CHAPTER 1

INTRODUCTION

1.1 OBJECT AND SCOPE

During the past few decades the chromatographic separation based on ion exchange resins has received a greater attention because of its unparalleled performance and unusual success in serving chemical, pharmaceutical, electronic, food, nuclear and power utility industries. The efficiencies of these industries would have been seriously impaired if several advances were not made in this direction. Many products now available to consumer would not be available at the low cost and high purity now enjoyed. In fact, certain products might not be available at all - or, if so, at much higher costs. Vitamin B-12, the antibiotics (streptomycin, neomycin and gentamycin, etc.) and uranium are but a few such examples made possible by the various advances in the field of ion exchange and adsorption.

Besides the unusual success in certain fields, the ion exchange technique based on molecular sorption has got one more important point of attraction and that is its economy. For the process does not require chemical regeneration of the resin as there is no ion exchange involved. It is simple in operation and uses simple and cheaper chemicals as solvents and eluents. This has prompted many research workers to try and turn it in to economically and industrially feasible and acceptable process.

In this work attention is given to carboxylic acids - a class of organic compounds which includes a wide variety of substances ubiquitous in both plant and animal kingdom and are of direct interest to organic and bio-organic chemists because of their occurrence in nature, physiological activity and uses in pharmacy and industry. Recognition of the presence of these acids and related compounds in many biological systems has naturally stimulated the development of numerous chromatographic methods for their separation and identification.

In the present work sorption behaviour of some of the carboxylic acids on synthetic ion exchange resins has been studied and the possibilities of separating some closely related acids such as members of the homologous series, position isomers and geometrical isomers, depending upon their sorption behaviour, have been explored. The work is in continuation with the studies in this area over a period of past three decades based on concept and methodology developed here, widely and well accepted internationally. The object of the present work is to take the understanding of the subject a step further by postulating equations for the calculations of sorption and resolution and thereby making the study useful both industrially and academically.

Further, as the sorption coefficient of a solute is determined by the nature of nucleus of solute molecule and its environment ; it calls for the scope of correlating sorption coefficient with the structure of solute molecule. In the thesis some efforts have been made to focus light in this direction also. This is quite interesting and it should be worthwhile to further the investigation and to reveal the structure sorption relationship on the basis of ion exchange technique.

1.2 ION EXCHANGE MATERIALS (1-25)

Ion exchange may be defined as the reversible interchange of ions between a solid phase (Ion exchange material) and a liquid phase in which there is no permanent change in structure." Reversible" and " no permanent change " are the key points in this definition. However, a study of ion exchange, either in the laboratory or in literature, shows that the use of ion exchange materials extends considerably beyond this definition and now in many cases depends on non-exchange properties. Applications such as catalysis, drying, plant-nutrition and separation of inorganic and organic solutes may be cited to illustrate this point (26-30).

Ion exchange materials are of a wide variety. These may be organic or inorganic and natural or synthetic. Synthetic materials are usually superior, because their properties can be better controlled. Synthetic organic exchangers are the most significant of the ion exchange materials. These are gels and the matrix consists of an irregular macromolecular three dimensional network of hydrocarbon chains containing ionogenic groups distributed more or less uniformly through out its structure. Depending upon the ion-active group attached to the matrix, the ion exchange resins are classified as cation exchange resins (weakly or strongly acidic) and anion exchange resins (weakly or strongly basic). Not all the significant ion exchangers have been organic in nature, the oldest materials such as ionic clays, green sands, zeolites and some of the newer products such as the synthetic aluminates, phosphates, silicates, molybdates(31) and ferrocyanides(32) show specific sorptive properties.

Granular ion exchange resins were first described in 1935 by Adams and Holmes(33). They discovered the ion exchange properties of a phenol-formaldehyde condensate resin, cation exchange was possible due to the presence of some ionized phenolic groups. This discovery led to the recognition, study and solution of the problem of introducing more efficient ionic groups on polymer " back bone " structure. Most of the early resins were based on a variety of condensation polymers. The advent of commercial ethylenic polymers, particularly the styrenes, led to a major switch in the late 1940s and early 1950s to the addition polymers. However, a few condensation polymer products remain still important.

