day (24hours) on water-bath incubator shaker. Allowing, all the solutions for half 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 its 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 estimation of solubility with distribution coefficient is calculated by applying the below given formula-

- (1) In moles/litre, the benzoic acid concentration for aqueous layer;

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

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

Where, the N_1 is normality of aqueous layer written as, $N(aq)$ and the

$$N(aq) = 0.01 V_2 / 10 \quad (ii)$$

And, the N_2 is normality of NaOH which involve for titration as $N(org) = 0.01$ N, thus, the

$$N(aq) = C(aq) \quad (iii)$$

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 concentration for organic layer;

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

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

Where, the N_3 is organic layer normality as

$$N(org), = 0.1 V_4 / 5 \quad (v)$$

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

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

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 partition coefficient (K) for water-benzene phase;

The K for water-benzene layer concentration which is determined from applying equation (vii)-

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

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

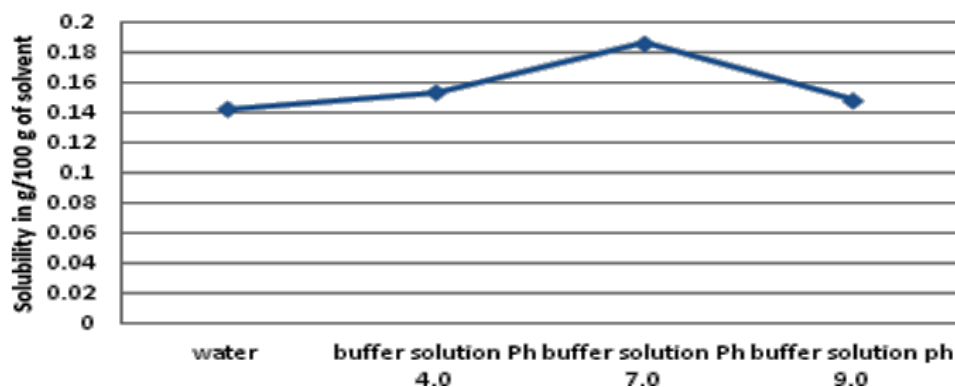
Result and Discussion

Notably, the benzoic acid solubility is depends on temperature, pressure, interaction of solute-solvent with solute dissociation in solvent in form of ionic and H-bonding etc. At room temperature (25°C) the analysis of solubility of solute 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 ± 0.033 g/100g of aqueous and at different pH since 4.0, 7.0 and 9.0 it is varies to 0.153 ± 0.012 , 0.186 ± 0.145 and 0.148 ± 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.

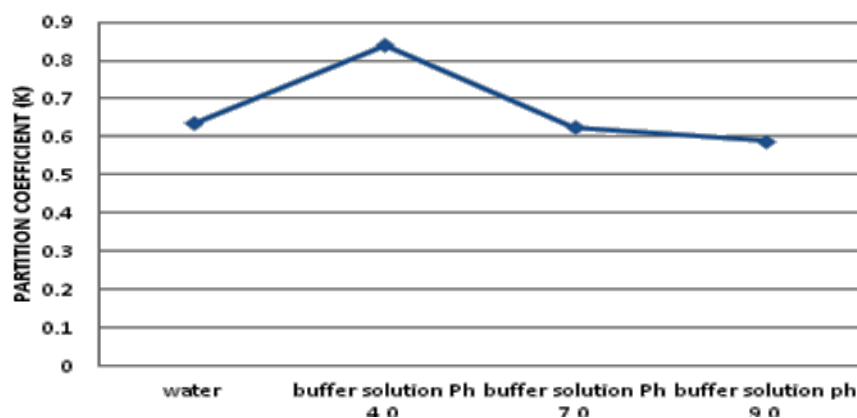
Table 1 At 25°C, Solubility analysis of Benzoic Acid

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

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 [17]. As from **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.

**Figure1** The pH effect on benzoic acid solubility**Table 2** pH analysis on partition coefficient 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

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

The **Figure 2** have been shown, where, the graph is plotted between partitioning (*K*) and the different pH value. Graph observation indicate that, the benzoic acid partitioning in acidic pH medium is higher in comparison of neutral as well as in basic medium. In study of benzene and water phase, the both graphs have plotted for solute solubility (*S*) and distribution coefficient (*K*) with 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 H-bonding formation

between benzoic acid molecules in organic benzene layer and in aqueous water layer the remaining monomer molecules [6, 18].

Conclusion

Herein, we have reported the solubility of benzoic acid at room temperature and their distribution or partition coefficient between the two immiscible liquid solvents like hydrophilic water and hydrophobic benzene with buffer solutions which are well studied. At different range of pH buffer solutions the solute benzoic acid solubility (in g/100g of solvent) have analyzed by using titration method, where the partitioning of this acid for water and benzene-buffer solvents by shake flask method. The solubility and partition analysis of concentration of benzoic acid in prepared distilled water and in benzene-buffer solution at three variety pH 4.0, 7.0 and 9.0 as in acidic, neutral and basic medium have determined with expected table value. The graph observation reveals about the solubility of benzoic acid in pH buffer solution in acidic pH (4.0) is slightly higher than basic medium and distribution coefficient of that acid in acidic medium higher than neutral (7.0) and basic pH (9.0) medium.

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