



PROTON TRANSFER EQUILIBRIA OF HYDROXY ACIDS

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ABSTRACT:

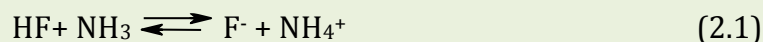
A number of studies have been reported on dissociation constant of hydroxyl acids in aqueous media but a little information is available on dissociation constants of Hydroxy acids in water-organic solvent mixtures. Practically no evidence is available for the theoretical calculations on dissociation energy and on solvation behaviour in periodic boundary conditions.

KEY WORD: Proton Transfer Equilibria, Hydroxy Acids,

INTRODUCTION:

The most important class of reactions taking place in water solutions are those in which a hydrogen ion is transferred from one molecule or ion to another. Since hydrogen atoms, with one electron, are the simplest atoms, a positive hydrogen ion is the same as a hydrogen nucleus. In the predominant fraction of hydrogen atoms, which is the isotope of mass one, the nucleus is a single proton, and hydrogen-ion transfer is generally known as proton transfer. After centuries of progressively refined definitions of what is meant by the terms acid and base, J. N. Bronsted [1] and T. M. Lowry [2] proposed that reactions involving the transfer of a hydrogen ion be called acid-base reactions; the proton donor is called a Bronsted acid, and the proton acceptor a Bronsted base. (The terms “donor” and “acceptor” put a polite face on the transaction; the proton goes where it can bond most strongly, and the Bronsted base has more realistically been termed a proton snatcher and the acid a proton loser.) When a Bronsted acid loses a proton, it is converted into a species which can

gain one; that is, every acid has its conjugate base, a substance which differs from the acid only in that a proton is missing. Conversely, of course, every Bronsted base has its conjugate acid. For example, in the acid-base reaction,



The HF is converted to its conjugate base F^- , and the NH_3 to its conjugate acid NH_4^+ .

MATERIALS AND METHOD:

Irving-Rosotti technique [3] was used for the calculating protonation constants for selected amines.

[I] Materials Used:

All reagents were used of AR Grade. All the solutions were prepared in doubly distilled water and standardized by different methods [4].

(i) Water:

Conductivity water was used throughout the work. Conductivity water was redistilled over alkaline potassium permanganate. The distillate was boiled to expel carbon dioxide and stored in airtight pyrex aspirator. The pH of this water was found to be ~6.8. This water was used for preparing solution of reagents.

(ii) Hydroxy acids and other chemicals:

All the hydroxyl acids (Salicylic acid, DL-Malic acid, DL-Mandelic acid and DL-Lactic acid) used were A.R. Grade. These were obtained from different chemical companies and their purities checked by noting their melting points and crystallisation methods [5]

(iii) Ethanol:

Ethanol was used after purifying it.[6-7].

[II] Preparation of Stock Solution :

(i) Sodium Hydroxide Standardisation :

Nearly 20gm of sodium hydroxide was dissolved in conductivity water in well-covered pyrex flask and was kept for two days. The clear liquid was filtered rapidly through sintered glass crucible of porosity G-4 using vacuum pump into another well-cleaned 500ml measuring flask. It was diluted up to 500ml shaken well and titrated against standard 0.1N oxalic acid solution using phenolphthalein as an indicator. Thus the strength of the sodium hydroxide solution was determined and also checked pH metrically. From this standard sodium hydroxide stock solution, 0.2M solution was prepared by proper dilution. Sodium Hydroxide must be free from carbon dioxide,so it is necessary to keep NaOH air tight and also kept out from sunlight because of photochemical reaction.

(ii) Sodium perchlorate Solution :

1M solution was prepared by dissolving the required amount of the sample in the conductivity water.

(iii) Perchloric acid Solution :

A definite volume of 80% acid was diluted with conductivity water to obtain 0.2 M Solution of HClO_4 in 500 ml flask. The exact strength was determined by titration against standard alkali solution pH metrically.

(iv) Hydroxy Acid Solutions :

Since all the hydroxy acids were of A.R. Grade and their standard solution of 0.1M concentration were prepared by dissolving the required quantity in conductivity water.

[III] Instrumentation:

Systronic 361 μ - pH meter with combined glass electrode and temperature probe with readability ± 0.01 was used for pH metric studies. It was calibrated with Buffer solution (7 pH and 4 pH or 9.2 pH) and calibration was checked intermittently.