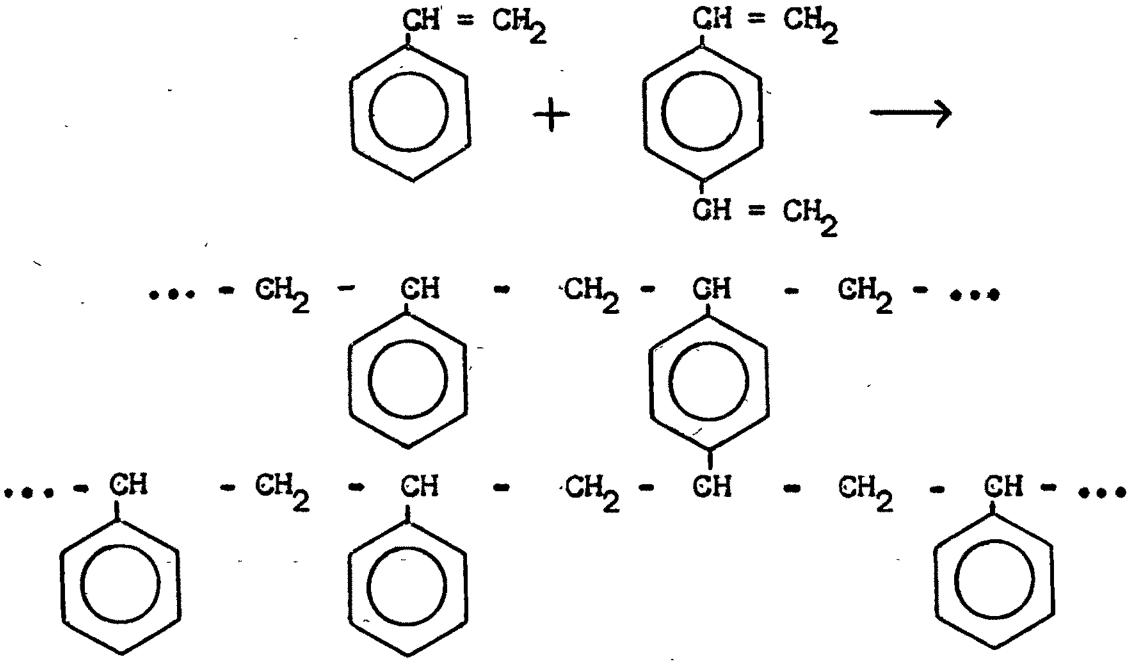
There have been considerable efforts to produce products having new chemical structure and specific selectivity as exemplified by the chelate resins. The major product requirements might be placed in three categories : quantitative performance, quality and economics. Of which, performance includes the closely related capacity, equilibrium(34-46) and kinetic properties. Total capacity, that is, the number of functional groups available for exchange per unit weight or volume in a prescribed ionic form and environment, is normally the prime property evaluated following the synthesis of an exchanger. Dry-weight capacity provides the best measure of the degree of substitution of functional groups during synthesis.

The selectivity, a resin shows for one ion with respect to another is dependent primarily on the chemical nature of the functional group, however, it is also dependent to a very great extent on the equilibrium swelling, the concentration of functional groups, the nature of the polymeric backbone structure and the nature of the external solution. The same factors affect diffusional processes and exchange rates, with resin particle size exterting a significant additional control.

1.2.1 Condensation and Addition " Backbone " Polymers :

Condensation polymers useful as ion exchange resin " backbones " are high molecular weight, crosslinked structure formed, usually by an ionic reaction mechanism, from small polyfunctional monomers by splitting out small molecules such as water, alcohol and ammonia and forming new C-C , C-N , C-O , or other bonds. Relatively easy hydrolytic or oxidative cleavage of the polymer chains are major problems with many condensation polymers.

Addition polymers useful as the backbone for ion exchange resin synthesis are crosslinked structures formed by the freeradical polymerization of mixtures of olefinic and diolefinic compounds. No new compounds are formed as by-products, and the polymer chains contain only C-C bonds. Consequently, such products resist hydrolytic cleavage and are relatively stable to heat and pH changes. Styrene thus may add to itself and to the difunctional divinylbenzene to give a crosslinked polymer network :



Most of the commercial ion exchange products, including strong acid and strong base exchangers, currently are built on the styrene-divinylbenzene backbone. However, acrylic acid or methacrylic-divinylbenzene copolymers are significant among the weak-acid-resins. Condensation products still find particular utility in the area of weak-base-resins.

1.2.2 Cation Exchange Resins (47-57)

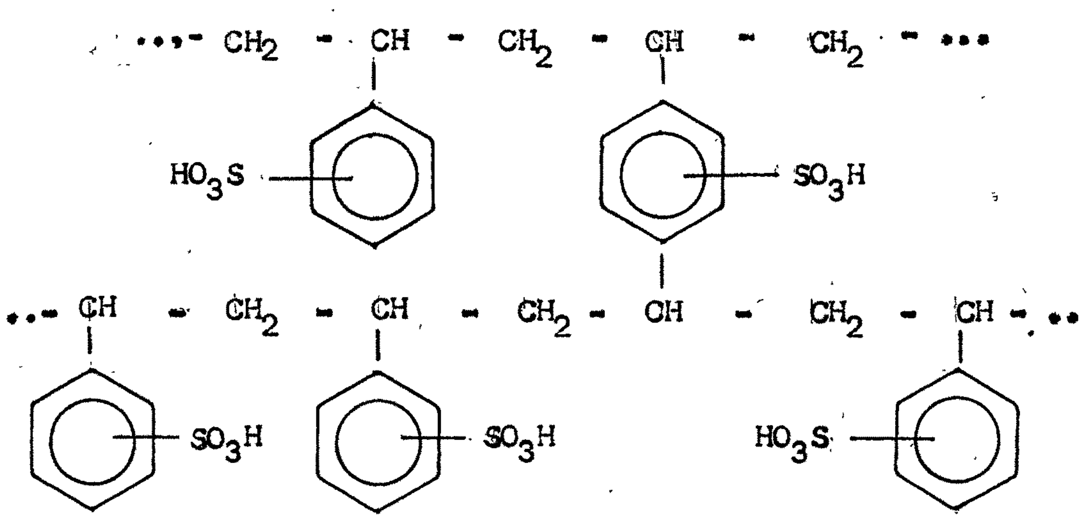
The exchange activities of cation exchange resins are associated with nuclear sulfonic, methylene sulfonic, carboxylic, phosphoric and phenolic groups.

