Review Article

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

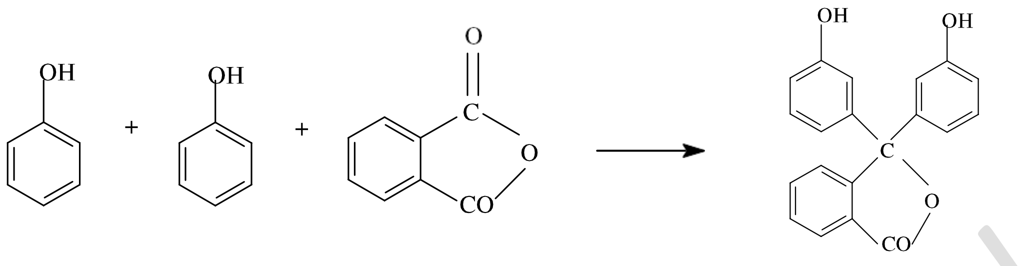
ABSTRACT

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 form in taking solvents. Here, we reported the benzoic acid (solute) solubility in g/100g of solvent in different pH benzene-buffer solutions which are analyzed by using titration method and partitioning study of these acid in water and benzene solvents layer by shake-flask acid-base titration method, at room temperature (25°C) for 24 hours. In titrimetric estimation the solubility of benzoic acid and their partition between water and in different pH buffer solutions in acidic, neutral and basic medium a phenolphthalein indicator have been used well. The water 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 in water and benzene layers is may calculated by applying normality determination equation and distribution coefficient as from Nernst distribution law equation.

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

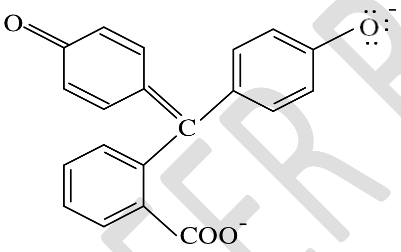
[1]. INTRODUCTION:

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 condensation reaction 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 (the right most structure in the above scheme). The colored form (that corresponds to a salt) adopts the following structure (one resonant structure of the anion is shown)-



(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 of known concentration which remains in burette to be delivered during the reaction is called as titrant. In this case the phenolphthalein indicator is added 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 benzoic acid's solubility and its distribution in water and benzene buffer solutions. Although, 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 [9,10]. Here the described temperature is 25 °C or 298 K, but as a temperature increases the capability of benzoic acid to dissociate decreases which that leads to reduce the value of dissociation constant (*K*) and process in this range is certainly exothermic as compatibility with Le Chatelier's principle [11,12]. 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 tetra chloride (CCl_4), chloroform ($CHCl_3$), alcohol (C_2H_5OH), acetone (CH_3COCH_3) and in liquor ammonia (liq.NH_3), etc. The benzoic acid (C_6H_5COOH; m.p. 121°C) is one of the simplest organic acids of aromatic series with poor solubility in water. It 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^+) [13]. In saturated aqueous solution (*aq*), the benzoic acid has little molar solubility with the following equilibrium-

$$C_6H_5COOH(aq) \rightarrow H^+(aq) + C_6H_5COO^-(aq)$$

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 dissociation constant of benzoic acid, which is affected by several factors including temperature, pH and ionic strength *etc* [14,15].

The solubility and distribution of benzoic acid in reported solvents as hydrophilic aqueous (water) and in hydrophobic organic (benzene) is 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 of Khouri [13]. Mathematically, the expression of Nernst distribution equation which is given as- $\boldsymbol{K= C_A/C_B}$. Where, the C_A and C_B equilibrium concentration of reporting substances for solvent-1 and 2, and the *K* is a constant known as partition or distribution coefficient, and its value is independent of actual concentration of the solutions [16]. 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) [17], 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. Here, *n* is known as degree of association. The study of this relationship is important because it provides a means for determining the association or dissociation of a substance in specific solution [18].

