Review Article

Gibbs Free Energy change (*ΔG*) in Aqueous Dissociation of Benzoic Acid at Temperature 'K' : A Thermodynamic Study

ABSTRACT

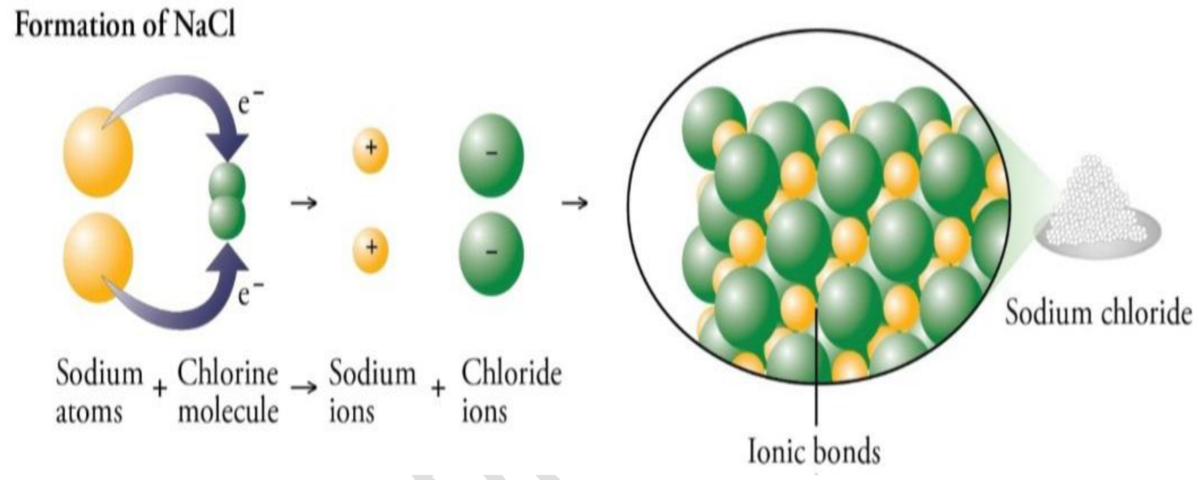
In article, we have reported a thermodynamic based study of a Gibbs free energy change (*ΔG*) in aqueous dissociation of benzoic acid at Kelvin temperature range in between of 288 K to 318 K. Thermodynamically, at this Kelvin temperatures range the acid dissociation constant (*Ka)* of benzoic acid into aqueous solutions have been determined by applying of titration method against standard basic solution of NaOH with different value of ionic strength of NaCl concentrations. In observation, the value of *Ka* is being inversely proportional with respect to temperature in between 289 K to 303 K and it is in contrast at higher temperature in between 303 K to 314 K it being directly proportional. In graph, the plot has shown the value of *Ka* of benzoic acid is being 4.176 at 298 K temperature. This is reported that, there are no regular correlation in between temperature and *Ka* of that acid. Thus, in finding of precious results for benzoic acid dissociation into water an applying the Gibbs free energy change relationship ($\Delta G = \Delta H - T\Delta S$) for endothermic or exothermic reaction process at standard condition of thermodynamic parameters. These parameters value (in kJ.mol^{-1}) are being as ΔG = 12.507, ΔH = 3.823 and ΔS = -29.14. And, at 298 K, it is show that the acid dissociation into aqueous solvent is an endothermic and non-spontaneous process with ordered entropy (*ΔS*).

Keywords: Benzoic acid; ionic strength; dissociation constant; Van't Hoff equation; Gibbs free energy change.