Sulfonated copolymers of styrene and divinylbenzene (DVB) constitute a class of resins most widely used. The copolymer matrix has excellent physical strength and is not easily subjected to degradation by oxidation, hydrolysis and elevated temperature. Typical examples of styrene - DVB copolymers based strong cation exchanger are Amberlite IR-120, Dowex 50, Duolite C-20, Ionac C-240 and permutit Q. In the present work studies have been carried out on such type of resin, so it would be of interest to see the synthesis of this resin in detail.

The initial step in the synthesis of the resin is the production of copolymer beads of proper size, crosslinking and internal physical structure. This is carried out by suspension or pearl polymerization technique. The monomer mixture, containing appropriate quantity of each monomer and a free radical catalyst such as benzoyl peroxide, is agitated in water containing a small amount of suspension stabilizer such as inorganic clays, alumina, organic methyl cellulose or polyvinyl alcohol. The purpose of the suspension stabilizer is to disperse the monomer liquid in globules of the proper particle size and to prevent agglomeration during the transition from the liquid to the solid phase. The polymerization temperature ranges from 70°C to the reflux temperature. The rate of agitation, nature of the stabilizer and the viscosity of the solution would determine the particle size distribution. After polymerization, the beads are washed to remove adhering material and then dried.

The molecules of styrene form the polymeric chains while the DVB provides crosslinks between the chains. The degree of crosslinking is controlled by the ratio of divinylbenzene to styrene in the original mixture. However, pure DVB is too expensive to be used for this purpose, a mixture of about equal weights of DVB and ethylstyrene is used industrially. Both the DVB and ethylstyrene, in turn, consist of a mixture of their three isomers. The conventional numerical measure of degree of crosslinking is the mole percent of the pure divinylbenzene in the original polymerization mixture. The presence of ethylstyrene results in the ethyl substituent in some of the benzene rings. The variation in composition of the commercial DVB accounts in part for the difference observed among different batches of supposedly identical resins.

The next step is the sulfonation of the beads. The sulfonation may be carried out with any of the several sulfonating agents including H_2SO_4, SO_3, oleum or chlorosulfonic acid or with mixtures, by stepwise addition of these at about $100^{o}C$ in appropriate amount to ensure good mixing during the reaction. The reaction is exothermic and temperature must be carefully controlled to avoid cracking of the polymer beads. Practically every benzene ring, including those belonging to the bridge is sulfonated preferentially in para position and the double sulfonation of a single ring is unlikely for steric reasons. An exchange capacity of about 5.1 meq/gm of dry resin is normally realized which agrees with the monosulfonation of the aromatic rings. The structure of the resin may be imagined as :



For very low crosslinked resins the bridging of aromatic rings through sulfone can occur by electrophilic ring substitution mechanism. Sulfonated beads are then hydrated and converted to the sodium salt. Care must be exercised in both of these steps to avoid bead breakage. In the hydration procedure the concentrated acid is replaced by concentrated electrolyte solution which is gradually diluted with water. Another technique designed to minimize bead breakage includes swelling of the beads in an organic solvent such as toluene or chlorinated hydrocarbons prior to sulfonation. This has proved helpful in improving the physical properties of the finished product, increasing the reaction rates and decreasing the tendency for extra sulfone crosslinking. Less completely sulfonated resins are desired sometimes for industrial and analytical purposes.

There is considerable evidence that incorporation of moderate amounts of a polar monomer such as acrylonitrile, methyl vinyl sulfone, vinyl esters etc., with the monomer mixture considerably improves the physical properties of the resultant ion exchange product (58-67), possibly due to the uniform and easier penetration of the polymer beads by H_2SO_4, owing to the easy protonation.

Carboxylic-type cation exchange resin can be prepared directly by the copolymerization of either methacrylic or acrylic acid with divinylbenzene. Wofatit C is considered to be the first carboxylic-type exchanger prepared in Germany. These resins are useful for the removal of cations from basic solutions as well as for " splitting " (replacement of salt cation with a proton) the weakly alkaline salts of multivalent cations.

