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RESEARCH ARTICLE

BUFFER SOLUTION BEHAVIOUR ON SOLUBILITY AND DISTRIBUTION COEFFICIENT OF BENZOIC ACID BETWEEN TWO IMMISCIBLE LIQUIDS

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Abstract

The two immiscible solvents such as hydrophilic (water) and hydrophobic (benzene) have been reported for study of solubility and distribution of benzoic acid in it. The solubility of benzoic acid in water and in different acidic, neutral, and basic pH benzene-buffer solutions are analyzed by titrimetrically, and concentration of acid in both solvents by acid-base titration method. The shake-flask method are involved for where the partitioning or distribution coefficient of benzoic acid in these two solvents layer at room temperature (25°C). Observation reveals that, the benzoic acid solubility in g/100g for water is being 0.142±0.033 and at different buffer solutions with pH 4.0, 7.0 and 9.0 it being 0.153±0.012, 0.186±0.145 and 0.148±0.708, in respect of partition coefficient of that acid where it for water-benzene solvent as 0.636 and in buffer solutions is being 0.841, 0.624 and 0.589 respectively. In graphically, at different pH buffer solutions the solubility plot of acid in neutral pH (7.0) is higher than other acidic and basic, but it for distribution coefficient of acid in acidic (pH 4.0) medium is higher than both neutral and basic pH (9.0) medium.

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Introduction:-

Although, the solubility with partition ratio of solute in solvent have reported firstly by Berthelot and Jungfleisch [1], but it clearly proven by Nernst (1891). A various literature reveals about solubility and distribution coefficient of solute in solvents with its application [2-7], as well as partition of water-octanol [8], and salvation thermodynamics in water-chloroform system have also been well reported [9]. The benzoic acid solubility and its dissociation process between water and benzene solvents have reported by titrimetrically [10], or adapting of various physico-analytical methods [11-13]. Concerning the study of solubility and partition coefficient of benzoic acid at 25°C as room temperature which having compatibility with Le Chatelier's principle [14]. In series of aromatic acids the benzoic acid (C_6H_5COOH) having less solubility in ordinary water through the carboxylic acid group polarization during on dissociation partially in water by forming H-bonding attachment to produce benzoate anion ($C_6H_5COO^-$) and hydronium cation (H_3O^+) [10].

$$C_6H_5COOH + H_2O \rightarrow C_6H_5COO^- + H_3O^+$$

In saturated aqueous solution (*aq*), a little molar solubility of benzoic acid which has following equilibrium-

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

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The molar solubility of benzoic acid in aqueous (water) is determined by titrimetrically against NaOH solution as standard strong base, then equilibrium can be expressed as-

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

Where, the Kc is dissociation constant of benzoic acid.

Here, we have been reported the buffer solution behavior on solubility and distribution coefficient (K) of benzoic acid (solute) between two immiscible liquid solvents such as water and benzene. In this work we are using equation derived from Nernst distribution coefficient law, which have used and improved to finding an accurate results with value of K. Mathematically, the expression of Nernst distribution equation which is given as- **'K' = C_A/C_B** . Here, the C_A and C_B are concentration of substances as for solvent A and B, and K is a constant of Nernst equation and it also known as partition or distribution coefficient where 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, the distribution ratio K becomes- $K = C(aq)/C(org)^{1/n}$ [15]. Here, $C(aq)$ is equilibrium concentration of solute (benzoic acid) in aqueous solution (water), and $C(org)$ is 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 i.e., $K = C(aq)/n\sqrt{}C(org)$. Where, n is known as degree of association with K as partition ratio or coefficient.

Benzoic acid is a colorless crystalline solid substance having M.F. C_6H_5COOH and M.P. 121-122°C with pleasant smell [16], and in early 20th century its salt has been used in industrial and medicinal purposes [17,18]. In present study we have been selected a benzoic acid because its suite solubility in variety of polar and non-polar solvents such as in water (H_2O) 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 benzoic acid solubility in water and in benzene with buffer solutions of pH acidic (4.0), neutral (7.0) and basic (9.0) medium are determined by using titration method and partitioning study of that acid in both liquid solvents by shake-flask method. The solute benzoic acid concentration in water and benzene solution is analyzed by applying acid-base titration method as well.