[IV] Preparation of Titration Sets:

To study the behavior of protonation constants in different organic-aqueous mixtures following sets were prepared as 0%,10%,20%, 30%,40%, and 50% V/V Ethanol-Water systems keeping ionic strength at 0.2 and temperature $30 \pm 0.1^\circ\text{C}$.

CALCULATION:

Each set was titrated pH-metrically against 0.2M NaOH solution. Alkalimetric titration data were pruned by computer programs PKAS. It contains more information than noise and value of protonation constants given by the programs are used as initial value for final refinement by the computer program BEST [8]. For the computation of species from given proton ligand stability constants, a FORTRAN computer program SPE is used

RESULTS AND DISCUSSION:

Moreover, dissociation constants are very important data to calculate microscopic constants of corresponding Hydroxy acids.

I. Determination of CO₂ content in NaOH solution

The carbonate contamination of base is seemingly inevitable the equivalence point derived from the Gran Plot [9] in alkaline region was always larger than that obtained from acid region. The presence of carbonate in the base should be regarded as systematic error to be reduced as much as possible by good laboratory practice.

Accurate calibration of electrode is necessary for the determinations of stability constants by potentiometric titrations, as any error in the calibration becomes a systematic error in interpretation of titration data. However the process is far from easy because inter dependence of all parameters involved. The program [10] provides an estimate of carbonate contamination of the base, the pseudo-Nernstian standard potential and slope of the electrode and optionally, the concentration of base and PK_w .

The principle of carbonate contamination determination is based on the method given by Gran. Gran's function (Φ) is given as under.

$$\Phi = V_o + V_{\text{NaOH}} \times 10^{\pm R}$$

Where, V_o = Initial Volume, V_{NaOH} = Volume of NaOH added

R = Reading of pH meter, (+) = Reading of pH meter in acid region

(-) = Reading of pH meter in alkaline region

The results are presented in Figure: II-2.0. Suitable percentage of carbonate correction is made at BEST input files during data processing.

II. Calculation of Dissociation constant

Dissociation constants of Hydroxy Acids are calculated with point wise calculation method. The results are compared with results of PKAS & BEST [11]. The results are comparable showing the authenticity of the BESTFIT models selected in the present. The results of point wise calculation are given in Table: II- 1.1 to 1.4 and Comparison data is given in Table:II-1.5

III. Dissociation Energies of Hydroxy Acids (A Theoretical Calculation).

To calculate dissociation energy three structures (i) un dissociated (ii) one dissociated (iii) Two dissociation sites were used as models for carrying molecular simulations. Charges were added at respective atoms. Ab-initio calculations (non-semi empirical methods) using minimal basis (STO-3G) are carried out. Geometry optimization conditions are specified as total charge=1 or 2, spin multiplicity=1, spin pairing= RHF, Convergence limit = 0.01, iteration limit = 50 and acceleration convergence = Yes.

Total energies of protonated structure at MP2 level and SCF (Self Consistent Field level) with STO-3G basis are reported in Table: II-2.1 to 2.4. From these energies correlation energies are computed.

IV. Solvation Energies of Hydroxy Acids

(Solvation behaviour and periodic Boundary Conditions).Solvation can have a profound effect on the results on a chemical calculation. The solvent effect is expressed in several ways, including

[i] The solvent can strongly influence [the energies of different solute conformations or configuration of atoms.

[ii] The nature of solute-solvent interaction is dependent on solvent environment. Solvent influences the hydrogen bonding pattern, solute surface area and hydrophilic and hydrophobic group exposures. T1P3P water model for solvation is used [12] in present study. Here the solute is placed in a box of T1P3P water model and impose periodic boundary conditions. Before running a molecular dynamics

simulation with solvent and a molecular mechanics method, a constant dielectric of 1.0 with T1P3P water molecule in a periodic box is imposed. Because of paramagnetism of T1P3P molecules using a distance-dependent dielectric or a value other than 1.0 gives unnatural results.

In the present study, to solvate a system following periodic Box size is specified 10.0 by 12.0 by 12.0 Angstroms (A°). This places 48 water molecules in the box. Solvated and unsolvated solute molecules (Hydroxy Acids) are optimized using molecular mechanics after assigning required conditions like electrostatic 0.5 and van der Waals 0.5, outer radius 5.0 A° and inner radius 1.0 A°.