[2]. EXPERIMENTAL:

(A)- Materials: In 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 [19]. The provided benzoic acid, (C_6H_5COOH) 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.

(B)- Methods: Here, by applying acid-base titration method, we have estimated the benzoic acid solubility on varies pH buffer solution at 25 °C maintaining room temperature [20]. 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 as are freshly prepared, by using an indicator as phenolphthalein. The appearing pink color show it end point and recorded these reading. In g/100g of solvent the solubility (*S*) 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.

If,
the conical flask weight (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).

At different pH range the 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 solutions in separating funnel having same pH (4.0) for all and it is given below-

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

At 25 ^{0}C (room temperature) these samples 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 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 (solute) concentration for aqueous (water) layer:*

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

N1V1 = N2V2 ………….(i)

Where,

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

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

$N(aq) = C(aq)$…………………..(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 (solute) concentration for organic (benzene) layer:*

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

N3V3 = N4V4………………(iv)

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

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

thus, $N(org) = C(org)$……………. (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 distribution coefficient (K) of benzoic acid for water-benzene solution:*

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

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

or, $K = [(C_w)] / (C_O)^{1/2}]$……..(vii)

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. At room temperature (25°C) the analysis of solubility (*S*) of benzoic acid and its partition 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. 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 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-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

In study of benzene-water system, where the both graphs are plotted in respect of distribution 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 $Cw/Co^{1/n}$ 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 [17]. 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 [21]. Here, 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 as well as in basic medium.

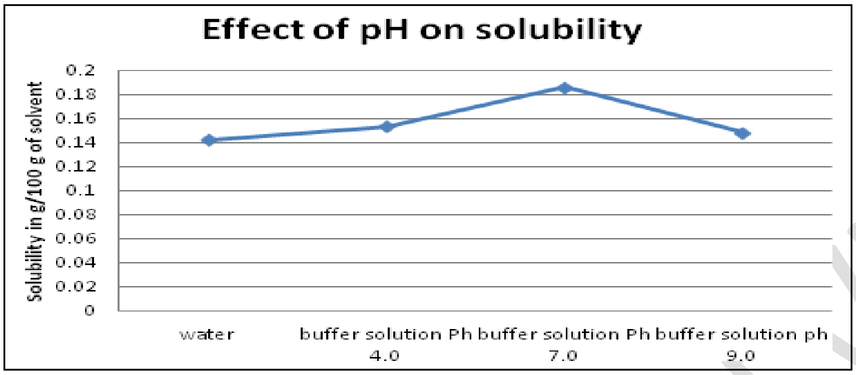


Figure-1. The pH effect on solubility of Benzoic Acid

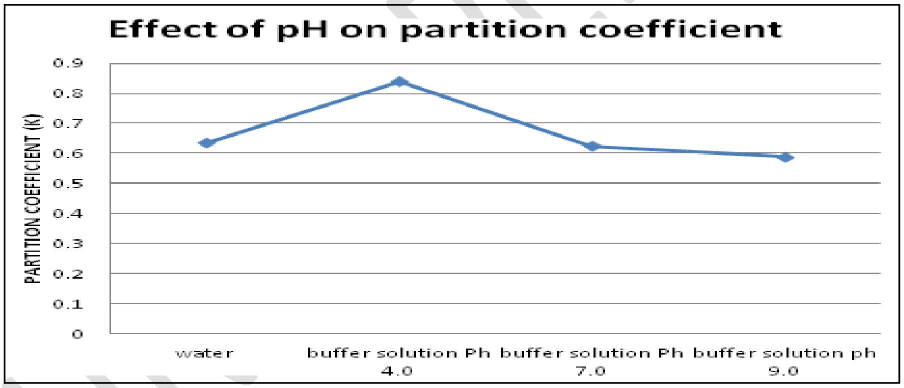


Figure-2. The pH effect on partition coefficient of benzoic acid

[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 room temperature (25°C) for 24 hours, the benzoic acid solubility in g/100g 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 DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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