Phenolphthalein Indicator in Titrimetric Estimation of Benzoic Acid Solubility and Distribution in Water and Benzene-Buffer Solutions

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Author's contribution

The sole author designed, analysed, interpreted and prepared the manuscript.

Original Research Article

ABSTRACT

In solubility and partitioning process of benzoic acid, the various factors are involved such as temperature, solute-solvent interaction and dissociation of acid into ionic state in taking solvents. Here, we reported the benzoic acid (solute) solubility in gram/100gram of solvent in different pH benzene-buffer solutions which are analyzed by using of titration method and partition study of these acid into solvents like water and benzene layer by shake-flask acid-base titration method, at room temperature (25°C) for 24 hours. In titrimetric estimation the solute benzoic acid solubility and their partition in between of water and in different pH buffer solutions as in medium of acidic, neutral and basic, a phenolphthalein indicator have been used well. The solvents and benzene-buffer solutions having different pH 4.0, 7.0 and 9.0 is titrated against as 0.01, 0.05 and 0.1N NaOH solutions by using phenolphthalein as indicator, where the end point show a pink color for each reading. Concentration of benzoic acid into water and solvent benzene layers is being calculated as by applying the equation of normality determination and distribution coefficient as from Nernst distribution law equation.

Keywords: Benzoic acid; pH effect; solubility; partition coefficient; phenolphthalein indicator.

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1. INTRODUCTION

Chemically, phenolphthalein is a organic compound of the well known phthalein family with molecular formula $C_{20}H_{14}O_4$ and often widely used as an acid-base indicator [1]. The melting point of crystalline phenolphthalein is in between of 258-263 °C and its solubility in water as 400 mg/L. It is synthesized by the reaction of condensation of phenol and phtalic anhydride. When two moles of phenol reacts with anhydride of phthalic acid (one mole) and heated in presence of concentration H_2SO_4, an water molecule is eliminated and phenolphthalein obtained [2]. The reaction is given below-
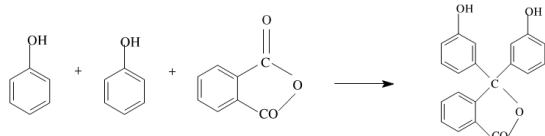

Phenol   Phthalic anhydride   Phenolphthalein

The phenolphthalein in aqueous solutions where the pH value is below 8.5, it is colorless and hue above pH 9.0 its colour is attains a intensive pink to deep red. Below 8.5 it is present entirely as phenol lacton (a right most structure in the above scheme). The colored form (that corresponds to a salt) adopts the structure, where, one resonanting structure of the anion is shown following-
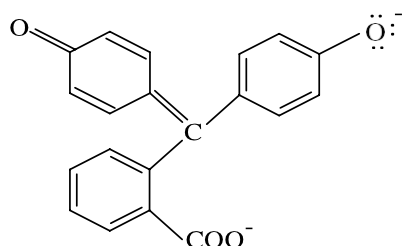
(deep red colour)

Phenolphthalein is a dye and chosen as indicator because in a pH range of 8.3 to 10, it changes colour as appears pink in basic solution and in acidic and neutral it remain colorless. The reactant of unknown concentration (in flask) is known as analyte and other reactant with concentration(known) which remains in the burette to be delivered during the reaction is called as titrant. In these case a phenolphthalein indicator is adding to the analyte concentration. Literature survey reveals about indicators as phenolphthalein and methyl orange [3], that is used as acid-base indicators in titration [4,5], and in variety of reactions at pH dependence well [6-8]. In this article, we have been reported the study of phenolphthalein indicator behaviour in titrimetric estimation of the solubility of benzoic acid with its distribution in water and benzene buffer solutions. Although, the many physical and analytical methods have been reported over the years in study of solubility and the process of dissociation for various weak acids as well as the benzoic acid into aqueous and benzene solvents [9,10]. Here the described temperature is 25 °C or 298 K, but as the temperature rises the capability of dissociation of benzoic acid is decreasing which leads the reducing of dissociation constant (K) value with exothermic process, accordingly to compatibility of Le Chatelier's principle [11,12]. Presently, here in study, we have been reported a solute benzoic acid (C_6H_5COOH; m.p. 121°C) because it has the fair solubility into solvents (in polar and nonpolar both) such as benzene (C_6H_6), carbon tetra chloride (CCl_4), chloroform ($CHCl_3$), alcohol (C_2H_5OH), acetone (CH_3COCH_3), and in liquor ammonia (liq.NH_3), etc. In aromatic organic acids series the benzoic acid is an one of the simplest acid with poor solubility into cold water partially. It is slightly dissolve during on dissociation into water through the polarization of carboxylic group by forming of H-bonding and to producing benzoate anion ($C_6H_5COO^-$) and hydronium cation (H_3O^+) [13]. This acid has a little molar solubility in saturated aqueous solution (*aq*), with in equilibrium which is as following-