1.INTRODUCTION :

Indeed, the each solute substances having a specific solubility or dissociation into a given solvent, which is depends on various factors such as pressure, temperature, intermolecular forces, bonding and polarity of substances etc [1-3]. A slightly changing is appears due to solute-solvent interactions when by addition of small amount of solute into water like solvent, then it trying to dissolve in it and get ionizes with their ionic strength in respect of temperature [4-7]. Although, the dissociation of solute into solvent have earlier reported [8], but, it proved well by Nernst in 1891 with given partition law, $K = C_A/C_B$ [9]. Here, we described the aqueous dissociation behavior of solute benzoic acid (C_6H_5COOH) in NaCl (sodium chloride) medium at specific range of temperature. An electrical attraction in between the oppositely charged end of the solute and the solvent molecules results to form a solution. When ionic substance is placed in polar solvent which ionized to solute with furnishes of cations (+) and anions (-). The salt of NaCl is formed by the reaction of strong (HCl) acid and strong (NaOH) base, thus, it ionize easily in aqueous solvent with high solubility. Crystalline NaCl (pH 7; M.P. 801°C) is an electrolyte and it easily dissolves into water to give a solvated or hydrated Na^+ and Cl^- ions [3], on enthalpy (ΔH) change for Born-Haber process [10]. Here, the figure 1 (a and b) have shown the ionic and crystalline form of NaCl and benzoic acid.

(a)-



(b)-

Figure 1. The crystalline form of NaCl salt (a), and solute benzoic acid (C_6H_5COOH), (b).

In this article, we have reported the thermodynamically based study of Gibbs free energy in aqueous dissociation of benzoic acid at Kelvin temperature range in between of 288 K to 318 K. In series of aromatic acids the benzoic acid (C_6H_5COOH) is a colorless crystalline solid (M.P. 121-122°C) substance having a very poor solubility into cold water with pleasant smell and used in food additives [11,12]. In aqueous solutions, a weak electrolytic behavior has been showing by solute benzoic acid (C_6H_5COOH) with little molar solubility [13], where the carboxylic (COOH) group of that acid is being polarizes with producing a benzoate anion ($C_6H_5COO^-$) and hydrogen (H^+) or hydronium cation (H_3O^+). The general reaction of acid dissociation equilibrium is given below-

$HA\,(aq) + H_2O\,(l) \rightarrow A^-(aq) + H_3O^+(aq)$

These reaction equilibrium is expressed in equilibrium constant (Kc),then-

$Kc = [H_3O^+]\,[A^-] / [HA]$

This Kc is called the dissociation constant (Ka) of acid and with correlated [14]. The figure 2 is show the structure of benzoic acid (C_6H_5COOH) and its benzoate ion ($C_6H_5COO^-$).

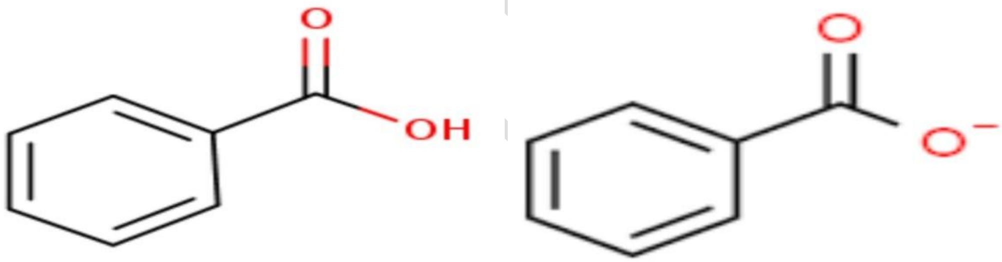


Figure 2. The structure of benzoic acid (C_6H_5COOH) and benzoate ($C_6H_5COO^-$) ion

2. MATERIALS AND METHOD :

Herein, experimental, the all required reagents and chemicals are being analytical graded which have been used further as without purification for study. Typically, the carbonate free a basic NaOH solution is prepared well by adopting of Vogel procedure [15]. This reagent graded solutions which are made of as NaCl stock solutions with ionic strength, NaOH, C_6H_5COOH (benzoic acid) and purified distilled water. By using of titration against standard NaOH basic solution the protolytic purity of benzoic acid are checked. Like an aqueous solvent the distilled water is using throughout the complete work. All the calibrated as well as volumetric glassware which of A class are used.

