NORMALITY EQUATION IN DETERMINING OF BENZOIC ACID CONCENTRATION BETWEEN AQUEOUS AND ORGANIC LAYERS

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ABSTRACT

In solubility of benzoic acid at different pH range, the distribution or partition coefficient (K) study of these acid between two two immiscible liquid-liquid solvents as hydrophilic water and hydrophobic organic benzene at room temperature (25°C) have been reported here. The methods which involved for the partitioning of benzoic acid in two solvents such as shake-flask and concentration analysis of acid in these solvents are acid-base titration methods. The benzoic acid solubility as well as partition in distilled water and in benzene-buffer solution having range pH 4.0, 7.0 and 9.0 with expected value have well determined. Observation is may reveals that as in aqueous layer an undissociated monomer molecular form of benzoic acid but in organic layer an associated dimer form. For such solvents system, there are applyingnormality determination equation to calculate aqueous (water) and organic (benzene) layer concentration in moles per litre.

Keywords: Benzoic Acid, Solubility, Partition Coefficient, Ph Effect, Normality Equation.

[1]. INTRODUCTION

Indeed, a various literature has revealed about the solubility of solute and their distribution or partition with its application as well [1,2]. The partitioning 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 different solvents as water-chloroform system have also been well reported [8]. The solubility and dissociation process of many 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]. 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 [11].

The benzoic acid (C_6H_5COOH) is one of the simplest organic acids of aromatic series with low solubility in water. In cold water the benzoic acid dissolves only in little amount 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[6]-

$$C_6H_5COOH(aq) \rightarrow H^+(aq) + C_6H_5COO^-(aq)$$
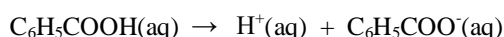
In water the molar solubility of benzoic acid is determined by titrimetrically against a standardized strong base solution, then equilibrium can be expressed as-

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

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

Herein, we have reported the concentration of benzoic acid when it maximum solubilized and distributed or partitioned between aqueous and benzene layers may calculated by applying normality determination equation. The both solvents such as hydrophilic aqueous water and hydrophobic organic benzene phase 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 [12]. 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.=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 benzoic acid has been used in early 20th century as in industrial purposes, therapeutically, medicinal and other respective way[6,13,14]. The benzoic acid (M.F.C_6H_5COOH & M.P. 121°C) is a colourless crystalline organic solid substance with pleasant odour. 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 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, 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 ispartitioning between the liquid water and liquid benzene system by applying of shake-flask method and concentration of acid in both solvents is analyzed by acid-base titration method as well.

[2]. EXPERIMENTAL
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 [15]. The provided benzoic acid, (C_6H_5COOH) is of Research Lab Fine Chemicals Industries, Mumbai, and using buffer solutions with pH 4.0, 7.0 and 9.0 as of Merck Specialties Private Limited, Mumbai, India.

By applying acid-base titrimetric method, we have estimated the benzoic acid solubility at varies pH buffer solution at 25^0C 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 this solution is heated. Cooling these prepared solutions 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 x 0.05 x 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) x 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 buffersolution, (40ml, pH4.0) + BB solution, 40ml.
2. The buffer solution, (40ml, pH 4.0)+ BB solution, 30ml +benzene, 10ml.
3. The buffersolution, (40ml,pH4.0)+ BB solution, 25 ml + benzene, 15 ml.
4. The buffersolution, (40ml,pH4.0)+ BB solution,20 ml + benzene, 20 ml, .