Some phosphorous containing resins, although not now commercially important, offer interesting possibilities as intermediate-strength cation exchangers having novel selectivity characteristics and high capacity.

1.2.3 Anion Exchange Resins

Most of the methods involve the formation of anionic resin by the polymerization of an aromatic amine and formaldehyde or polyamine, a phenol and formaldehyde. Recently much work has been directed toward the epoxide-amine condensates.

Weak-base anion exchangers based on addition polymers also are well known, but they have apparently passed through a peak of commercial acceptance and are now being replaced to a considerable extent by epoxy-amine condensates. Commercial resins with styrene-DVB backbone have been prepared by the series of steps : polymerization, chloromethylation and amination with alkyl amines or alkylene polyamines.

Mixed-base resins, contain both weak-base and strong-base groups. 2-methyl-5-vinyl-pyridine polymerizes with divinylbenzene or a glycoldimethylacrylate to yield a weak-base anion exchange resin which in turn may be further alkylated, e.g. with benzylchloride, to give a commercially useful mixed-base resin.

Strong-base anion exchange resins can be readily prepared by reacting chloromethylated copolymers with trialkyl amines e.g. using ammonium persulfate as catalyst, tetraallylammonium chloride has been polymerized in suspension to yield a strong-base exchanger.

A typical ion exchanger has been prepared in which diphenyl ether is the basic structural unit for a wide variety of developmental ion exchange materials. Diphenyl ether may be chloromethylated to give from one to four chloromethyl groups per ether unit and then undergo condensation polymerization to an insoluble resinous mass by the contact with an active Friedel-Crafts catalyst such as ferric chloride. The resulting crosslinked polymer, containing a quantity of residual unreacted chloromethyl groups, may then be further suitably aminated to give the desired anion exchange resin. These products have been shown to have high capacity and unusual chemical stability.

1.2.4 Amphoteric Ion Exchange Resins

Special bipolar ion exchange resins carrying both positive and negative ion active groups are known as amphoteric ion exchange resins. Both types of active groups are able to participate in ion exchange processes, frequently carried out simultaneously on the same solution. Studies have shown that the single group react independently and stoichiometrically.

They consist of a linear crosslinked mixture of polymers comprising a cation exchanger entwined within an anion exchanger. This structure is achieved by polymerizing the cation exchanger monomer within the structure of the previously formed anion exchanger producing the ' snake cage ' structure required for ion retardation. Such resins are employed to remove electrolytic impurities from liquids by the preferential retardation of the electrolyte due to the formation of ion pairs with the resin.

1.2.5 Gel Type Resins (19)

The gel-type resins of the styrene DVB type date back to 1947. These materials do not contain any true porosity. Ions to be exchanged must diffuse through the gel structure to the exchange sites. The intermolecular distances which limit the size of the ion that can migrate through the gel is often referred to as the apparent porosity. Even in low crosslinked gel-type resins, the apparent porosity is usually no greater than 40 Angstrom units.

1.2.6 Macroreticular Resins

In late 1950 s, a polymerization technique has been developed that yields a crosslinked ion exchange structure entirely different from the conventional gels and having a rigid macroporous structure, similar to that of conventional adsorbents such as alumina, silica and the carbons, which is superimposed on the gel structure. In contrast to the conventional ion exchange resins, these resins have been designed as macroporous or macroreticular ion exchangers. The descriptive term was introduced by personnel of Rohm and Haas company. Accordingly, these resins can best be described by comparing them with a small ball of tough, rigid sponge-like material, having large discrete pores (19). The first macroreticular resin was placed in to field service in 1959. Preparation technique of these resins includes a solvent system in which the solvent dissolves the monomer but tends to precipitate the polymer (63,68-91). Generally such polymers are formed by the addition polymerization of a monofunctional monomer (styrene) with a polyfunctional monomer (DVB) in presence of an inert (to polymerisation) solvent such as alcohol or hydrocarbon.

Carboxylic acid resins of the macroporous type have been prepared from crosslinked acrylic acid (74,92,93) and maleic acid (69) derivatives. Macroporous anion exchange resins have been prepared from epichlorohydrin-polyethyleneimine condensations in presence of water immiscible solvents (94,95). The term ' isoporous ' has been applied by Kressman (96) to describe ion exchange resins structures in which the crosslinks are introduced not during copolymerization, but by a chemical reaction in the performed resin bead. It is specifically applied to methylene bridging caused by condensation reaction during the chloromethylation with chloromethyl methyl ether, of styrene-DVB copolymers.