Firstly, in preparation of the all solutions we taking a dry cleaned six 250 ml stopper bottles and salt of benzoic acid. Firstly, weigh the benzoic acid as 1.0 gram and it placed in each of six dry cleaned bottles. Now, a 100 ml of sodium chloride (NaCl) solution we prepared in each bottle by using of volumetric flask (100 ml) of different as 0.00, 0.05, 0.10, 0.30, 0.40 and 0.50 M concentrations. Poured this prepared molar solutions in each benzoic acid containing bottles and vigorously shaking it and for 2 hours it put in a thermostat, at about 298 K. Now then with filtering to prevention of withdrawing small solids in pipette we are pipette out a 20 ml of solutions from each bottles. Then it discharged into another conical flask (250 ml) after removing the filtering. The NaCl concentrations in each of solutions with benzoic acid by applying titration method is determined against basic 0.05 M NaOH solution. The pH of each solutions have measured well by using of digital pH meter at given specific temperature in between that of 288 K - 298 K to 318 K ranges.

3. RESULTS AND DISCUSSION :

Indeed, by applying of many physico-chemical analysis we all are concerning the equilibrium studies for solubility and dissociation process of benzoic acid (C_6H_5COOH) into aqueous solutions from over the years. The addition of small amount solute or salts into water has shown an interaction in between solute and solvent. In aqueous the dimerization of crystalline benzoic acid and its carboxylic group is may polarize by formation of H-bonding with water molecule [16,17]. In this work, thermodynamically, at Kelvin temperature range in between 288 K to 318 K, the dissociation constant (*Ka)* of benzoic acid into aqueous solutions have been determined well by applying of titration method against standard basic solution of NaOH with different value of ionic strength of NaCl. The value of *Ka* (6.28×10^{-5}) of benzoic acid and the activity coefficient (γ) at indicated some ionic strength (I) of ions have been reported in table 1, where the ionic strength of a 0.120 M solution of benzoic acid that is also 0.05 M in NaCl concentrations. Although, the experimental data from table 2 is represented that, there six different ionic strengths are influenced at 298 K temperature for dissociation of benzoic acid in range of 0.00 to 0.50 M by adding NaCl. In observation, from volume of NaOH the solubility of that acid into aqueous and pH is inversely related with concentrations of NaCl. Notable, in titration the volume of benzoic acid (20 ml) have been used for each solutions with 0.05 M of basic NaOH. Here, the molar concentrations of NaCl is used to raising the ionic strength (I) of benzoic acid for each solutions and followed the measuring of pH value also for each particular solutions.

Table 1. The Activity coefficient (γ) of ions at different ionic strength (I)

S.N.	**Ions**	**0.001 M**	**0.005 M**	**0.01 M**	**0.05 M**	**0.1 M**
1.	Cl^-	0.964	0.925	0.899	0.805	0.755
2.	Na^+	0.964	0.928	0.902	0.820	0.775
3.	$C_6H_5COO^-$	0.965	0.929	0.907	0.835	0.800
4.	H_3O^+	0.967	0.933	0.914	0.860	0.830

Table 2. The ionic strength (I) of NaCl on dissociation constant (*Ka*) of benzoic acid into water at 298 K

S. N.	***V* of benzoic acid solution (in /ml)**	**Ionic strength of NaCl (in mol/l)**	***V* of (0.05 mol /l) of NaOH (in /ml)**	**pH**	**Molar solubility (α)**
1.	20 ml	0.00	10.61 ± 0.014	2.884 ± 0.005	0.0265
2.	20 ml	0.05	10.19 ± 0.010	2.832 ± 0.005	0.0255
3.	20 ml	0.10	9.92 ± 0.009	2.813 ± 0.003	0.0248
4.	20 ml	0.30	9.51 ± 0.012	2.789 ± 0.005	0.0238
5.	20 ml	0.40	9.09 ± 0.011	2.763 ± 0.003	0.0227
6.	20 ml	0.50	8.58 ± 0.011	2.747 ± 0.007	0.0215