Two structures are merged, isolated one and solvated one. The changes in structure can be seen by overlapping two structures by selecting one specific bond.

By checking bond lengths and bond angles, it is found that there is difference (i) in energy of solvated and unsolvated molecules (ii) there is difference in bond angles and bond torsions of two structures. Solvation Energy and other parameters of Hydroxy acids in water as solvent are presented in the Table: II-3.1

IV. Best Fit models of acido-base equilibria:

Protonation constants for hydroxyl acids and percentage of various species like H₂L, HL, L in different water-organic solvent mixtures are presented in Tables: II-4.1 to 4.4.

Best fit models of acido-base equilibria for Malic acid, Lactic acid, salicylic acid and mandelic acid show that with decrease in dielectric constant of medium there is increase in protonation constants of hydroxyl acids [13].

The spontaneous dissolution of Hydroxy Acids in a solvent mixture must be accompanied by a reduction of free energy ΔG_{sol} .

The following four forces are possible

- (a) Creation of a 'cavity' or space within the solvent (reduction of Solvent-solvent forces)
- (b) Separation of solute molecule from bulk solute (reduction of solute- solute forces)
- (c) Insertion of solute molecule in cavity (creation of solute- solvent forces (solvation))
- (d) Entropy of mixing of solute and solvent for higher solubility, solvation forces (c) should be balance by both (a) and (b) forces.

The solute and surrounding solvent molecules exert a natural net attraction (otherwise there would be no solution). The aggregation of solvent molecules around a solute is known as solvation. The presence of a solute molecule affects the properties of its immediate environment, which is known as the cybotactic region and may extend well beyond the inner solvation shell though, at present, detailed and exact knowledge of its structure is not available.

The total solvent-solute interaction energy is key to all solvent effects upon physical and chemical phenomena. These forces are dependent on (i) Polarity (ii) Polarizability (iii) Hydrogen bonding (iv) Donor-acceptor interaction. There are number of solvation scales based on any physical or chemical property, sensitivity, nature of solvent. These scales are also related to solvation forces, to which experiment responds. There is rarely a solvation scale which is measure of purely of one type of intermolecular interaction. Hybrid scales are usually used for comparison of responses to solvent changes by different reactions. The scales based on physical propertties are Dielectric constant, Refractive index, Reaction field calculations, Solvent cohesive energy- the solubility parameter.

The protonation constants are considered in detail to give more information about the effect of solvent on protonation equilibria of hydroxy acids.

The presence of cosolvent in the medium influences the equilibrium in solution closely due to change in dielectric constant of equilibria, which varies the electrostatic and non-electrostatic interaction. The thermal motion permits more or less free rotation and rapid interchange of solvent molecules. The extent of cybotactic region is greater for the solvent with low dielectric constant because fall of electric potential is possible, as the distance varies inversely with dielectric constant. As a result of solvation forces the density of cybotactic region is higher than that of bulk of solvent. So solvation is accompanied by reduction in volume or electriristiction.

Further alter of dielectric constant has direct influence on the dissociation constant equilibria. The charge decrease is encouraged in medium of decreasing dielectric constant.

Dielectric constant of solvent is an important parameter affecting protonation constant of Hydroxy Acids. In present study, $\log pK_1^H$ values are decreasing with increase in value of dielectric constants as expected. The behavior of dissociation constants in solutions of dielectric constant less than pure solvent is unpredictable .

The distribution of LH₂, LH and L species of both selected aliphatic and aromatic Hydroxy Acids at different pH values are shown in Figure: II-2.11 to 2.45.

The H₂L species are maximum with 99% at lower pH in range of 2.0 pH and decreases to minimum at pH 5-6 in case of selected aliphatic and aromatic hydroxyl acids. But H₂ species has maximum concentration at pH 6.00 to 6.80 and with variable percentage 40-99% in case of aromatic diamines.

As pH increases the concentration of these LH₂ species decrease exponentially and becomes almost zero at pH ~6.0 in case of both aliphatic and aromatic Hydroxy acids. HL species has maximum concentration at pH 6.2-6.9 in case of all Hydroxy Acids. The free ligand concentration progressively

increases and attains maximum value at higher pH values. This conclusion is useful for predicting the bioavailability of ligands and possible metal ligand complexation behavior at a given pH.