Macroreticular resins offer a number of advantages over the conventional gel-type resins. Some of them are as follows :

1. Because of the open high-internal-surface structure, these resins can be more rapidly and nearly completely sulfonated with gaseous SO_3, than gel-beads,
2. The open structure of the macroreticular resins permits the use of tough copolymers which would be too dense to effectively act as ion exchange resins if they were used in a strictly gel-type system.
3. Certain functional groups can not be synthesized properly from gel-type copolymers because of steric hindrance while the macroreticular copolymers are excellent substrates for many of these bulky functional groups.
4. These resins are relatively insensitive to osmotic shock both during preparation and subsequent usage. Whereas great care must be taken to avoid breakage during sulfonation and washing of gel-type beads, the macroporous-type may be sulfonated in the absence of a solvent and diluted and washed rapidly without excessive fracturing.

5. By virtue of large discrete porosity, high molecular weight ions (or colloids) can be more completely removed or recovered from solution and more completely eluted from the resin on regeneration than would be the case with other materials.

6. Because of the high degree of crosslinking and the extensive internal void structure these resins exhibit small volume change on transfer from a highly polar to an essentially non-polar solvent or on drying.

7. Because of the composition i.e. high crosslinkage, high selectivity for one ion with respect to another is realized.

8. These resins are useful as catalysts for reactions, particularly in nonpolar or gas phase systems where gel-type resins do not perform satisfactorily as all reactants do not dissolve in the hydrophilic gel structure of conventional resins.

9. Certain macroreticular resins are more oxidative resistant than the gel-type analogues.

Although the macroreticular resins, on the whole, do have somewhat lower capacity and higher regeneration costs than the gel-type resins, these are often offset by the longer operating life and enhanced kinetic behaviour of the macroreticular resins or the fact they will effect removals not possible by the gel-type resins.

1.2.7 Pellicular Resins(97)

Pellicular ion exchange materials were the first major development in column technology in High pressure liquid chromatography (HPLC). In 1967 Horvath et al (98) polymerized a thin film of styrene-divinylbenzene resin onto a spherical glass bead. The resin-bonded bead was treated chemically to make either a cation or anion exchanger. The pellicular cation exchange resin, the strongly acidic type, had sulfonate functionality. The pellicular anion exchange resin was strongly basic, possessing quaternary ammonium groups. Both resins had small ion exchange capacities in the order of eight to ten microequivalents per gram.

The thin, bonded coating of resin permits rapid solute mass transfer to occur for the same reasons that superficially porous packings demonstrate good efficiencies of liquid-solid chromatography (LSC) and liquid-liquid chromatography (LLC). The bonded-resin coating has the same advantages as the silicone-bonded phases used in Bonded-phase chromatography (BPC). Organic solvents, high buffer strengths, and high temperatures (up to 80°C) do not affect the bonded resin. Extremely acidic or basic conditions may affect bonded coatings.

Resins have been coated on the superficially porous surface of Zipax-SAX and -WAX are strong and weak anion exchange resins, respectively. Zipax-CAX is a strongly acidic cation exchanger with $-SO_3H$ groups extending from the surface. Care should be exercised when using resin coated superficially porous beads with organic solvents, high buffer concentrations, extreme pH values, or temperatures much higher than ambient because of instability of the resin coating.

Aromatic compound including phenols, carboxylic acids and aldehyde can be rapidly separated on pellicular anion exchange resins in the acetate form by elution with sodium acetate solution (99).

1.2.8 Adsorbent Resins (15)

These are distinguished from ion exchange resins in that their activity is generally based on van-der-waals' adsorption rather than coulombic ion exchange. Examples of such resins are Duolites S-30, S-33 and S-37. All three are characterized by having a large active surface (macroporosity) and weak-electrolyte activity.

These resins are used for the adsorption of high molecular weight organic compounds, usually from aqueous media. Applications include pretreatment of surface water supplies to prevent fouling of strong base resins and removal of colour and proteins from sugar solutions and wines.

1.2.9 Redox Resins (15)

These are resins capable of undergoing oxidation reduction cycles. The active groups may be part of the polymer molecule, as with addition polymers of vinyl hydroquinone or condensates of hydroquinone ; or an ion capable of undergoing oxidation reduction may be introducted into an ion exchange resin, in which case operating conditions must be such as to result in no ion exchange. Examples of such resins are strong-base anion exchangers containing adsorbed sulfite, bisulfite or hydrosulfite ions and weak-base resins containing reversibly (redox-wise) active copper. Duolite S-10 is used for removing dissolved oxygen from solution.

1.2.10 Ion Exchange Membranes (7)

Three basic techniques have been developed for preparing the permeselective ion exchange memberanes. The first involves the casting of homogeneous film from an ionic monomeric system or from a solution of an ionic polymer. The second technique consists of incorporating finely ground, highly crosslinked ion exchange resins into a plastic but inert matrix. Third a porous reactive substrate such as paper, cellophane, etc., is impregnated with monomers or polymeric solutions substantive to cellulose. These resins have become significant particularly for desalination of saline water.

1.2.11 Chelate Resins

Resins containing as part of their structure organic radicals which will undergo chelate ring formation with metallic ions subject to such activity (100). e.g. Resins containing the iminodiacetate groupings.