$$C_6H_5COOH(aq) \rightarrow H^+(aq) + C_6H_5COO^-(aq)$$
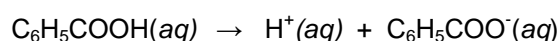
In titrimetrically, the benzoic acid molar solubility is determined as by against of strong base standard solution, where, the equilibrium is beig expressed as-

$$Kc = [H^+][C_6H_5COO^-] / [C_6H_5COOH(aq)]$$

Where, Kc is the dissociation constant of benzoic acid, which is affected by several factors including temperature, pH and ionic strength *etc* [14,15]. In this work, the solubility and distribution of benzoic acid into aqueous (hydrophilic) and into organic benzene (hydrophobic) like solvents is determined by titrimetrically. From the law of Nernst distribution coefficient which is used for to finding the more improved and accurate results as in comparing of reported its value of K in study of literature of Khouri [13]. In mathematically, the Nernst distribution equation

is as- $K = C_A/C_B$. Here, the C_A and C_B are the equilibrium concentrations of given substances for 1 and 2 solvents. And, the K is a constant known as distribution or partition coefficient, where, these value is independent of actual concentration of the solutions [16]. Notably, the solute benzoic acid exists in dimeric form into aprotic solvents (benzene) [17]. Although, the Nernst partition coefficient law study having importance because of providing a determining means for the association or dissociation (n) of a substances in given solutions [18].

2. EXPERIMENTAL MATERIALS AND METHODS

2.1 Materials

In experimental and procedure studies, there required all the solvents and chemicals reagents which is used as being a laboratory based analytical graded as well as the distilled water as solvent is freshly prepared also which is using in during throughout the hole work. The supplied stock solutions are as solute benzoic acid, (C_6H_5COOH) is of Research Lab Fine Chemicals Industries, Mumbai, India, as well as the using of readymade buffer solutions as of pH 4.0, 7.0 and 9.0 of Merck Specialties Private Limited, Mumbai, India. The (NaOH) sodium hydroxide solutions have prepared well with carbonate free as the work suggested by Vogel [19].

2.2 Methods

Here, by the applying titration (acid-base) method, we have been estimated the solubility of benzoic acid on variety of pH buffer solution at maintaining to room temperature (25 $^{\circ}$C). Now, taking the different beakers of100ml and then in every beaker is added about 200mg of solid benzoic acid and buffer solution of containing pH as 4.0, 7.0 and 9.0, then, for producing a saturated solution, it well stirred with using glass rod. Some undissolved solid must be left and then these solution is heated. Now, we cooling it at room temperature to these prepared solution then about a 5.0ml of these solution is withdrawn into dry conical flask (W_1) as previously weight. Now, weight (W_2)) again of 5.0ml containing conical flask and then start titrate to this solution against basic solution of of 0.05N NaOH which are prepared in freshly manner, here, we using an introduced indicator as phenolphthalein. During on titration an appearing of just pink color which show its end point of reaction and then we recorded to these (burette) reading. By the

described formula, as given below, the solubility (*S*) of benzoic acid is well determined as well comparing the solubility against distilled water which prepared as blank. In between gram/100gram of solvent the solubility of benzoic acid in an using solvent and in buffer solutions of different pH is being plotted in graphically. In graph method, the benzoic acid solubility and the pH effect has been studied already [20].

If, the weight of conical flask (empty) = W_1 and, conical flask weight (with 5.0 ml solution) = W_2

then weight of solution ($W_2 - W_1$) = W_3

where, the solute weight (C_6H_5COOH) = W_4

the W_4 is a (g of substance x N of solution x V ml of solution used (burette reading)

then weight of solvent ($W_3 - W_4$) = W_5

thus, *S* of benzoic acid (in g/100g of solvent) = solute weight (W_4) x 100/ solvent weight (W_5).

