Journal Homepage: - www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)

Article DOI: 10.21474/IJAR01/16006
DOI URL: http://dx.doi.org/10.21474/IJAR01/16006

ISSN NO. 2320-5407

RESEARCH ARTICLE

THERMODYNAMIC BASED AQUEOUS SOLVATION AND DISSOCIATION OF BENZOIC ACID

Shiv Prakash Mishra[1] and R.P. Singh[2]

1. Faculty of Science (Chemistry), Dr. Rammanohar Lohia Avadh University, Ayodhya-224001, (U.P.), India.
2. Professor in Chemistry, Kamla Nehru Institute of Physical & Social Sciences, Sultanpur-228118, (U.P.), India.

……………………………………………………………………………………………………....

Manuscript Info

……………………….

Manuscript History
Received: 10 November 2022
Final Accepted: 14 December 2022
Published: January 2023

Key words:-
Benzoic Acid, Ionic Strength, Salvation, Dissociation Constant, Thermodynamic Parameters

Abstract

………………………………………………………………….

In article, we have reported a thermodynamic based study of aqueous solvation of benzoic acid (C_6H_5COOH) at 288 to 318 Kelvin temperature. At this temperature range the dissociation constant (*Ka)* of benzoic acid into aqueous solvent has been determined by applying of titration method against standard basic solution of NaOH at different ionic strength of NaCl. Although, in observation, the value of *Ka* is being inversely proportional in respect of temperature in between 289 K to 303 K, and at higher temperature in between 303 K to 314 K, it being directly proportional. This reports that, there are no regular correlation in between temperature and *Ka* of that acid. Graphically, the plot has shown the value of *Ka* of benzoic acid is being 4.176 at 298 K temperature. In finding of precious results for benzoic acid solvation and its dissociation into water the applying Van't Hoff equation with Gibbs free energy change relationship ($\Delta G = \Delta H - T\Delta S$) for reaction (endothermic or exothermic) process at standard condition of thermodynamic parameters as in terms of enthalpy (H) and entropy (S). Where, 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.

……………………………………………………………………………………………………....

Introduction:-

Notably, the each solute substances having a specific solvation and dissociation properties 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 distribution of solute into solvent have well reported by W. Nernst (1891) with given a partition law, $K = C_A/C_B$ [8]. Here, we described the aqueous salvation behaviour of solute benzoic acid (C_6H_5COOH) in NaCl 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, on enthalpy (ΔH) change for Born-Haber process [9]. Here, the Figure 1 has shown the monoclinic crystalline form of solute benzoic acid.

Corresponding Author:- Shiv Prakash Mishra
Address:- Faculty of Science (Chemistry), Dr. Rammanohar Lohia Avadh University, Ayodhya-224001, (U.P.), India.

Figure 1:- The crystalline form of solute benzoic acid (C_6H_5COOH).

In this article, we have reported the thermodynamic based study of aqueous solvation and 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. 395 K) substance having a very poor solubility into cold water with pleasant smell and used in food additives [10, 11]. In derivatives of benzoic acid the ortho-hydroxybenzoic acid (salicylic acid) have solubility in respective solvents with greater importancy for medicinal purposes as anti-bacterial, anti-inflammatory and in skin diseases well [12]. In aqueous, 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 as in dissociation constant (*Kc*) then-

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

This *Kc* is called the equilibrium or apparent dissociation constant of acid at given temperature, and, it correlated with their thermodynamic dissociation constant (*Ka*) of acid at infinite dilution at a given temperature [14]. Although, the overall thermodynamic dissociation constant (*pKa*) is a negative logarithmic scale of *Ka*, (as $pKa = -\mathrm{Log}_{10}\, Ka$) with respect of temperature [15]. Figure 2 has shown the chemical structure of benzoic acid (C_6H_5COOH) and its derivative of ortho-hydroxybenzoic acid ($C_6H_4(OH)COOH$).