A. Dipicrylamine resins : Resins with selective affinity for potassium, made by incorporating the diphenylamine radical into a polymeric structure.

B. Polyol resins : Adsorbents having specific affinity for borate, made by incorporating multiple hydroxyl radicals into polymeric matrices.

1.3 CARBOXYLIC ACIDS (101-108)

The carboxyl group is one of the most interesting entities met in organic molecules. The presence of the carboxyl group makes a molecule an acid. Organic acids comprise a very large and diverse class of substances ubiquitous in the plant kingdon and are used in almost all synthetic organic products, either as part of the final composition or in one or more of the processing stages. Organic acids can be broadly classified as : Aliphatic acids, Alicyclic acids, Aromatic acids, Heterocyclic acids and Amino acids of which aliphatic and aromatic acids are of considerable interest.

Physical properties of the acids studied in this work are summarized in Table 1.3-1. Below is given their natural sources and various uses.

1.3.1 Aliphatic Dicarboxylic Acids

The acids studied are saturated aliphatic dicarboxylic acids of the series beginning with oxalic acid, with the general formula $C_nH_{2n}(COOH)_2$, in which n = o to 8. These acids are generally weak acids having much higher melting points and ionization constants than monocarboxylic acids of comparable molecular weight. The acidic character decreases with increase in molecular weight. Thus, oxalic acid is the strongest of all the non-substituted dicarboxylic acids. This is because one unsaturated carboxyl group in oxalic acid promotes the ionization of second directly. The strength of an acid is expressed in terms of dissociation constant Ka or more conveniently by the negative logarithm of dissociation constant pKa (Table 1.3-1). Among the series an interesting alternation is observed in both the melting points and solubilities in water. The acids having an even number of carbon atoms invariably are higher melting and less soluble than their immediate higher or lower homologs having an odd number of carbon atoms. This is due to the closer packing of even series molecules in the solid state, which can be explained only if the structure of these molecules were considered to be of swinging flexible zigzag chain rather than rigid straight chain. These contrasts become less marked in acids with higher molecular weights. The acids with odd number of carbon atoms have found little application because they are less readily available and more expensive as they are considerably more difficult to prepare than are the acids having an even number of carbon atoms.

Oxalic acid : Oxalic acid is one of the most important dicarboxylic acids, very widely spread in plants. It occurs in rhubarb, sorrel and other plants of the Oxalis group (hence the name) and as potassium and calcium salt in plants of Rumex family. Algae, fungi, lichens and ferns are rich in it. It is also found in Salicornia, Salsoia and in the leaves of Graminea, Bryophytes, Funaria and Sphagnum. Oxalic acid formed by moulds and this process is used commercially. It is present in urine of man and animals and animal organs. Ferrous and calcium oxalates are sometimes found as minerals.

Oxalic acid is used in industry as a mordant in clothprinting, for the manufacture of dyes, dextrins, ink, as a bleaching agent (straw, wood and leather), for removing stains of rust and ink, as a reagent and standard in volumetric analysis and as a developer in photography.

Malonic acid : It was discovered by Dessaignes who isolated it as a product of oxidation of malic acid and for this reason named it malonic acid. It occurs as calcium salt in beet root.

Due to presence of reactive $-CH_2$ group this compound is used for preparative work. Its ester, diethylmalonate commonly known as malonic ester, finds great application as an important synthetic reagent. Malonic acid derivatives are used in the preparation of barbituric acid, Vitamins B_1 and B_6, amino acids and hypnotics.

Succinic acid : The acid was first obtained by Agricola in 1550 by distilling amber (L. Succinum = amber) and hence the name. It is also found in many plants (e.g. in unripe gooseberries, graps, beet juice and rhubarb), in some varieties of lignites, in resins, in fossil woods and in terpentine oils. It is formed in large quantities in both the chemical and biochemical oxidation of fats, in the fermentation of calcium malate or ammonium tartarate, and in the alcoholic fermentation of sugar.

The acid has many unique properties. The most interesting of which is the reactivity of the $-CH_2$ groups. so that it has been used advantageously as an intermediate in the synthesis of a wide variety of complex organic compounds. It is used as an important intermediate in the manufacture of pharmaceuticals. It is also a valuable ingredient in the synthesis of plastics, elastomers, protective coatings, electrical insulation, dyes, perfumes and many other industrial products. It is used as a reagent in volumetric analysis.

Glutaric acid : It is so named because of its relationship with glutamic and tartaric acid. It occurs in beet juice and in the wash water from raw sheep's wool. It is less available, but can be prepared by the oxidation of certain cyclic compounds, chiefly cyclopentanol and cyclopentanone by nitric acid or by air in the presence of catalyst. It can also be synthesized from trimethylene glycol.

It is used in organic synthesis and in diabetes studies with animals.

Table 1.3-1 : Some physical constants of the acids studied.