Here, the g is stand for gram and N is for normality with volume, V. The benzoic acid partition coefficient at different pH range is estimated by using of two shake flask method and acid-base titration method. In next beaker, a solution of solute benzoic acid (10 %) into solvent benzene (BB solution) have been prepared. There are four different solutions which are prepared in separating funnel having equal pH (4.0) for all, it is below given-

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

At room temperature, 25 ^{0}C, the each separate flask of prepared samples solutions are shaken well by using water-bath incubator shaker for one day (24hours). Now, for a half hour we allowing, all the solutions to stand for obtaining the equilibrium which is containing two layers such as a lower aqueous with upper as benzene layer. In new dry beaker a removing the lower aqueous layer of each flask by retaining of layer of benzene in separating flask. Now, we pipette out aqueous layer of about 10ml into a dry conical flask and it titrated against with solution of 0.01N

NaOH, in indicator we using also as phenolphthalein. An pink colour appeared and these show its end point or completion the reaction, then, we record this reading. Now, in a another dry conical flask we pipette out the benzene layer of 5.0 ml and adding distilled water to 10 ml. From NaOH (0.1N) solution we titrate it against of these solution by using of phenolphthalein indicator. A appearing of pink colour which is end point of reaction and also observed reading is record. For pH 7.0 and 9.0 of buffer solutions, the same procedure is followed with blank sample as distilled water. In calculation of partitioning (K) estimation for such system we applying the below given formula-

2.2.1 The benzoic acid (solute) concentration for aqueous (water) layer (In moles/litre)

The normality determination, it is calculated by applying following normality equation-

$$N_1V_1 = N_2V_2 \tag{1}$$

here, N_1 is normality of aqueous layer written as,

$$N(aq) \text{ and the } N(aq) = 0.01 \ V_2 / 10 \tag{2}$$

N_2 is normality of NaOH which involve for titration as,

$$N(org) = 0.01 \text{ N, thus, the } N(aq) = C(aq) \tag{3}$$

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

2.2.2 The benzoic acid (solute) concentration for organic (benzene) layer (in moles/litre):

The normality determination, it is calculated by applying following normality equation-

$$N_3V_3 = N_4V_4 \tag{4}$$

here, N_3 is organic layer normality as

$$N(org), = 0.1 \ V_4 / 5 \tag{5}$$

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

$$\text{then, } N(org) = C(org) \tag{6}$$

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

2.2.3 The distribution coefficient (K) of benzoic acid for water-benzene solution:

The distribution coefficient of water-benzene system which is determined from applying equation-

hence, $K = C(aq) / C(org)^{1/2}$

$$\text{or, } K = [(Cw)] / (C_O)^{1/2}] \tag{7}$$

here, the Cw is stand for concentration of water and Co as for concentration of organic layer.

3. RESULT AND DISCUSSION

Knowing, the solubility and distribution (partition) of benzoic acid in solvents is temperature dependent. The solubility (S) and partition (K) analysis of solute benzoic acid at the room temperature (25°C) have been showing in Table 1. In solubility observation of benzoic acid at about25°C into distilled water is being found to 0.142 $\pm$ 0.033 gram/100gram for water solvent and these are at different pH to 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. From table-1, we have also reported the partition coefficient (K) of benzoic acid with their pH analysis into water and benzene as well as in buffer solution where these value are being as 0.636 and the combine value as being 0.841, 0.624 and 0.589 for buffer solutions at different range as of pH 4.0, pH 7.0 and pH 9.0, respectively.

As for benzene-water system we have studied that in respect of distribution coefficient (K) and buffer solutions of different pH (4.0, 7.0 and 9.0) range as well as partitioning of benzoic acid with pH effect, where the both graphs are plotted. The partition study of solute into solvent reveals that the concentration ratio (Cw/Co) of water (aqueous) and organic (benzene) layers is not remain constant equally but these are remain constant with ratio $Cw/Co^{1/n}$, during in distribution of solute (benzoic acid) between water-benzene system. These indicated that the association or dimerization of acid molecules in dimer form,

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Table 1. The solubility and partition analysis for benzoic acid at 25°C