At room temperature (25^0C) these containing flasks have shaken for one day (24hours) on water-bath incubator shaker. Allowing, all the solutions for ½ 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 another dry conical flask and adding 10ml of distilled water. From 0.1N NaOH we titrate against of these solutions 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-
$N_1V_1 = N_2V_2$.............................(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 for organic layer concentration;
As determination of normality, it is calculated by applying following normality equation-
$N_3V_3 = N_4V_4$………………(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 the,
$N(org) = C(org)$……………. (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 partition coefficient (K) for water-benzene system;
The partition coefficient of aqueous-organic system which is determined from applying equation-
Hence, $K = C(aq) / C(org)^{1/2}$ …..(vii)

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

[3]. RESULT AND DISCUSSION

Knowing, the benzoic acid solubility is depending on temperature, pressure, interaction of solute-solvent with solute dissociation in solvent into ionic form, hydrogen bonding formation and substances polarity-nonpolarity, etc. At room temperature (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 + 0.033 g/100g of aqueous and at different pH since 4.0, 7.0 and 9.0 it is varying 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
(The result at 25^0C expressed as; n=3, and, Mean + SD)

S.N.	Using Solvents	Specific Solubility(S) (gm/100gm of solvent)
1-	Distilled water	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

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 Cw/Co (concentration of water and organic) of layer may not remain constant but the $Cw/Co^{1/n}$ ratio isremaining 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 [16].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].
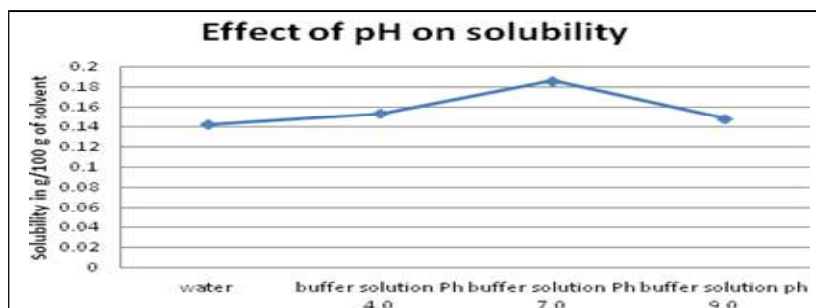

Figure-1. The pH effect on benzoic acid solubility

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.

Table-2. pH analysis on partition coefficient of Benzoic Acid

S.N.	Using Solvents	Partition coefficient (K)
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 as well as in basic medium.
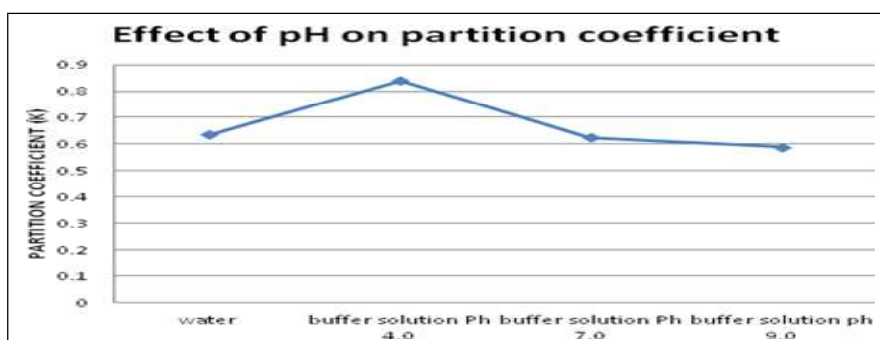

Figure-2. The pH effect on partition coefficient of benzoic acid

[4]. CONCLUSION

In present article, we are reported the applying of normality equation to determination of normality for aqueous layer and organic layer concentration of benzoic acid. The solubility and distribution or partition of benzoic acid between the two immiscible liquid-liquid solvents like hydrophilic nature containing aqueous water and hydrophobic organic benzene have been studied well. Here, the solubilization study of solute benzoic acid at room temperature (25℃) are analyzed by titrimetrically and their partitioning by using of shake flask method for water and benzene solvent system. The analysis of concentration of benzoic acid with solubility and partition coefficient in distilled water as well as in different pH buffer-benzene solutions having pH 4.0, 7.0 and 9.0 as in acidic, neutral and basic medium, respectively.

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