At increasing temperature which causes a rise in the solubility and dissociation of solute, but not always rise for all substances due to continuous and discontinuous solubility with terms ‘γ’ for dissociated or un-dissociated ions of solute at infinite dilution of solutions. The mean activity coefficient (γ±) of ions is given by this expression as $Ka = Kc.\gamma^2\pm$ [18]. Literature survey reveals that an ionic strength of solute substances have dependent or effected by the physical properties of solutions including an electrolytic property [19], pressure [20], and temperature [21]. The solubility of benzoic acid into saturated aqueous solution is in least amount and followed the reaction equilibrium-

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

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

Thus, the equilibrium expression is as-

Ka (acid) = [conjugate base]$[H_3O^+]$ / [acid], and thus-

$Ka = [H_3O^+]\ [C_6H_5COO^-] / [C_6H_5COOH(aq)]$……..(1)

Where, the molar solubility (α) of benzoic acid is $[C_6H_5COOH(aq)]$ plus aqueous $[C_6H_5COO^-] = [H^+]$ or 10^{-pH}, and can be determined by using of standardized titration method against basic solution of NaOH. Hence,

$Ka = (10^{-pH})^2 / \alpha - 10^{-pH})$ ………………………………..(2)

Where, $\alpha = (V_{NaOH} \times M_{NaOH}) / V_{(Benzoic\ Acid)}$………..(3)

Here, the V_{NaOH}, $V_{(Benzoic\ Acid)}$ are the volume of sodium hydroxide and benzoic acid in litre^{-1}, and M_{NaOH} as the molarity of NaOH (mol^{-1} /litre), respectively.

Actually, at 298 K temperature, the estimated value of thermodynamically dissociation constant (Ka) for benzoic acid is may obtained by extrapolation to zero ionic strength [18]. From plot (as shown in figure 3), the observed value of Ka is about 4.176 at 298 K (room temperature) and it having similarity with other literature value [22-25]. Also, the same above described procedure is repeated for reported temperatures in between 289 K to 314 K, and measured the pH of each solution. At this temperature range the results average is show a high precision with given volume of NaOH and pH values for each NaCl concentration. Often, the molarity which used in thermodynamics way is not convenient, due to thermal expansion in the solutions volume because it depends on temperature. Thus, by resolving to this problem in correction of temperature to maintaining the same concentration of NaCl for applied all temperatures. These correction have involved the testing of decrease or increase in volume of solutions at each applied temperature in inside the volumetric flask which is relative to the standard volume of 100 ml flask at 293 K, then we prepared a solution NaCl upto the starting volume less or more than 100 ml in comparison to be exactly 100 ml, when a thermal equilibrium is attained with selected temperature inside the thermostat. By using temperature probe we see saw that about selected range of temperatures and the pH of each solution is measured by digital pH meter.