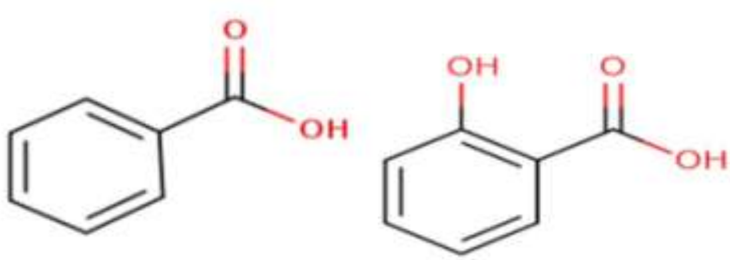


Figure 2:- The structure of benzoic acid (C_6H_5COOH) and ortho-hydroxybenzoic acid (Salicylic acid) ($C_6H_4(OH)COOH$).

Experimental:-

In experimental, the all required reagents and chemicals are being laboratory based with 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 [16]. 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. In aqueous solvent the distilled water is prepared which using throughout the complete work. All the calibrated as well as volumetric glassware of A class are used. The solute benzoic acid is of Research Lab Fine Chemical Industries, Mumbai, India. By using of titration method against standard NaOH basic solution the protolytic purity of benzoic acid are checked. First of all, 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 NaCl solution 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 concentrations of NaCl for each of solutions with benzoic acid is determined against basic 0.05 M NaOH solution by applying titration method. 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 range.

Results and Discussion:-

Athough, by applying of many physico-chemical analysis we all are concerning the equilibrium studies for solvation 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. Chemically, in benzoic acid the carboxyl group (-COOH) is attached to a benzene ring. In aqueous the dimerization of crystalline benzoic acid and its carboxylic group is may polarize by formation of H-bonding with water molecule [17, 18]. 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. At 293 K temperature the aqueous solubility of benzoic acid as well as some other common solute in g/100 ml of water are reported in Table 1. 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 also been reported in Table 2, 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 3 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 aqueous solubility of benzoic acid and some solute at 293 K.

S.N.	Name Solute	Chemical Formula	Molar Mass (in g/mol)	Solubility (*S*), (in g/100 ml)
1.	Common salt	NaCl	58.44	36
2.	Table sugar	$C_{12}H_{22}O_{11}$	342.30	200
3.	Benzoic Acid	C_6H_5COOH	122.12	0.30
4.	Salicylic acid	HOC_6H_4COOH	138.121	0.22
5.	Aspirin	$CH_3COOC_6H_4COOH$	180.158	0.33

Table 2:- The activity coefficient (γ) of some ions at different ionic strength (I).

S.N.	0.001 M	0.005 M	0.01 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 3:- The molar solubility (α) of benzoic acid at different ionic strength (I) of NaCl 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

Although, at increasing temperature which causes a rise in the solubility and dissociation of solute, is 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 $Ka = Kc.\gamma^2\pm$ [19]. Literature survey reveals that an ionic strength of solute substances have dependent or effected by the physical properties of solutions including an electrolytic property [20], pressure [21], and temperature [22]. 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)

The aqueous salvation of benzoic acid solution at described temperatures (288-318 K) is may calculated by using equation (2),

Solubility (S) = W × 1000 / d × M gram mol / 1000 gram solvent ….. (2)

Where, W is the weight of one ml of benzene- water solution, M is the molecular weight of benzoic acid and the d as density of solvent (water) used. In mathematically terms, however, the reported three quantities such as *Ka, Kc* and I are linked by the relation,

$\log Ka + 2B\sqrt{I} = \log Kc$............................... (3)

