

**DETERMINATION OF EQUILIBRIUM CONSTANT
OF ASCORBIC ACID AND BENZOIC ACID AT DIFFERENT
TEMPERATURE AND IN AQUEOUS AND
NON- AQUEOUS MEDIA**

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ABSTRACT

Dissociation constant studies of ascorbic acid and benzoic acid has been carried out potentiometrically at various temperature from 25 to 50°C and in 10, 20, 30 and 40 percent dioxane-water solvent system at 25°C. Effect of temperature and solvent concentration on pKa values has been observed. The resolution of acid strength in dioxane-water relative to that in water has been determined for both compounds by plotting pKa values vs percent composition of solvent. The results show greater resolution in non-aqueous media as compare to aqueous media. Data obtained is analyzed by Computer program written in GW-Basic for calculation of pKa values for monobasic acid.

Introduction

Ascorbic acid occurs naturally in fruits and vegetables, however the concentration vary greatly in different canned juices. In some fruit juices it is purposely aid for attracting consumers and to act as antioxidant to increase shelf life of commercial product (Sing et al., 1985). Severe ascorbic acid deficiency produces Scurvy. The pathalogic signs of this deficiency are almost entirely confined to supporting tissues of mesenchymal origin (bone, dentine, cartilage and connective tissue).

Scurvy is characterized by failure in the formation and maintenance of intercellular materials, which is turn causes typical symptoms, such as hemorrhages, loosening of teeth, poor wound healing and the easy fracturability of the bones (Harlod, 1971). Owing to the wide use and importance of ascorbic acid in fruit vegetable and drug it is necessary to know the dissociation constant of this acid.

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Benzoic acid is a simplest carboxylic acid of aromatic series it is used as food preservative, because it inhibits the growth of yeasts and moulds. Also used for this purpose in the form of sodium salt, which is highly water soluble.

There are different methods (Albert et al., 1984; Cooksen, 1974; McBryde, 1974; Ramettee, 1967) by which dissociation constant of weak acids and bases can be determined. The potentiometric methods are widely used since they are fast and easy to study ionic equilibria in aqueous and non-aqueous solvents, while other methods such as spectrophotometric and conductometric are laborious and time consuming but they are very accurate (McBryde, 1974; Ramttee, 1967; Serjeant, 1984).

The ionization constant describe the proportion of different ionic species in which the substance is divided at different pH. The ionic species differ in physical and biological properties as well (Meloun et al., 1988).

The survey of literature shows that the ionization constant data in aqueous and non-aqueous solvents at different temperatures are not frequently available (Sing et al., 1985, Meloun et al., 1988; Pappastasiou, 1989). The pKa values are temperature and solvent concentration dependent therefore these data re very important in pharmaceutical industries, in spectroscopy and in biology (Sing et al., 1985; Meloun et al, 1988; Guillen et al, 1988; Barsoum et al., 1987).

The technique of potentiometric method for the determination of pKa values, has been improved to obtain better and accurate results as compared to reported pKa values in the literature. Further refinement to get better result was achieved through computer program which was used for analyzing the experimental data without any approximation. The program has been written to work on IBM PC XT/AT or compatible computers.

Theory:

Any monobasic acid dissociation as follows



$$K_a = [\text{H}^+][\text{A}^-] / [\text{HA}] \quad (2)$$

$$\text{p}K_a = \text{pH} + \log. \{[\text{HA}] / [\text{A}^-]\} \quad (3)$$

When titrating an acid with base, electrical neutrality gives

$$[\text{A}^-] + [\text{OH}^-] = [\text{Na}^+] + [\text{H}^+] \quad (4)$$

$$[\text{A}^-] = [\text{NaOH}] - [\text{OH}^-] + [\text{H}^+] \quad (5)$$

If C_a is total ion concentration of acid taken then

$$C_a = [A^-] + [HA] \quad (6)$$

$$[HA] = [C_a] - [A^-] \quad (7)$$

Substituting the value of $[A^-]$ in Eq. (7), we get

$$[HA] = [C_a] - [NaOH] + [OH^-] - [H^+] \quad (8)$$

Eq. (3), Eq.(5) and Eq.(8) have been used to calculate pK_a using no approximation.