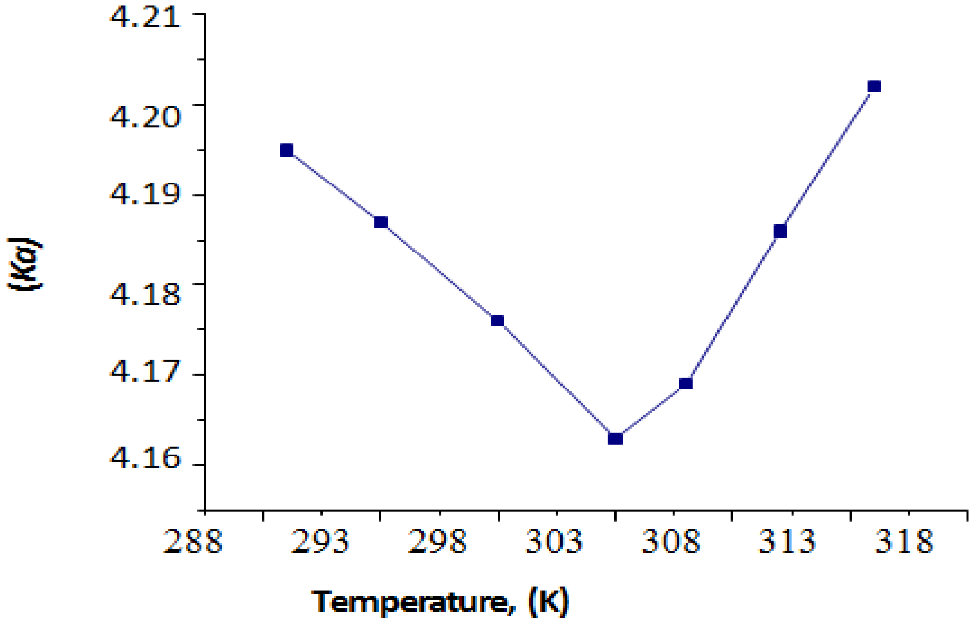


Figure 3. The plot of acid dissociation constant (*Ka*) of benzoic acid into water against Kelvin temperature (T) range

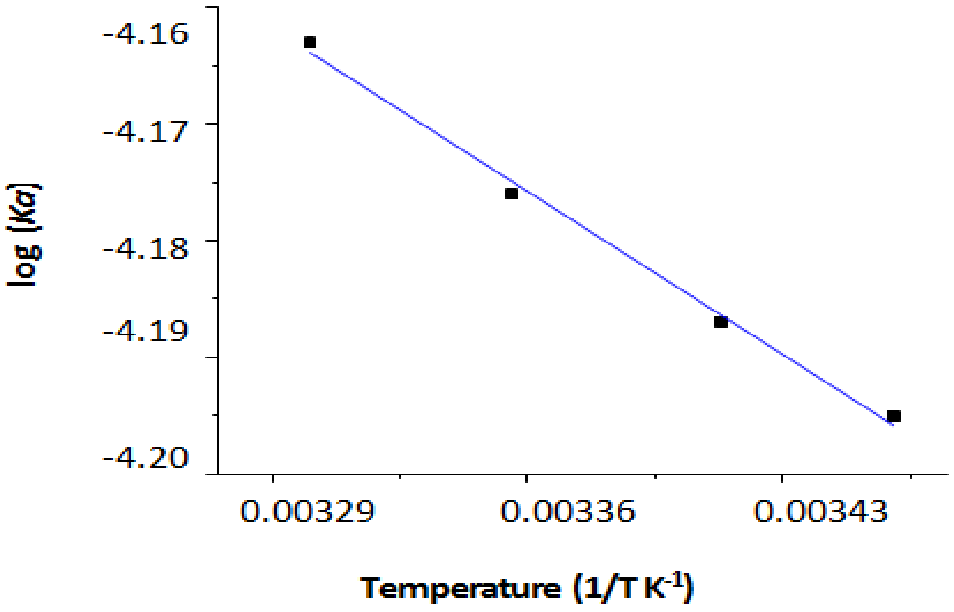


Figure 4. The plot of acid dissociation constant (*Ka*) against temperature (1/T K^{-1}) of benzoic acid into water