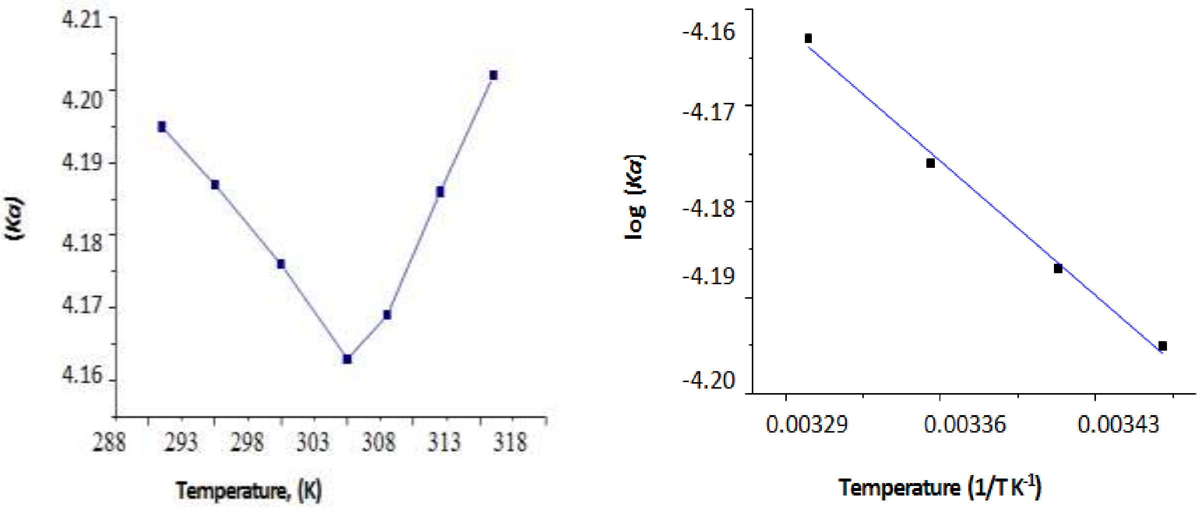
Here, the B is a quantity that depend on physical properties of solutions. In aqueous solution, the molar solubility (α) of benzoic acid is [$C_6H_5COOH(aq)$] plus aqueous [$C_6H_5COO^-$] = [H^+] or 10^{-pH}, and can be determined by using of standardized titration method against basic solution of NaOH. Hence,

$Ka = (10^{-pH})^2 / \alpha - 10^{-pH})$ …...............................(4)

Where, $\alpha = (V_{NaOH} \times M_{NaOH}) / V_{(Benzoic\ Acid)}$…….(5)

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.

Indeed, at 298 K temperature, the estimated value of thermodynamically dissociation constant (*Ka*) for benzoic acid is may obtained by extrapolation to zero ionic strength. From plot as shown in Figure 3 (a), the observed value of *Ka* is about 4.176 at 298 K (room temperature) and it having similarity with other literature value [23-26]. 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.



(a) **(b)**

Figure 3:- The plot of acid dissociation constant (*Ka*) of (a)- benzoic acid into water against Kelvin temperatures (T), (b)- against temperature ($1/T\ K^{-1}$) of benzoic acid in water.

From the 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, (a), 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 (6) in benzoic acid dissociation process [27].

$$log\,Ka = \frac{-\Delta H}{2.303\ R} 1/T + \frac{\Delta S}{R} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

Here, thermodynamic Gibbs free energy equation is,

$$\Delta G = \Delta H - T\Delta S \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

These equation (7) 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,

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = - RT\ ln\ K \quad \ldots\ldots\ldots\ldots\ldots (8)$$

$$\text{Or, } \Delta G^{\circ} = - 2.303\ RT\ log\ K \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

Here, equation (8) allow us to calculate the equilibrium constant for any reaction from the standard state free energy reaction. And, from equation (7), the $\Delta H = \Delta E + P\Delta V$, then combining equation 7, in to equation 10,

$$\Delta G = \Delta E + P\Delta V - T\Delta S \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

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

$\Delta G = \Delta A + P\Delta V$……………….……………….(11)

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 6), 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 3 (b). 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. In finding of precious results for benzoic acid salvation into aqueous we are applying Gibbs thermodynamic relation (7) 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 $kJ.mol^{-1}$. From using of equation 9 we can calculated the salvation free energy change of benzoic acid. By applying of equation 10 and 11 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 [28]. 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 [29]. 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 [19]. 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].