Experimental

The double quartzed and degassed water was used for the preparation of all solutions. The chemical reagents used were of analytical grade and were used without further purification. Stock solutions of 0.1 M sodium hydroxide in water and in 10, 20, 30 and 40 percent dioxane-water, 0.01 M ascorbic acid and 0.0197 M benzoic acid were prepared. Fresh and distilled dioxane was used in preparation of solutions. All sodium hydroxide solutions prior to use were standardized with primary standard by potentiometric method. The PHILIPS PW 4920 digital pH-meter was coupled with Ingold combined glass and Ag/AgCl saturated with potassium chloride reference electrode, was used. The glass electrode was calibrated against standard buffers of 0.05 M sodium phthalate ($pH\ 25^\circ C = 4.00$) and 0.01M sodium tetra borate ($pH\ 25^\circ C = 10.012$). All measurements of sample solution were performed in double walled glass cell of which temperature was maintained constant by circulating water from JULABO thermostated bath accurate to $\pm 0.01^\circ$. The sample was kept inert by bubbling a purified and dried nitrogen gas and mixed by stirring with magnetic stirrer. For dispensing titrant the Mettler DV-210 burette readable to 0.01 ml was used.

The potentiometric measurements were performed by titrating 50 ml of sample in cell at 20, 25, 30, 35, 40, 45 and $50^\circ C$ with sodium hydroxide prepared in water in 10, 20, 30, 40 percent dioxane- *water* solvent at $25^\circ C$.

Results and Discussion

The thermodynamic pK_a values of ascorbic and benzoic acids were calculated from the corresponding titration of 50 ml of 0.01 M ascorbic acid with 0.1M sodium hydroxide. The pK_a value were calculated by means of computer program in GW-Basic for monobasic acids. The experimental data and computer out put is presented in Table 1.

Results summarize in Table 2 shows the effect of temperature on pKa values of ascorbic acid. Fig.1 further shows that as temperature increases from 25 to 50°C then pKa values of ascorbic acid decreases from 4.159 to 3.550 and total decrease is 0.690 unit and parabolic curve is seen. Value obtained at 25°C is closed to the reported value (Sing et al., 1985).

Table 3 and Fig.2 shows that as temperature increases from 25 to 50°C there is no regular decrease in pKa values of benzoic acid. As temperature increases from 20 to 30°C then pKa values decrease while further increase in temperature upto 50°C again increase the pKa values. Effect of solvent concentration on pKa value for both acids also investigated. Mixture of water and organic solvents particularly dioxane in popular media for studying acids behaviour (Sergeant et al., 1984). In present case we used dioxane as non-aqueous solvent. The influence of composition of dioxane on dissociation equilibria was investigated by plotting pKa vs percent composition.

Fig.3 shows that as percent composition of solvent increases from 10 to 40 then pKa values of ascorbic acid increase from 4.235 to 4.133 and total increase is 0.898 unit.

Fig. 4 shows that as percent composition of dioxane-water increases from 10 to 40 then pKa values of benzoic acid increase from 4.57 to 5.16 and total increase 0.59 unit.

Effect of composition of solvent on pKa values shows the effect of dielectric constant. The dielectric constant (E) of a solvent expresses its effect on the electrostatic force between ions. The work of separation of ions will vary inversely with dielectric constant of the solvents. Results shows greater resolution in non-aqueous media as compare to aqueous media.

The change in thermodynamic parameters i.e. Gibb's free energy (AG), ethalpy (OH) and entropy (AS) can be found from the variation of its equilibrium constant with temperature.