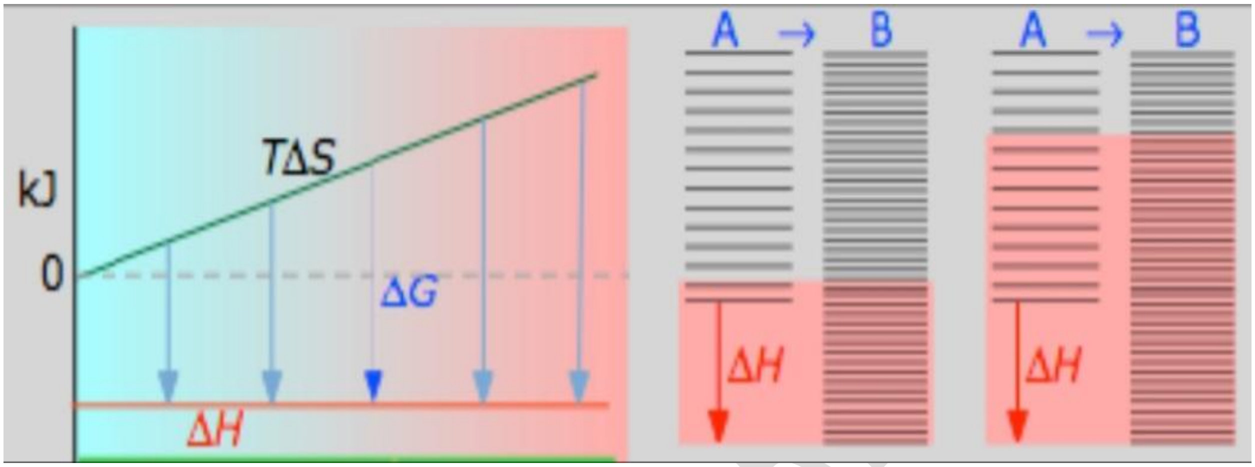


Figure 5. The Gibbs free energy (*G*) change diagram for *ΔG* < 0, at standard conditions of temperature, 298 K

From experimental data, the volume of NaOH which is used in titration and the pH value at used each temperature, the benzoic acid solubility into aqueous based is directly proportional to temperature and the dissociation capability of benzoic acid is not increases always as temperature increases. In graphically (figure 3), the dissociation constant (*Ka*) value are being inversely proportional with respect to temperature in between 289 K to 303 K and it is in contrast at higher temperature in between 303 K to 314 K it being directly proportional. This is reported that, there are no regular correlation in between temperature range and *Ka* of benzoic acid. Thus, in process of dissociation of benzoic acid into water the thermodynamic parameters have been reported at a standard condition. These thermodynamic parameters are being as in term of entropy (*S*), heat content or enthalpy (*H*) and Gibbs free energy (*G*) in respect to temperature and pressure. Although, there are no well described process of dissociation in thermodynamic study, but, at ordinary temperature (288 K to 303 K to 318 K) range the changing in value of both entropy (*ΔS*) and enthalpy (*ΔH*) is obtained by introducing a Van't Hoff equation (eq.4) in benzoic acid dissociation process [26].

$$log\,Ka = \frac{-\Delta H}{2.303\,R} 1/T + \frac{\Delta S}{R} \text{………………….} \ (4)$$

Here, thermodynamic Gibbs free energy equation is,

$\Delta G = \Delta H - T\Delta S$……….………………………..(5)

These equation (5) provides, how the components of ΔG is influence the magnitude of the equilibrium constant. Therefore, we can apply this equation at standard condition for the relationship in between ΔG° and K. Thus,

$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = - RT \ln K$ ……………………(6)

These equation (6) allow us to calculate the equilibrium constant for any reaction from the standard state free energy reaction. Here, from equation (5), the $\Delta H = \Delta E + P\Delta V$, then combining equation 5, in to equation 7,

$\Delta G = \Delta E + P\Delta V - T\Delta S$……………………………(7)

Also in term of work function (A) change, the $\Delta A = \Delta E - T\Delta S$, then

$\Delta G = \Delta A + P\Delta V$………………………………….(8)

All relations are summarized as in follows –

If, $\Delta G < 0$: The reaction (A → B) can spontaneously proceed to the right.

If, $\Delta G > 0$: The reaction (A → B) can spontaneously proceed to the left.

If, $\Delta G = 0$: The reaction is at equilibrium and the quantity of reactants and products (A → B), will not change.