Acid	Formula	Mol. Wt. gms.	pK^{25°		Specific gravity	M.P.	B.P.	Solubility i 100 parts of water
			1	2				
Oxalic (ethandioic)	$HO_2C.CO_2H$	90.04	1.27	4.28	1.900	186-7 d	subl>100	10^{20°
Malonic (propandioic)	$CH_2:(CO_2H)_2$	104.06	2.77	5.71	1.631^{15°	130-5 d	-	138^{16°
Succinic (butandioic)	$(CH_2.CO_2H)_2$	118.09	2.20	5.60	1.572^{25°	189-90	$235(-H_2O)$	6.8^{20°
Glutaric (pentandioic)	$CH_2(CH_2.CO_2H)_2$	132.11	4.33	5.54	1.429^{15°	97.50	200^{20mm}	63.9^{20°
Adipic (hexandioic)	$(CH_2CH_2CO_2H)_2$	146.14	4.42	5.62	1.360^{25°	151-3	265^{10mm}	1.4^{15°
Pimelic (heptandioic)	$(CH_2)_5(CO_2H)_2$	160.17	4.51	5.43	1.291^{25°	103-5	272^{100mm}	2.5^{14°
Suberic (octandioic)	$(CH_2)_6(CO_2H)_2$	174.19	4.59	5.41	1.266^{25°	140-4	279^{100mm}	0.14^{16°
Azelaic (nonandioic)	$(CH_2)_7(CO_2H)_2$	188.22	4.54	5.55	1.029^{20°	106.5	286.5^{100mm}	0.20
Sebacic (decandioic)	$(CH_2)_8(CO_2H)_2$	202.24	4.59	5.40	1.207^{25°	134.5	294.5^{100mm}	0.10

cont...

contd. ...

Benzoic	$C_6H_5.CO_2H$	122.12	4.20	-	1.266^{15°	121.7	249.2	0.21^{17°
3,5-dihydroxybenzoic (α-resorcylic)	$(HO)_2C_6H_3.CO_2H$	154.12	4.05	-	-	subl > 237(anh)	-	v.s.h.
2,4-dihydroxybenzoic (β-resorcylic)	$(HO)_2C_6H_3.CO_2H$	154.12	3.29	-	-	194-200 (anh)d.	-	0.26^{17°
2,6-dihydroxybenzoic (γ-resorcylic)	$(HO)_2C_6H_3.CO_2H$	154.12	1.22	-	-	148-67 (anh)d.	-	v.s.h.
3,5-dimethoxybenzoic	$(H_3CO)_2C_6H_3.CO_2H$	182.17	-	-	-	-	-	-
2,4-dimethoxybenzoic	$(H_3CO)_2C_6H_3.CO_2H$	182.17	4.36	-	-	-	-	-
2,6-dimethoxybenzoic	$(H_3CO)_2C_6H_3.CO_2H$	182.17	-	-	-	-	-	-
Maleic (cis) (butendioic)	$(:CH.CO_2H)_2$	116.07	2.00	6.26	1.609	130.5	135 d.	79^{25°
Fumaric (trans) (butendioic)	$(:CH.CO_2H)_2$	116.07	3.03	4.47	1.635^{20°	286-7	290	0.7^{17°
Crotonic (trans)(α) (butenoic)	$CH_3.CH:CHCO_2H$	86.09	4.70	-	0.964^{80°	72	189	8.3^{15°

d. = decomposes, v.s.h. = very soluble in hot

subl. = sublimes, anh. = anhydrous

Adipic acid : It is so named as it is formed by the oxidation of various fats (L. adipis = fat). It is available particularly from Russian minerals oils, which are rich in cyclohexane. The acid is not found in natural products as such, but occurs in natural products that have become rancid owing to oxidation. It was first synthesized in 1902 from tetramethylene bromide and was described by Thorpe in 1909.

It is used as a substitute for tartaric acid in the manufacture of baking powders and in the manufacture of mineral waters. Certain of its esters are used as gelatinizing agents and as plastisizers. Its most important use is in the manufacture of an extraordinarily strong synthetic fiber " Nylon ", produced by E.I. du pont de Nemours (U.S.A.) by condensing it with hexamethylene diamine (derived from adipic acid).

Pimelic acid : The name of this acid is derived from its occurrence in fats (Gr. pimele = fat). It is also an oxidation product of castoroil. It occurs in urine of herbivarous animals and can be prepared by a Novel reaction. It was first prepared by the oxidation of suberone (cycloheptanone).

It may be used as a precursor in the biological synthesis of biotin.

Suberic acid : It is so named as it is an oxidation product of cork (L. suber = cork). Suberic acid can be prepared by the oxidation of castor oil (chiefly glycerol, ricinoleate) or ricinoleic acid. It can also be obtained by oxidation of cyclooctene. It is not a readily accessible substance.

Suberic acid has found some uses in alkyd resin manufacture. On condensation polymerization with diamines, suberic acid gives rise to polyamides ; the product formed with octamethylenediamine (derived from suberic acid) is sometimes called an " 8-8 Nylon ", in distinction from the " 6-6 Nylon " derived from adipic acid.