Fig. 5 shows the effect of temperature on AG values for ascorbic acids while Fig.6 shows the effect of temperature for benzoic acid.

It is concluded that both temperature and solvent nature effect on pK. values.

Table 1

Substance = Ascorbic Acid
 Molecular weight = 176.13
 .0881 G Dissolved in 50 ml of water
 Concentration of acid = CS = 1.000397E-02 M
 Concentration of alkalie = CA = .1 M
 Temperature = 25 Degree Celcius

Volume	pH	HA	A	Log (HA/A)	% Ion	pK _a M	pK _a T	Dalta
1.80	3.95	0.0061	0.0036	0.000	0.000	0.000	0.000	0.000
2.00	4.01	0.0057	0.0039	0.158	39.359	4.168	4.198	0.030
2.20	4.07	0.0053	0.0043	0.089	43.121	4.159	4.190	0.031
2.40	4.14	0.0049	0.0047	0.022	46.904	4.162	4.194	0.032
2.60	4.20	0.0045	0.0050	-0.046	50.743	4.154	4.187	0.033
2.80	4.28	0.0041	0.0054	-0.114	54.595	4.166	4.200	0.034
3.00	4.35	0.0037	0.0057	-0.184	58.505	4.166	4.201	0.035
3.20	4.41	0.0033	0.0061	-0.257	62.466	4.153	4.189	0.036
3.40	4.48	0.0030	0.0064	-0.334	66.460	4.146	4.183	0.037
3.60	4.57	0.0026	0.0067	-0.416	70.483	4.154	4.192	0.038
3.80	4.66	0.0022	0.0071	-0.506	74.556	4.154	4.193	0.039
4.00	4.76	0.0018	0.0074	-0.606	78.672	4.154	4.193	0.039
4.20	4.89	0.0015	0.0078	-0.724	82.829	4.166	4.207	0.040
4.40	5.03	0.0011	0.0081	-0.868	87.039	4.162	4.203	0.041
4.60	5.22	0.0007	0.0084	-1.062	91.296	4.158	4.199	0.042
4.80	5.44	0.0004	0.0088	0.000	0.000	0.000	0.000	0.000

Average of pK^M = 4.159 ± 0.006

Average of pK^T = 4.195 ± 0.006

Gibb's free energy of pK^T = 5.722 KCal/Mole

Table 2: Benzoic Acid

S. No.	Temp.	pK_a^{M}	pK_a^{T}	Rep* pK_a	$-\frac{d(\text{pK}_a)}{dt}$	$\Delta^\circ\text{G}$ k cal/ mole	ΔH Cal/ mol	ΔS Cal/ mol/k
1.	20	4.170 ± 0.004	4.202 ± 0.007	4.206	0.011	5.636	-1496.26	
2.	25	4.153 ± 0.006	4.184 ± 0.01	4.204	0.011	5.708	-1546.33	-24.32
3.	30	4.111 ± 0.004	4.143 ± 0.006	4.203	0.010	5.746	-1629.13	
4.	35	4.167 ± 0.004	4.199 0.009	4.207	0.010	5.920	-1547.05	
5.	40	4.210 ± 0.007	4.242 ± 0.005	4.219	0.010	6.077	-1541.03	
6.	45	4.221 ± 0.005	4.253 0.008		0.010	6.191	-1549.62	
7.	50	4.260 ± 0.005	4.293 0.009	4.229	0.010	6.347	-1514.88	

Rep* Reported pK_a values, Ref. Alber et al. (1984).**Table 3: Ascorbic Acid**

S. No.	Temp. $^\circ\text{C}$	pK_a^{M}	pK_a^{T}	Δ	$-\frac{d(\text{pK}_a)}{T}$	ΔG	ΔH	ΔS
1.	25	4.159 ± 0.006	4.195 ± 0.006	0.04	0.011	5.722	10019.2	14.41
2.	30	3.393 ± 0.004	3.970 ± 0.005	0.04	0.010	5.506	9875.2	
3.	35	3.927 ± 0.005	3.964 ± 0.003	0.04	0.010	5.588	10029.6	
4.	40	3.808 ± 0.004	3.845 ± 0.007	0.04	0.010	5.508	10021.8	
5.	45	3.681 ± 0.005	3.699 0.008	0.01	0.01	5.384	9969.3	
6.	50	3.552 ± 0.007	3.589 ± 0.005	0.03	0.03	5.307	9963.3	