Conclusion:-

In conclusion, we have reported a thermodynamically base study for aqueous solvation and dissociation of benzoic acid (C_6H_5COOH) at 288 to 318 Kelvin temperature range. Thermodynamically, at this different Kelvin temperature range the dissociation constant (*Ka)* of benzoic acid into aqueous solvent are determined by applying of titration method against standard basic solution of NaOH with different NaCl concentrations. In observation, the value of *Ka* is being inversely proportional with respect to temperature in between 289 K to 303 K, but in contrast at higher temperature because it is just reverse in between 303 K to 314 K, as it being directly proportional. Graphically, the plot value of *Ka* for benzoic acid is about 4.176 at 298 K (room temperature). These reports that, there are no regular correlation in between temperature and *Ka* of that acid. Thus, in finding of results for acid dissociation into water the applying a Van't Hoff equation and Gibbs free energy change relationship ($\Delta G = \Delta H - T\Delta S$) for endothermic or exothermic reaction 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).

Acknowledgements:-

This work have been supported by various respective Journals and books as well. The author thanks to gratefully acknowledge support of Faculty of Science and Department of Physics and Electronics, Dr. Rammanohar Lohia

Avadh University, Ayodhya-224001, (UP), India, for providing help me in useful discussion, suggestion and providing of necessary facilities to finding the valuable data.

References:-

[1] Finar IL. Organic Chemistry, 6th Edition, Dorling Kindersley (India) Pvt. Ltd. 2007.

[2] Cotton FA, Wilkinson G, Murillo CA, Bochmann M. Advanced Inorganic Chemistry, 6th Edition, John Wiley and Sons, Inc. 1999.

[3] Mishra SP. Titrimetric study of solubility of benzoic acid and their partition in water and benzene solvents. Chemical Sci. Int. J. 2021;30(3):40-45. Mishra SP. Concentration effect of sodium chloride salt on benzoic acid solubility and dissocation into water at 298 K temperature. Int. Res. J. Pure & Appl. Chem. 2021;22(6):47-52.

[4] Kilpatrick M, Eanes RD, Morse JG. The dissociation constants of acids in salt solutions. IV. Cyclohexanecarboxylic acid. Journal of the American Chemical Society. 1953;75(3):588-9.

[5] Kettler RM, Wesolowski DJ, Palmer DA. Dissociation quotient of benzoic acid in aqueous sodium chloride media to 250 C. Journal of solution chemistry. 1995;24(4):385-407.

[6] Sergeeva VF. Salting-out and salting-in of non-electrolytes. Russian Chemical Reviews. 1965;34:309-317.

[7] Mishra SP. Introducing of thermodynamic Van't Hoff equation in process of dissociation of benzoic acid at ordinary temperature range. Chemical Sci. Int. J. 2022;31(1):8-14. Mishra SP, Singh RP. Gibbs free energy change in aqueous dissociation of benzoic acid at temperature K : A thermodynamic study. Chemical Science Int. J. 2022;31(2):44-52.

[8] Nernst W. Distribution of a substance between two solvents and between solvent and vapor. Z. phys. Chem. 1891;8:110-39.

[9] Treptow RS. Determination of ΔH for reactions of the born-haber cycle. Journal of chemical education. 1997;74(8):919.

[10] Ramesh H, Huda N, Hossain M, Bhuyan AK. Food Additives Benzoic Acid and its Methyl and Propyl Parahydroxy Derivatives Aggregate Proteins. ACS Food Science & Technology. 2021;1(11):2162-73.

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

[12] Young Jay A. Salicylic acid. J. Chem. Educ. 2008;85(12):1617. Fakhree M A A, Ahmadian S, P-Azar V, Jr. Acree W E, and Jouyban A. Solubility of 2-hydroxybenzoic acid in water, 1-, 2-propanol, and 2-propanone at (298.2 to 338.2) K and their aqueous binary mixtures at 298.2 K. J. Chem. Eng. Data. 2012;57(11):3303-07.

[13] Bolton PD, Fleming KA, Hall FM. Linear free energy enthalpy entropy relation for the ionization of benzoic acids. Journal of the American Chemical Society. 1972;94(3):1033-4.

[14] Huh Y, Lee JG, McPhail DC, Kim K. Measurement of pH at elevated temperatures using the optical indicator acridine. Journal of solution chemistry. 1993;22(7):651-61.