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 [19]. A Research Lab Fine Chemicals Industries, Mumbai, have provided solid benzoic acid, (C_6H_5COOH) and the Merck Specialties (Pvt.) Limited, Mumbai, to buffer solutions as of pH 4.0, 7.0 and 9.0 value.

[A]- The solubility (S) determination:

At 25°C temperature we are applying the acid-base titration method, for estimation of benzoic acid solubility at varies pH buffer solution. Now, in different beakers take 100ml buffer solution of pH 4.0, pH 7.0 and pH 9.0, and then in every beaker we added solid benzoic acid about 200mg, and for producing saturated solution it stirred with glass rod. Notably, some solid un-dissolved and must be left. If required these solution is heated. At 25°C, cooling these solution which are prepared and into dry conical flask (say W_1) it withdrawn a 5.0ml of these solution. Again weight (say W_2)) of 5.0ml solution contained conical flask and indicator phenolphthalein is used and it titrate against to these solution with prepared of 0.05N NaOH solution. Records the burette reading (V) as appearing pink colour show it end point. As given below described formula we determine the benzoic acid solubility (S) in gram/100gram of solvents and to compare with water (distilled) as blank against solubility [20].

If, conical flask weight (empty) = $W_{1,}$ and conical flask weight with solution (5.0ml) = W_2
Thus, the solution weight, $(W_2 – W_1) = W_3$, and if the solute weight (C_6H_5COOH) = W_4
Here, W_4 is (g/w of substance x N of solution x ml of solution used) as 0.125 x 0.05N x V
Then, the solvent weight, $(W_3 – W_4) = W_5$
Thus, S = solute weight (W_4) x 100/ solvent weight = (W_5)

The partition coefficient (K) determination:

By the using acid-base and shake-flask method we estimated partition coefficient (K) of benzoic acid at different pH. Where, in a beaker we prepared 10 % benzoic acid solution in benzene (say 2B solution). Here, the four different type of solutions are prepared in separating funnel, where buffer solution having the same pH 4.0 for each all sample, is given below-

(1). Buffer solution (40 ml) + 2B solution (40 ml).
(2). Buffer solution (40 ml) + 2B solution (20 ml) + benzene (20 ml).
(3). Buffer solution (40 ml) + 2B solution (25 ml) + benzene (15 ml).
(4). Buffer solution (40 ml) + 2B solution (30 ml) + benzene (10 ml).

At 25^0C, we used a water-bath incubator shaker for where all prepared solutions with in flasks have been shaken for one day (24hours) and allowing to stand it about half hour to get equilibrium. After then we obtained that the used separating funnel or flask is containing lower aqueous with upper as benzene layer. In dry beaker, firstly we removed the lower layer (aqueous) from each flask by retaining of upper layer (benzene) within separating flask. Now, in a dry conical flask we pipette out aqueous layer of 10 ml, and against with 0.01N NaOH solution we titrated it, by using indicator as phenolphthalein. The pink color as it end point. We record this reading well. Benzene layer (5.0 ml) is pipette out in an another using dry conical flask with adding a 10 ml of distilled water. Using of indicator as phenolphthalein also, these prepared solution with 0.1N NaOH solution against titrated. A pink color is appearance as it end point of reaction and record this observe burette reading. Notably, we have followed for buffer solution of pH 7.0 and pH 9.0, the same above described procedure with to blank sample as distilled water. By applying normality and modify Nernst partition formula for aqueous water and organic benzene phase or layer, we are estimate as well as to calculate the partitioning (*K*) behavior of solute in solvent (in moles/litre). The following formula have been given below-

(1)- *Solute (benzoic acid) concentration for aqueous (water) layer* :
As determination of normality it is calculated by applying following normality equation-
N1V1 = N2V2...................... (i)
Here,
the N_1 is aqueous layer normality written as, N(*aq*) and the N(*aq*) = 0.01 V_2 / 10 …….(ii)
and, the N_2 is normality of base 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 as burette reading of volume of base NaOH.

***Solute (benzoic acid) concentration for organic (benzene) layer* :**
As determination of normality it is calculated by applying following normality equation-
N3V3 = N4V4…………….(iv)
Here,
the N_3 is organic layer normality as N(*org*), = 0.1 V_4 / 5……….(v)
and the N_4 is normality of base 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 (5.0 ml), and V_4 as the burette reading (consumed) of volume of base NaOH.