 $\Delta\text{G} \pm \text{Kcal/mol}$ $\Delta\text{H} \pm \text{Kcal/mol}$ $\Delta\text{S} \pm \text{Cal/mol/K}$

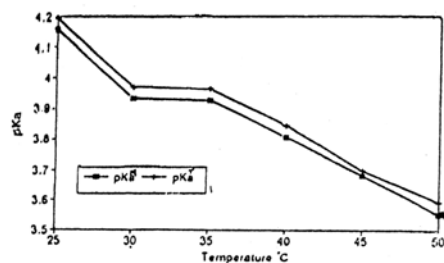


Fig. 1: Graph showing the effect of temperature on pK_a^M and pK_a^T values of ascorbic acid.

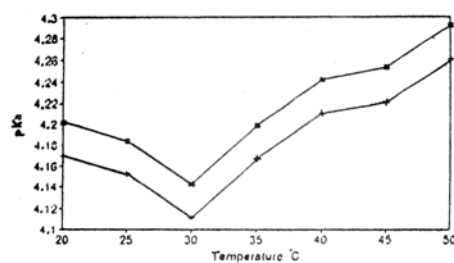


Fig. 2: Graph showing the effect of temperature on pK_a^M and pK_a^T of benzoic acid.

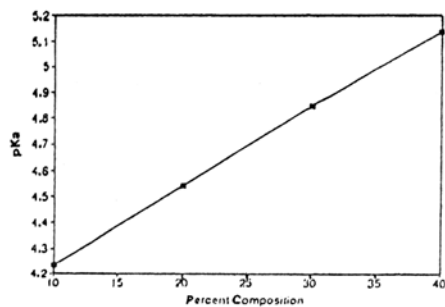


Fig. 3: Graph showing the effect of percent composition on pK_a values of ascorbic acid.

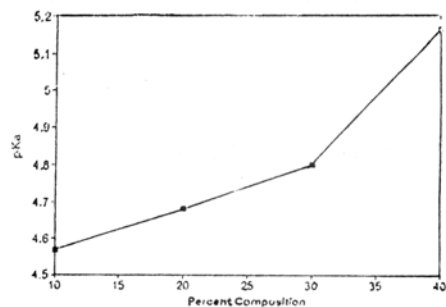


Fig. 4: Effect of percent composition on pK_a values of benzoic acid.

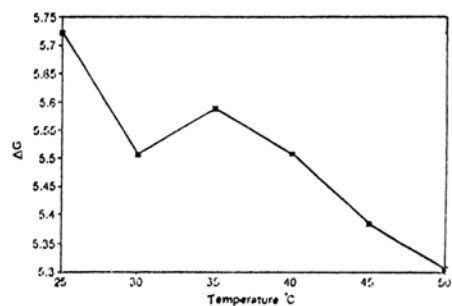


Fig. 5: Graph showing the effect of temperature on DG values of ascorbic acid.

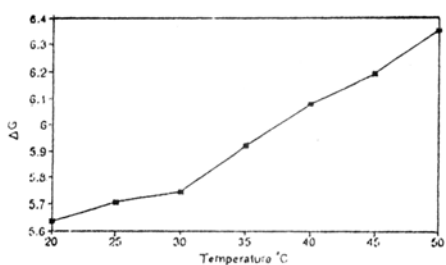


Fig. 6: Graph showing the effect of temperature on DG values of benzoic acid.

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