[15] Wang Z, Deng H, Li X, Ji P, Cheng J-P. Standard and absolute p*K*a scales of substituted benzoic acids in room temperature ionic liquids. J. Org. Chem. 2013;78(24):12487-493.

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

[17] Remmers K, Meerts WL, Ozier I. Proton tunneling in the benzoic acid dimer studied by high resolution ultraviolet spectroscopy. The Journal of Chemical Physics. 2000;112(24):10890-4.

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

[19] Khouri SJ. Titrimetric study of the solubility and dissociation of benzoic acid in water: effect of ionic strength and temperature. American J. Analytical Chem. 2015;6:429-436.

[20] Steigman J, Sussman D. Acid-base reactions in concentrated aqueous quaternary ammonium salt solutions. I. Strong acids and bases, carboxylic acids, amines, and phenol. Journal of the American Chemical Society. 1967;89(25):6400-6.

[21] Read AJ. Ionization constants of benzoic acid from 25 to 250 °C and to 2000 bar. J. Solution Chem. 1981;10:437-450.

[22] Ellis AJ. The ionization of acetic, propionic, n-butyric, and benzoic acid in water, from conductance measurements up to 225°. Journal of the Chemical Society (Resumed). 1963:2299-310.

[23] Bosch E, Bou P, Allemann H, Roses M. Retention of ionizable compounds on HPLC. pH scale in methanol-water and the pK and pH values of buffers. . Analytical Chem. 1996;68(20):3651-3657.

[24] Matsui T, Ko HC, Hepler LG. Thermodynamics of ionization of benzoic acid and substituted benzoic acids in relation to the Hammett equation. Canadian Journal of Chemistry. 1974;52(16):2906-11.

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

[26] Sarmini K, Kenndler E. Capillary zone electrophoresis in mixed aqueous–organic media: effect of organic solvents on actual ionic mobilities, acidity constants and separation selectivity of substituted aromatic acids.: I. Methanol. Journal of Chromatography A. 1998;806(2):325-35.
[27] Lima EC, Hosseini-Bandegharaei A, Moreno-Piraján JC, Anastopoulos I. A critical review of the estimation of the thermodynamic parameters on adsorption equilibria. Wrong use of equilibrium constant in the Van't Hoof equation for calculation of thermodynamic parameters of adsorption. Journal of molecular liquids. 2019;273:425-34.
[28] Solomons GT, Fryhle CB. Organic Chemistry, 10th Edition, John Wiley & Sons, Hoboken; 2011.
[29] Strong LE, Brummel CL, Ryther R, Radford JR, Pethyridge AD. J. Solution Chem. 1988;17:1145-1167.
[30] Fernandez LP, Hepler LG. Thermodynamics of Aqueous Benzoic Acid and the Entropy of Aqueous Benzoate Ion. The Journal of Physical Chemistry. 1959;63(1):110-2.
[31] Mesmer RE, Marshall WL, Palmer DA, Simonson JM, Holmes HF. Thermodynamics of aqueous association and ionization reactions at high temperatures and pressures. Journal of Solution Chemistry. 1988;17(8):699-718.
[32] Stańczyk M, Boruń A, Jóźwiak M. Conductance studies of aqueous solutions of sodium salts of selected benzoic acid derivatives at temperatures from (288.15 to 318.15) K. Journal of Molecular Liquids. 2019;278:247-52.
[33] Baes CF, Jr, Mesmer RE. The Hydrolysis of Cations, John Wiley, New York; 1976.
[34] Berzins A, Semjonova A, Actins A, Salvalaglio M. Speciation of Substituted Benzoic Acids in Solution: Evaluation of Spectroscopic and Computational Methods for the Identification of Associates and their Role in Crystallization. Crystal Growth & Design. 2021;21(9):4823-36.
[35] Karimova NV, Luo M, Grassian VH, Gerber RB. Absorption spectra of benzoic acid in water at different pH and in the presence of salts: Insights from the integration of experimental data and theoretical cluster models. Physical Chemistry Chemical Physics. 2020;22(9):5046-56.