S.N.	Using solvents	pH	Mean solubility (*S*) (g/100g of solvent)	Partition coefficient (K)
1-	Distilled water	-	0.142 ± 0.033	-
2-	Benzene-water solvent	-	-	0.636
3-	Benzene-buffer solution	pH 4.0	0.153 ± 0.012	0.841
4-	Benzene-buffer solution	pH 7.0	0.186 ± 0.145	0.624
5-	Benzene-buffer solution	pH 9.0	0.148 ± 0.708	0.589
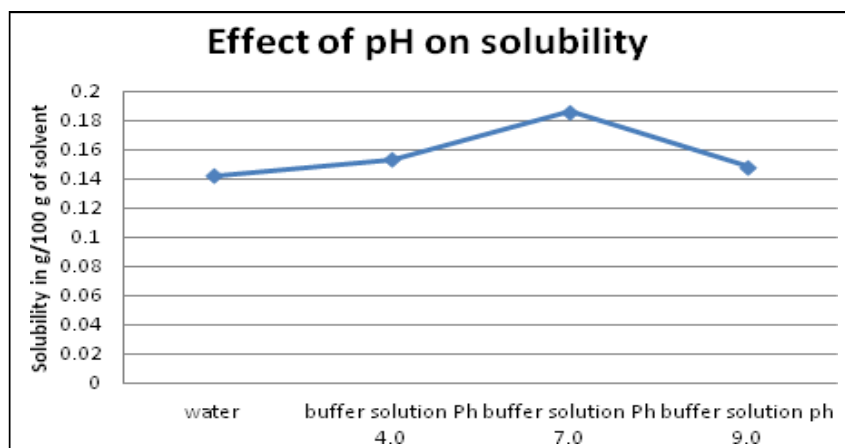
Fig. 1. The pH effect on solubility of Benzoic Acid
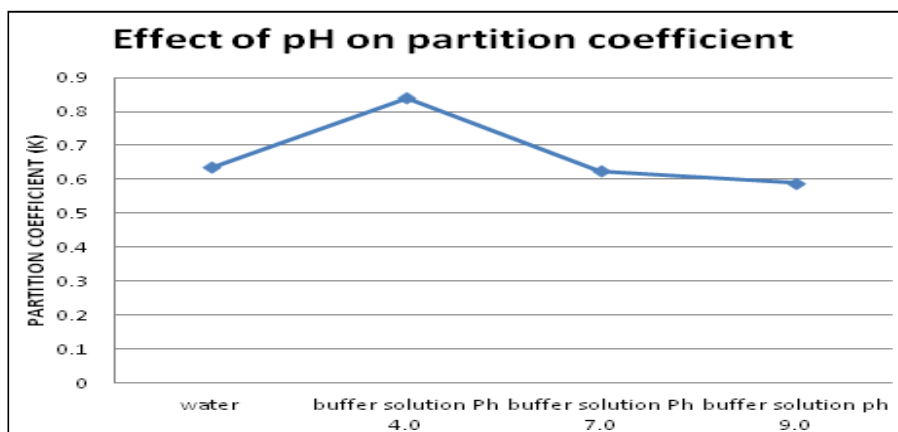
Fig. 2. The pH effect on partition coefficient of benzoic acid

due to formation of H-bonding in between of benzoic acid molecules in aqueous and organic layer and the remaining monomer molecules [17]. The benzoic acid solubility with pH effect have shown in Fig. 1, where plotting of graph in between to different pH containing buffer solution (in gram/100 gram of solvent). It is suggested that in variety of pH buffer solution as in acidic medium the benzoic acid solubility is being to slightly higher in comparative study to basic pH because of their ionic dissociation strength [21,22]. Here, the Fig. 2 have shown, where, the graph is plotted in between partitioning (*K*) and

the buffer solutions with different pH. The observation of graph indicates that, the partitioning of benzoic acid in acidic pH medium is higher in comparison of neutral or in basic medium [23]. Although, the solubility of benzoic acid is thermodynamically dependent [24,25], and follow to Van't Hoff equation [26].

4. CONCLUSION

In conclusion, we have reported a phenolphthalein indicator as in study of titrimetric estimation of benzoic acid solubility and their

distribution in water and benzene-buffer solution. In process of solubility and partitioning of benzoic acid (solute), there are various factors involved like solute-solvent interaction, dissociation of acid into ionic form in solvent, and temperature etc. At 25°C (room temperature) for 24 hours, the solubility of benzoic acid in gram/100gram of water and as well as in different pH benzene-buffer solutions have been determined by titrimetrically and partitioning of acid with its concentration in water and benzene layers by shake-flask acid-base titration method. In titrimetric estimation the solubility of benzoic acid and their partition or distribution between water and in using different pH buffer solutions are analyzed well in acidic, neutral and basic medium. For water and benzene-buffer solutions at different pH 4.0, 7.0 and 9.0 it has titrated against as 0.01, 0.05 and 0.1N NaOH solutions by using phenolphthalein as indicator, where the end point show a pink colour for each reading value. The concentration of benzoic acid between water and in benzene layers is calculated by applying of normality determination equation and distribution coefficient of acid from Nernst distribution law equation.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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