In Van't Hoff equation (equation 4), the R is a molar gas constant having value to 8.314 J.K^{-1}.mol^{-1} with account of ΔH and ΔS, which are on temperature independent because of the small change in values of temperature in relatively. A data analysis of Ka in mathematically terms as log Ka to 1/T between 289 K to 314 K ranges temperature has illustrated in figure 4. The value of ΔG is depends almost entirely on the entropy change (ΔS) associated with the enthalpy (ΔH) of process at condition of temperature and pressure (figure 5). In finding of precious results for benzoic acid dissociation into aqueous we are applying Gibbs thermodynamic relation (5) at constant condition where its parameters value are being as ΔG = 12.507 kJ.mol^{-1}, ΔH = 3.823 kJ.mol^{-1} and ΔS = -29.14 kJ.mol^{-1}. By applying of equation -7 and -8 we can calculate the value of total energy (ΔE) change with work function (A) of the system for endothermic or exothermic reaction process at constant P and T. Thermodynamically, the benzoic acid dissociation into aqueous solvent is a process of endothermic with positive (+ve) energy changes which has lead to non-spontaneous process of dissociation for that acid. And, if the value is becoming a negative (-ve) for energy changing, then it means, the benzoic acid having a highly ordered state (entropy) attain into water after during its dissociation process.

The temperature change from 288 K to 298 K to 318 is effected to the acidic strength of benzoic acid which lead to an inductive effect inside the benzoic acid molecules with movement of charge in continual state through acid atoms resulting the bond polarization [27]. At above temperature about 303 K, the benzoic acid dissociation into aqueous solvents is show different behavior and the molecules of acid show less acidic nature because of electron releasing group effect which decreases inside the acid molecules on acidic hydrogen [28]. As increases temperature, the dissociation capability of benzoic acid is be found to decreases with reducing of that *Ka* value. In these temperature range the process of dissociation is may be an exothermic with compatibility to principle of Le Chatelier [29]. At higher pressure (in bar) and temperature (K) the thermodynamic parameters are retrieved for dissociation of any solute or acid with infinity dilution [30,31], with conductance of ions like Na^+, Cl^-, H^+ and OH^- [32,33]. Though, in process of benzoic acid dissociation we can apply a Debye-Huckel limiting law in finding or improving of results with more accuracy. Also, the absorption spectra of benzoic acid in aqueous solution at different pH in presence of salt and others spectroscopic method have proven it well [34,35].

4. CONCLUSION :

In conclusion, we have reported a thermodynamically study of a Gibbs free energy change (ΔG) in aqueous dissociation of benzoic acid at Kelvin temperature range in between of 288 K to 318 K. In thermodynamically, at this different Kelvin temperatures the dissociation constant (*Ka)* of benzoic acid into aqueous solvents have determined by applying of titration method against standard basic solution of NaOH with different value of NaCl concentrations. In observation, the value of *Ka* is being inversely proportional with respect to temperature in between 289 K to 303 K and it is in contrast at higher temperature in between 303 K to 314 K it being directly proportional. Graphically, the plot value of *Ka* for benzoic acid is about 4.176 at 298 K (room temperature). This is reported that, there are no regular correlation in between temperature and *Ka* of that acid. Thus, in finding of good results for acid dissociation into water the applying a Gibbs free energy change relationship ($\Delta G = \Delta H - T\Delta S$) for reaction (endothermic or exothermic) process at constant condition. Here, the thermodynamic parameters value (in $kJ.mol^{-1}$) are being as ΔG = 12.507, ΔH = 3.823 and ΔS = -29.14, but, at 298 K it is show that, the acid dissociation into aqueous is an endothermic process and non-spontaneous with ordered entropy (ΔS).

REFERENCES :

1. Cotton FA, Wilkinson G, Murillo CA, Bochmann M. Advanced Inorganic Chemistry, 6th Edition, John Welly and Sons, Inc; 1999.

2. Mishra SP. Chemical Science Review and Letters. 2021;10(38):163-167. Mishra SP. Chemical Sci. Int. J. 2021;30(3):40-45.
3. Finar IL. Organic Chemistry, 6th Edition, Dorling Kindersley (India) Pvt. Ltd. 2007.
4. Sergeeva VF. Russian Chemical Reviews. 1965;34:309-318.