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Table: I

(1)	(0% Ethanol-Water Mixture)	
	Perchloric Acid(0.05M)	10.00 ml
	Hydroxy Acid Solution(0.10M)	5.00 ml
	Sodium Perchlorate (1.00M)	8.95 ml
	Conductivity Water	26.05 ml
	Total	50.0 ml

(2)	10% (V/V) Ethanol-Water	
	Perchloric Acid (0.05M)	10.00 ml
	Hydroxy Acid Solution (0.10M)	5.00 ml
	Sodium Perchlorate (1.00M)	8.95 ml
	Ethanol	5.00 ml
	Conductivity Water	21.05 ml
	Total	50.0 ml

(3)	20% (V/V) Ethanol-Water	
	Perchloric Acid (0.05M)	10.00 ml
	Hydroxy Acid Solution (0.10M)	5.00 ml
	Sodium Perchlorate (1.00M)	8.95 ml
	Ethanol	10.00 ml
	Conductivity Water	16.05 ml
	Total	50.0 ml

(4)	30% (V/V) Ethanol-Water	
	Perchloric Acid (0.05M)	10.00 ml
	Hydroxy Acid Solution (0.1M)	5.00 ml
	Sodium Perchlorate (1M)	8.95 ml
	Ethanol	15.00 ml
	Conductivity Water	11.05 ml
	Total	50.0 ml

(5)	40% (V/V) Ethanol-Water	
	Perchloric Acid (0.05M)	10.00 ml
	Hydroxy Acid Solution (0.1M)	5.00 ml
	Sodium Perchlorate (1M)	8.95 ml
	Ethanol	15.00 ml
	Conductivity Water	6.05 ml
	Total	50.0 ml

(6)	50% (V/V) Ethanol-Water	
	Perchloric Acid (0.05M)	10.00 ml
	Hydroxy Acid Solution (0.1M)	5.00 ml
	Sodium Perchlorate (1M)	8.95 ml
	Ethanol	15.00 ml
	Conductivity Water	1.05 ml
	Total	50.0 ml

Table: II - 1.1 Stepwise Method for Calculation of Dissociation Constants of Malic acid
Temperature $30 \pm 0.1^\circ\text{C}$, $\mu = 0.2\text{M dm}^{-3}$ (NaClO_4)

(i) Calculation of first dissociation constant						
pH	V'	V''	V'' - V'	$\bar{n} \text{H}$	$\log \frac{\bar{n}\text{H} - 2}{3 - \bar{n}\text{H}}$	$\text{pH} + \log \frac{\bar{n}\text{H} - 2}{3 - \bar{n}\text{H}}$
3.00	2.16	3.40	1.24	2.5483	0.08417	3.0842
3.01	2.16	3.42	1.26	2.5410	0.07138	3.0814
3.01	2.17	3.44	1.27	2.5374	0.06509	3.0751
3.02	2.18	3.46	1.28	2.5339	0.05898	3.0790
3.03	2.18	3.48	1.30	2.5266	0.04625	3.0763
3.04	2.19	3.50	1.31	2.5231	0.04016	3.0802
3.05	2.20	3.52	1.32	2.5195	0.03389	3.0839
3.06	2.20	3.54	1.34	2.5123	0.02137	3.0814
3.07	2.20	3.56	1.36	2.5049	0.00851	3.0785

$$pK_3^H = 3.0800$$

(ii) Calculation of second dissociation constant						
pH	V'	V''	V'' - V'	$\bar{n} \text{H}$	$\log \frac{\bar{n}\text{H} - 1}{2 - \bar{n}\text{H}}$	$\text{pH} + \log \frac{\bar{n}\text{H} - 1}{2 - \bar{n}\text{H}}$
4.74	2.47	6.50	4.03	1.5407	0.0709	4.8109
4.76	2.47	6.52	4.05	1.5334	0.0581	4.8181
4.77	2.47	6.54	4.07	1.5262	0.0456	4.8156
4.78	2.47	6.56	4.09	1.5189	0.0328	4.8128
4.80	2.47	6.58	4.11	1.5117	0.0203	4.8203
4.81	2.47	6.60	4.13	1.5045	0.0078	4.8178
4.83	2.47	6.62	4.15	1.4972	-0.0049	4.8251