(3)- *Partition coefficient (K) of solute for water and benzene solvents*:
The partition coefficient of aqueous-organic solvents system which is determined from applying equation-
$K = \sqrt{C(org)} / C(aq)$, or = $C(aq) / C(org)^{1/2}$ ….. (vii)
Thus, at equilibrium, $K = (C_w / C_O^{1/2})$
Where, C*w* is stand for concentration of solute (benzoic acid) in aqueous water layer and C*o* for concentration of solute in organic layer.

Results and Discussion:-

The solubility of solute is depends on various factors such as temperature, pressure, interaction of solute-solvent with solute dissociation in solvent as in ionic form and H-bonding *etc*. The addition of salts in water gives rise a slight changing because solute-solute and solute-solvent interaction [21]. The solute benzoic acid in aqueous solution has less solubility and having weaker electrolyte behaviour [22]. From table-1 we have reported that the solute benzoic acid's solubility in gram/100gram of solvent, at room temperature about 25°C, as in water (as distilled) is being to 0.142 ± 0.033 and at three pH 4.0, pH 7.0 and pH 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) for benzene and buffer solution. The figure-1 have shown benzoic acid solubility with pH effect, where graph is plotting between solubility of solute in g/100g of solvent versus varied pH of buffer solutions and water. These suggested that the acid solubility as in acidic range is becoming higher slightly in comparison of basic medium due to their strength of ionic dissociation.

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

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

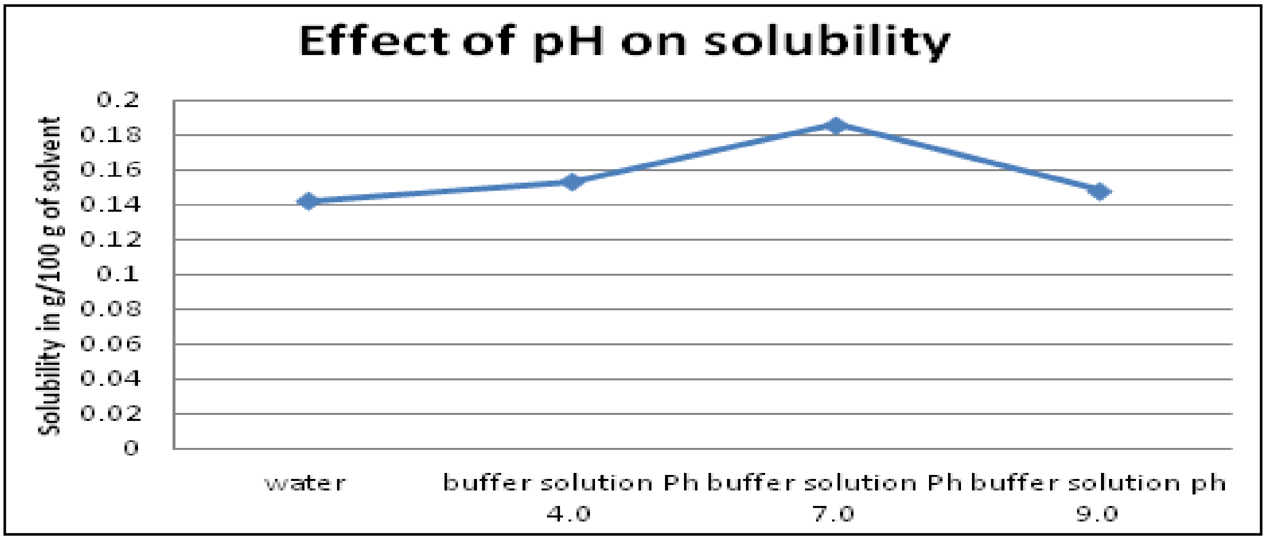

Figure-1:- The pH effect on benzoic acid solubility.