5. Kilpatrick M, Eanes RD, Morse JG. J. Am. Chem. Soc. 1953;75:588-589.

6. Kettler RM, Wesolowski DJ, Palmer DA. J. Solution Chem. 1995;24(4):385-407.

7. Mishra SP. Int. Res. J. Pure & Appl. Chem. 2021;22(6):47-52. Mishra SP. Chemical Sci. Int. J. 2022;31(1):8-14.

8. Berthelot M, Jungfleisch E. Ann. Chim. Phys.1872;26:396-407.

9. Nernst W. Z Phys. Chem. 1891;8:110-139.

10. Treptow RS. Chem. J. Educ. 1997;74(8):919-923.

11. Ruoyu L, Zeitler JA, Tomerini D, Parrott EPJ, Gladden LF, Day GM. Phys. Chem. Chem. Phys. 2010;12(20):5329-5340.

12. Ramesh H, Huda N, Hossain M, Bhuyan AK. ACS Food Sci. Technol.2021;1(11):2162-2173.

13. Bolton PD, Fleming KA, Hall FM. J. Am. Chem. Soc. 1972;94(3):1033-1034.

14. Huh Y, Lee JG, Mc Phail DC, Kim K. J. Solution Chem. 1993;22:651-661.

15. Vogel A. Text book of Quantitative Chemical Analysis, 5th Edition, Longman, Harlow; 1989.

16. Thomas LH, Jones Andrew OF, Kallay AA, Mclntyre GJ, Wilson CC. Cryst. Growth Design. 2016;16(4):2112-2122.

17. Remmers K, Leo Meerts W, Ozier I. J. Chem. Phys. 2000;112(24):10890-10894.

18. Khouri SJ. American J. Analytical Chem. 2015;6:429-436.

19. Steigman J, Sussman D. J. Am. Chem. Soc. 1967;89:6400-6406.

20. Read AJ. J. Solution Chem. 1981;10:437-450.

21. Ellis AJ. J. Chem. Soc.1963;2299-2310.

22. Matsui T, Ko HC, Hepler LG. Can. J. Chem. 1974;52:2906-2911.

23. Bosch E, Bou P, Allemann H, Roses M. Analytical Chem. 1996;68:3651-3657.

24. Sarmini K, Kenndler E. J. Chromatography A. 1998;811:201-209.

25. Cleveland JA, Benko MH Jr., Gluck SJ, Walbroehl YM. J. Chromatography A. 1993;652:301-308.

26. Lima EC, H-Bandegharaei A, M-Piraján JC, Anastopoulos I. Journal of Molecular Liquids. 2019;273:425-434.

27. Solomons GT, Fryhle CB. Organic Chemistry, 10th Edition, John Wiley & Sons, Hoboken; 2011.

28. Strong LE, Brummel CL, Ryther R, Radford JR, Pethyridge AD. J. Solution Chem. 1988;17:1145-1167.

29. Atkins P, de Paula J. Physical Chemistry, 9th Edition, W. H. Freeman and Company, New Yark; 2010.

30. Mesmer RE, Marshall WL, Palmer DA, Simonson JM, Holmes HF. J. Solution Chem. 1988;17:699-718.

31. Fernandez Le-V P, Hepler LG. J. Phys. Chem. 1959;63(1):110-112.

32. Baes CF, Jr, Mesmer RE. The Hydrolysis of Cations, John Wiley, New York; 1976.

33. Stanczyk M, Borun A, Jozwiak M. J. Mol. Liq. 2019;278:247-252.

34. Karimova NV, Luo M, Grassian VH, Gerber RB. Phys. Chem. Chem. Phys. 2020;22(9):5046-5056.

35. Berzins A, Semjonova A, Actins A, Salvalaglio M. Cryst. Growth Des. 2021;21(9):4823-4836.