$$pK_2^H = 4.8172$$

(iii) Calculation of Third dissociation constant						
pH	V''	V'	V'' - V'	$\bar{n}H$	$\log \frac{\bar{n}H}{1 - \bar{n}H}$	pH + $\log \frac{\bar{n}H}{1 - \bar{n}H}$
11.65	5.38	9.66	4.28	0.5316	0.0550	11.7050
11.66	5.38	9.68	4.30	0.5247	0.0429	11.7029
11.67	5.40	9.70	4.30	0.5252	0.0438	11.7138
11.68	5.40	9.72	4.32	0.5184	0.0320	11.7120
11.69	5.42	9.74	4.32	0.5189	0.0328	11.7228
11.70	5.42	9.76	4.34	0.5120	0.0209	11.7209
11.71	5.46	9.78	4.32	0.5200	0.0348	11.7448

$$pK_1^H = 11.7175$$

**Table: II - 1.2 Stepwise Method for Calculation of Dissociation Constants of Lactic acid
Temperature 30±0.1°C, μ= 0.2M dm⁻³ (NaClO₄)**

(i) Calculation of first dissociation constant						
pH	V'	V''	V'' - V'	$\bar{n}H$	$\log \frac{\bar{n}H - 1}{2 - \bar{n}H}$	pH + $\log \frac{\bar{n}H - 1}{2 - \bar{n}H}$
3.72	2.42	3.68	1.26	1.5433	0.0754	3.7954
3.73	2.42	3.70	1.28	1.5361	0.0628	3.7928
3.74	2.42	3.72	1.30	1.5288	0.0501	3.7901
3.75	2.42	3.74	1.32	1.5216	0.0375	3.7875
3.77	2.42	3.76	1.34	1.5143	0.0248	3.7948
3.78	2.42	3.78	1.36	1.5071	0.0123	3.7923
3.79	2.42	3.80	1.38	1.4998	-0.0003	3.7897

$$pK_2^H = 3.7918$$

(iv) Calculation of second dissociation constant						
pH	V'	V''	V'' - V'	$\bar{n}H$	$\log \frac{\bar{n}H}{1 - \bar{n}H}$	pH + $\log \frac{\bar{n}H}{1 - \bar{n}H}$
11.64	5.38	9.66	4.28	0.5316	0.0550	11.6950
11.65	5.38	9.68	4.30	0.5247	0.0429	11.6929
11.66	5.40	9.70	4.30	0.5253	0.0440	11.7040
11.67	5.40	9.72	4.32	0.5184	0.0320	11.7020

11.68	5.42	9.74	4.32	0.5189	0.0328	11.7128
11.69	5.42	9.76	4.34	0.5121	0.0210	11.7110
11.70	5.46	9.78	4.32	0.5200	0.0348	11.7348

$$pK_1^H = 11.7075$$

**Table: II - 1.3 Stepwise Method for Calculation of Dissociation Constants of Salicylic acid
Temperature 30±0.1°C, μ= 0.2M dm⁻³ (NaClO₄)**

(ii) Calculation of first dissociation constant						
pH	V'	V''	V'' - V'	\bar{n}_H	$\log \frac{\bar{n}_H - 1}{2 - \bar{n}_H}$	pH + $\log \frac{\bar{n}_H - 1}{2 - \bar{n}_H}$
2.74	1.86	3.2	1.34	1.5091	0.0158	2.7558
2.74	1.88	3.22	1.34	1.5092	0.0160	2.7560
2.75	1.88	3.24	1.36	1.5019	0.0033	2.7533
2.76	1.9	3.26	1.36	1.5021	0.0036	2.7636
2.77	1.92	3.28	1.36	1.5023	0.0040	2.7740
2.78	1.94	3.3	1.36	1.5025	0.0043	2.7843
2.79	1.94	3.32	1.38	1.4952	-0.0083	2.7817