From the table-2, we have reported the pH behavior analysis of partitioning of benzoic acid in phase of water and benzene with acidic, neutral and basic buffer solutions. Where, the value for benzene-water phase it is being 0.636 as well as the combine value as 0.841, 0.624 and 0.589 is being for benzene-buffer solutions at different range pH 4.0, 7.0 and 9.0, respectively. The figure-2 has 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's distribution coefficient in acidic pH medium is higher than in comparison that of neutral as well as in basic medium.

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

S.N.	**Using Solvents**	**pH**	**Partition coefficient (*K*)**
1-	Benzene-water solvent	-	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

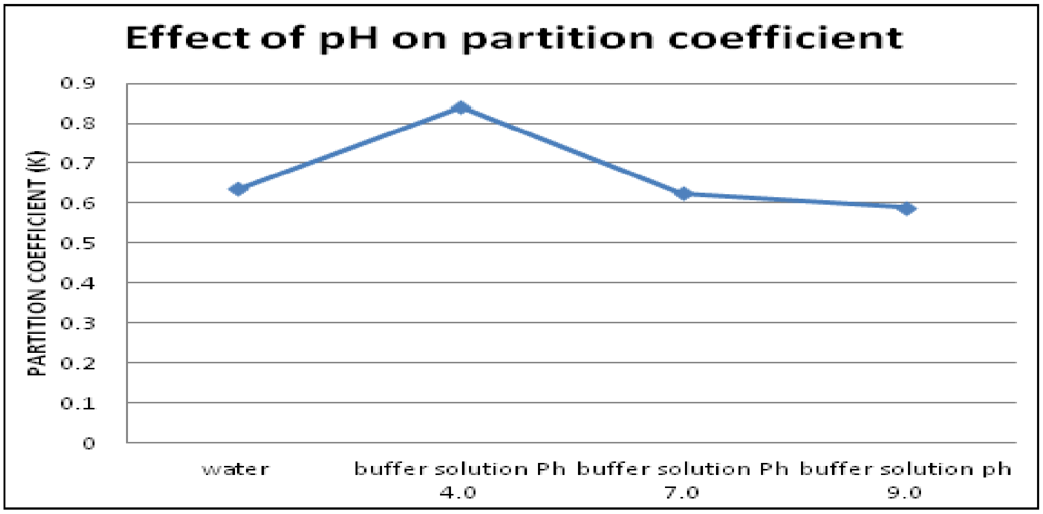

Figure-2:- The pH effect on partition coefficient of benzoic acid.

Graphically study for benzene-water system, where both graphs are plotted in respect of solubility (*S*) and partitioning or distribution coefficient (*K*) of solute in solvents with different pH containing buffer solutions and effect of pH on solubility and partitioning of benzoic acid. For distribution of solute in aqueous-organic solvents, the study reveals that as C*w* and C*o*$^{1/n}$ (concentration of water and organic layer) ratio is remain constant, whereas, the C*w* and C*o* ratio may not remain constant. It indicates the formation of H-bonding by association of molecules in dimerization phenomenon between molecules of benzoic acid in organic layer and in aqueous layer the remaining monomer molecules. In water the benzoic acid solubility is directly proportional with temperature, but at higher temperature than 30°C, the acid behaves differently where capability of acid to dissociate which leads to raduce the value of *K* [10], with polarization of bond [23].

Conclusion:-

In conclusion, we have reported the buffer solutions behaviour on solubility and distribution coefficient of benzoic acid at room temperature (25°C) between two immiscible liquid such as hydrophilic water and hydrophobic benzene solvents. In water and in benzene with buffer solutions of pH 4.0, pH 7.0 and pH 9.0, the solubility of benzoic acid (solute) in g/100g of solvents are analyzed by using titration method and partitioning of acid in water and benzene solvents by shake-flask method. The observation reveals the solubility of benzoic acid in distilled water is being 0.142±0.033 and in different buffer solutions with pH 4.0, 7.0 and 9.0 being 0.153±0.012, 0.186±0.145 and 0.148±0.708, as well as it for partition coefficient of acid in water-benzene solvent as 0.636 and in buffer solutions is being 0.841, 0.624 and 0.589 respectively. In graphically, at different pH buffer solutions the solubility of benzoic acid in neutral pH (7.0) is higher than that of acidic (4.0) and basic (9.0), but, it for distribution coefficient of acid in acidic medium is higher than both neutral and basic pH medium.

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