Azelaic acid : The name of this acid is derived from the fact that the substance is one of the products of the oxidation of oleic acid with nitric acid (az, from ' azotic '= nitric and Gr. ' elaidic ", an acid stereoisomeric with oleic acid = oleic acid). Azelaic acid is found in natural products only after exposure to the oxiative influence of the atmosphere, which results in the oxidation of the unsaturated acids of the natural product. Thus crushed castor beans, when rancid, contain Azelaic acid. It is also present in small quantities in pyrethrum extract. It is a rather expensive chemical.

It is used in the manufacture of lacquers, hydrotropic salts, polyamides, alkyd resins and plasticizers.

Sebacic acid : It is obtained by dry distillation of castor oil or dry distillation of ricinoleic acid with sodium hydroxide. It has been isolated from yeast.

The polyhydric alcohol esters of sebacic acid are important in alkyd resin applications when flexibility is required, as for coated fabrics. They are suitable, too, as plasticizers for other synthetic resins. Sebacic acid may be condensed with a diamine to produce Nylon. It is also used in the manufacture of candle, perfumes, lubricants and hydroulic fluids.

1.3.2 Disubstitutedbenzoic acids

Aromatic acids are weak acids. The ionization constants (Table : 1.3-1) of these acids depend upon the type and position of the substituents in the aromatic nucleus. The ionization constants of these acids can be increased by intramolecular hydrogen bond formation. For this reason 2,6-dihydroxy benzoic acid is a stronger acid than its α and β isomers.

Benzoic acid : Benzoic acid, the simplest aromatic acid, is found in small amounts in a few fruits, in resins and in essential oils as esters e.g. perubalsam, tolubalsam. It is widely used for preserving foods, curing tobacco and manufacturing benzoates and benzoyl compounds.

The following benzoic acids used in this study were synthesized according to the procedure given in the literature (107).

Dimethoxybenzoic acids : Dimethoxybenzoic acids were prepared by refluxing the corresponding dihydroxybenzoic acid (1 gm) in acetone (200 ml) with anhydrous potassium carbonate (12 g) and dimethylsulfate (12 ml) for 10-12 hours. The acetone was removed by distillation and potassium carbonate dissolved in water. The residue was boiled with 10% sodium hydroxide, Cooled and the solution on acidification yielded the dimethoxybenzoic acid which crystallized from dilute alcohol. 2,4-dimethoxybenzoic acid (108), m.p. 109°C, 2,6-dimethoxybenzoic acid, m.p. 186-7°C and 3,5-dimethoxybenzoic acid, m.p. 185-6°C.

Dihydroxybenzoic acids : 2,4-, 2,6- and 3,5-dihydroxybenzoic acids were of chemically pure (C.P.) grade obtained from reliable manufacturers.

1.3.3 Geometrical Isomeric Acids

Fumaric acid : The name of this acid is derived from its occurrence in Fumaria officinalis (Fumitory). It is often found in mushrooms (Boletus and Agaricus species) and also in many fungi and in the lichen cetraria islandica (Iceland Moss). It has been found in many higher plants of number of families. It can be formed by the fermentation of glucose and molasses by the action of certain moulds such as Rhizopus nigricans and Rhizopus japonicus. It appears to be a normal product of animal metabolism.

Certain fumaric acid resins have special properties not possessed by the corresponding maleic acid products e.g. when incorporated with glycerol-type resins in varnishes they give harder and more durable finish than the maleic containing resins.

Maleic acid : It does not occur naturally. It is used for making varnishes and lacquers, to inhibit rancidity in milk powder and as a anhydride in Diels Alder synthesis.

Crotonic acid : The name is derived from its occurrence in croton oil as a glyceride. It also occurs in the essential oils of the fermented tobacco leaf and in Kohlrabi. It is formed among other compounds in the dry distillation of wood and from crude wood tars. It has been detected in a patch of infertile soil in Texas. It is commonly prepared by the oxidation of crotonaldehyde.

It is mainly used in the preparation of synthetic resins, surface coatings, plasticizers and pharmaceuticals. It is used as a softening agent in synthetic rubber.

Knowledge of natural occurrence of these aliphatic and aromatic acids and corresponding compounds in both animal and plant matter has led bio-organic chemists to extensive studies in phytochemical and zoochemical (especially those directed towards their role in various matabolism and other vital processes) and organic chemist to find with them as many applications as possible in various fields(such as chemical, pharmaceutical, polymer etc.). This has naturally triggered the explosive growth of numerous chromatographic methods for their separation and identification. In this thesis, separation of mixture of such acids is discussed mathematically in terms of various chromatographic quantities and correlated with the sorption coefficient ; a basic parameter in chromatography whose determination was carried out by sorption equilibrium prior to the separation study. The separation possibilities of closely related acids are given in terms of resolution.