$$pK_2^H = 2.7670$$

(v) Calculation of second dissociation constant						
pH	V'hjhV'	V''	V'' - V'	\bar{n}_H	$\log \frac{\bar{n}_H}{1 - \bar{n}_H}$	pH + $\log \frac{\bar{n}_H}{1 - \bar{n}_H}$
11.44	4.22	8.42	4.20	0.5282	0.0490	11.4890
11.45	4.22	8.44	4.22	0.5212	0.0369	11.4869
11.46	4.22	8.46	4.24	0.5142	0.0247	11.4847
11.47	4.22	8.48	4.26	0.5072	0.0125	11.4825
11.48	4.22	8.50	4.28	0.5000	0.0000	11.4800
11.49	4.24	8.52	4.28	0.5000	0.0000	11.4900
11.50	4.24	8.54	4.30	0.4937	-0.0109	11.4891

$$pK_1^H = 11.4860$$

**Table: II - 1.4 Stepwise Method for Calculation of Dissociation Constants of Mandelic acid
Temperature 30±0.1°C, μ= 0.2M dm⁻³ (NaClO₄)**

(iii) Calculation of first dissociation constant						
pH	V'	V''	V'' - V'	$\bar{n}H$	$\log \frac{\bar{n}H - 1}{2 - \bar{n}H}$	$\text{pH} + \log \frac{\bar{n}H - 1}{2 - \bar{n}H}$
3.10	2.24	3.30	1.06	1.6144	1.5934	4.6934
3.15	2.30	3.41	1.11	1.5967	1.4795	4.6295
3.20	2.35	3.50	1.15	1.5826	1.3958	4.5958
3.25	2.35	3.57	1.22	1.5572	1.2584	4.5084
3.30	2.35	3.65	1.30	1.5282	1.1195	4.4195

$$pK_2^H = 4.5693$$

(vi) Calculation of second dissociation constant						
pH	V'	V''	V'' - V'	$\bar{n}H$	$\log \frac{\bar{n}H}{1 - \bar{n}H}$	$\text{pH} + \log \frac{\bar{n}H}{1 - \bar{n}H}$
11.55	2.69	5.45	2.76	0.5919	1.4504	13.0004
11.60	2.74	5.50	2.76	0.5315	1.1345	12.7345
11.65	2.78	5.60	2.82	0.5051	1.0206	12.6706
11.70	2.80	5.70	2.90	0.4863	0.9467	12.6467

$$pK_1^H = 12.7630$$

**Table: II - 1.5
Comparison of Dissociation Constants of Hydroxy Acids in water**

	Malic Acid			Lactic Acid		Salicylic Acid		Mandelic Acid	
	pK_1^H	pK_2^H	pK_3^H	pK_1^H	pK_2^H	pK_1^H	pK_2^H	pK_1^H	pK_2^H
Dissociation Constant	11.70	4.78	3.24	11.41	3.83	11.80	2.93	11.60	3.18
PKAS	11.71	4.71	3.20	11.40	3.80	11.69	2.89	11.53	3.09
BEST	11.68	4.53	3.12	11.32	3.84	11.71	2.92	11.59	3.12
Literature	11.70	4.72	3.28	11.42	3.75	12.23	2.93	11.61	3.19

Table: II - 2.1

Calculation of dissociation energy and other parameters in Malic acid

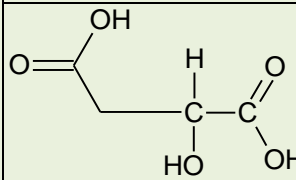
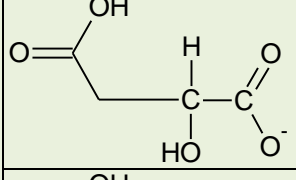
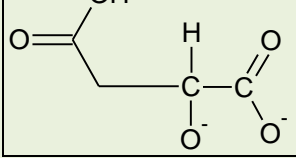
Different Forms	Energy		Gradience	Cycles points	Iteration & Difference	Basic Function & Paimates Gaussian	MP ₂ Correlation Energy	Dissociation energy of Malic Acid	
	SCF	MP ₂						SCF	MP ₂
	-137296.4	-137499.5	1.124	1+7 Points	1 It 0.0047 diff	24 basis + 84 primates Gaissian	-132.0812	-	-
	-137601.5	-137991.1	3.838	1+6 Points	2 It 0.0039 diff	25 basis + 87 primates Gaissian	-142.1221	282.11	288.10
	-1384411.3	-1386521.2	6.024	1+7 Points	2 It 0.0052 diff	26 basis + 90 primates Gaussian	-152.241	432.11	448.31

Table: II - 2.2

Calculations of dissociation energy and other parameters in Lactic Acid

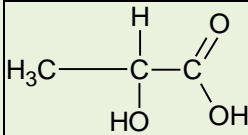
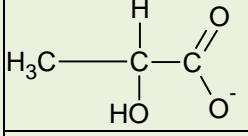
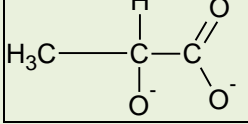
Different Forms	Energy		Gradience	Cycles points	Iteration & Difference	Basic function & paimates Gaussian	MP ₂ Correlation Energy	Dissociation energy of Lactic Acid	
	SCF	MP ₂						SCF	MP ₂
	-121112.10	-121320.22	1.12	1+6 Points	1 It 0.00019 diff	65 basis + 95 primates Gaissian	-128.02	-	-
	-121261.22	-121711.62	4.32	1+6 Points	2 It 0.00005 diff	66 basis + 98 primates Gaissian	-133.14	271.80	277.08
	-121308.32	-121822.13	6.81	1+6 Points	2 It 0.00376 diff	67 basis + 101 primates Gaussian	-148.22	410.20	432.7

Table: II - 2.3

Calculations of dissociation energy and other parameters in Salicylic Acid

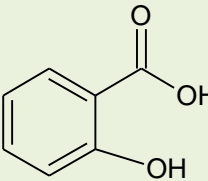
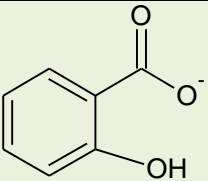
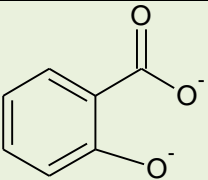
Different Forms	Energy		Gradience	Cycles points	Iteration & Difference	Basic function & paimates Gaussian	MP ₂ Correlator Energy	Dissociation energy Of Salicylic Acid	
	SCF	MP ₂						SCF	MP ₂
	-163012.31	-163192.03	2.620	1+6 Points	2 It 0.00019 diff	45 basis + 105 primates Gaussian	-140.6622	-	-
	-163241.31	-163381.41	3.404	1+6 Points	2 It 0.00005 diff	46 basis + 108 primates Gaussian	-163.7459	259.21	264.31
	-163431.09	-163598.13	100.26	1+6 Points	2 It 0.00376 diff	37 basis + 111 primates Gaussian	-178.7800	398.13	401.32

Table: II - 2.4

Calculations of dissociation energy and other parameters in Mandelic Acid

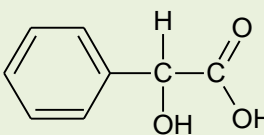
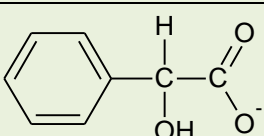
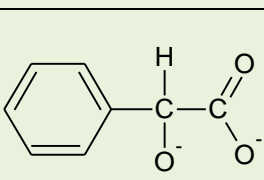
Different Forms	Energy		Gradience	Cycles points	Iteration & Difference	Basic function & paimates Gaussian	MP ₂ Correlator Energy	Dissociation energy Of Mandelic Acid	
	SCF	MP ₂						SCF	MP ₂
	-182121.11	-182324.40	1.620	1+6 Points	2 It 0.00019 diff	35 basis + 105 primates Gaussian	-140.6622	-	-
	-182342.9	-182413.1	5.404	1+6 Points	2 It 0.00005 diff	36 basis + 108 primates Gaussian	-155.7459	240.98	246.42
	-182436.2	-18251.3	125.26	1+6 Points	2 It 0.00376 diff	37 basis + 111 primates Gaussian	-167.78	370.45	382.01

Table: II - 3.1

**Calculation of Solvation Energy and other parameters of various Hydroxy Acids in aqueous media
Malic Acid**

Form	Energy	Gradience	Convergent	Cycles
Unsolvated	1.8132	0.01163	Yes	210 Cycles 1 pts
Solvated	814.2131	0.0112	Yes	216 Cycles 21 pts

Lactic Acid

Form	Energy	Gradience	Convergent	Cycles
Unsolvated	1.6100	0.0800	Yes	100 Cycles 80 pts
Solvated	629.3121	0.0121	Yes	132 Cycles 211 pts

Salicylic Acid

Form	Energy	Gradience	Convergent	Cycles
Unsolvated	6.3211	0.0132	Yes	32 Cycles 12 pts
Solvated	414.0021	0.0018	Yes	292 Cycles 512 pts

Mandelic Acid

Form	Energy	Gradience	Convergent	Cycles
Unsolvated	8.1121	0.0932	Yes	14 Cycles 45 pts
Solvated	322.3109	0.0113	Yes	535 Cycles 983 pts

Best fit Chemical Models of Acido-Basic Equilibria of
Hydroxy-acids in Ethanol-Water mixture at 30 ± 0.1 °C.
 $\mu=0.2\text{Mol.dm}^{-3}$ (NaClO₄) pH-readability ± 0.01

Table: II-4.1 DL - Malic Acid(pH = 2.00-12.00)

% V/V Ethanol	Pk ₁ ^H	Pk ₂ ^H	Logβ ₂	Species Distribution % (pH)		
				H ₂ L	HL	L
0	11.41	3.83	15.24	98.5 (2.0)	99.9 (6.9)	79.5 (12.0)
10	11.71	3.79	15.50	98.4 (2.0)	99.9 (6.8)	66.0 (12.0)
20	11.96	3.98	15.95	98.9 (2.0)	99.9 (7.0)	52.2 (12.0)
30	12.35	4.19	16.54	99.9 (2.0)	99.9 (7.2)	30.9 (12.0)
40	14.40	4.98	18.58	99.6 (2.0)	99.9 (7.5)	0.7 (12.0)
50	14.52	4.86	19.38	99.8 (2.0)	99.9 (7.9)	0.3 (12.0)

Table: II-4.2 DL - Lactic Acid (pH=2.00-12.00)

% V/V Ethanol	Pk ₁ ^H	Pk ₂ ^H	Logβ ₂	Species Distribution % (pH)		
				H ₂ L	HL	L
0	11.60	3.18	14.78	97.3 (2.0)	99.9 (6.6)	7.13 (12.0)
10	11.04	3.61	14.64	97.5 (2.0)	99.9 (6.7)	90.1 (12.0)
20	12.30	3.68	13.00	97.9 (2.0)	99.9 (6.7)	33.4 (12.0)
30	13.66	3.95	17.61	98.8 (2.0)	99.9 (7.0)	2.1 (12.0)
40	14.54	4.21	18.75	99.3 (2.0)	99.9 (7.3)	0.2 (11.9)
50	14.53	4.70	19.24	99.8 (2.0)	99.9 (7.8)	0.2 (11.9)

Table:II-4.3 DL - Salicylic Acid (pH=2.00-12.00)

% V/V Ethanol	Pk ₁ ^H	Pk ₂ ^H	Log β ₂	Species Distribution % (pH)		
				H ₂ L	HL	L
0	5.62	3.24	9.06	98.5 (2.0)	90.6 (4.5)	99.9 (8.9)
10	5.46	3.06	8.53	92.0 (2.0)	88.7 (4.3)	99.9 (8.5)
20	5.33	3.21	8.54	94.2 (2.0)	85.0 (4.3)	99.9 (8.4)
30	5.65	3.47	9.13	96.7 (2.0)	86.0 (4.5)	99.9 (8.7)
40	6.25	4.07	10.32	99.1 (2.0)	85.9 (5.2)	99.9 (9.3)
50	6.59	4.08	10.67	99.1 (2.0)	90.0 (5.3)	99.9 (9.6)

Table:II-4.4 DL - Mandelic acid (pH=2.00-12.00)

% V/V Ethanol	Pk ₁ ^H	Pk ₂ ^H	Logβ ₂	Species Distribution % (pH)		
				H ₂ L	HL	L
0	11.80	2.93	14.73	89.4 (2.0)	99.9 (6.0)	7.82 (12.0)
10	10.97	3.12	14.09	92.9 (2.0)	99.9 (6.2)	91.4 (12.0)
20	11.08	3.34	14.42	95.5 (2.0)	99.9 (6.4)	89.2 (12.0)
30	13.40	3.34	16.74	95.6 (2.0)	99.9 (6.4)	3.8 (12.0)
40	14.12	3.61	17.73	97.6 (2.0)	99.9 (6.7)	0.7 (12.0)
50	14.46	3.86	18.32	98.6 (2.0)	99.9 (6.9)	0.3 (12.0)