PART I

INTRODUCTION

1.1
The Object

The object is to contribute to the sorption studies with ion exchange resins and the application to separations.

1.2 Synthetic ion exchange resins : (1-17).

Ion exchange materials are of a wide variety. These may be inorganic or organic and of different shape and size. The common general structural principle is a framework with electric surplus charge and mobile counter ions. However, the various types of materials behave markedly differently. Ion exchange resins 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. The ionic groups attached to the matrix may be of various types such as

$$-SO_3^- \ , \ -COO^- \ , -PO_3^{-2} \ , -AsO_3^{-2}$$

for cation exchangers and

$$-NH_3^+ \ , \quad >NH_2^+ \ , \quad >N^+< \ , \quad >S^+$$

for anion exchangers. Hence, ion exchange resins are crosslinked polyelectrolytes. They are insoluble, but have a limited swelling in water, depending on the crosslinking. The ion exchange behaviour of the resins is mainly dependent on the nature of the fixed ionic groups.

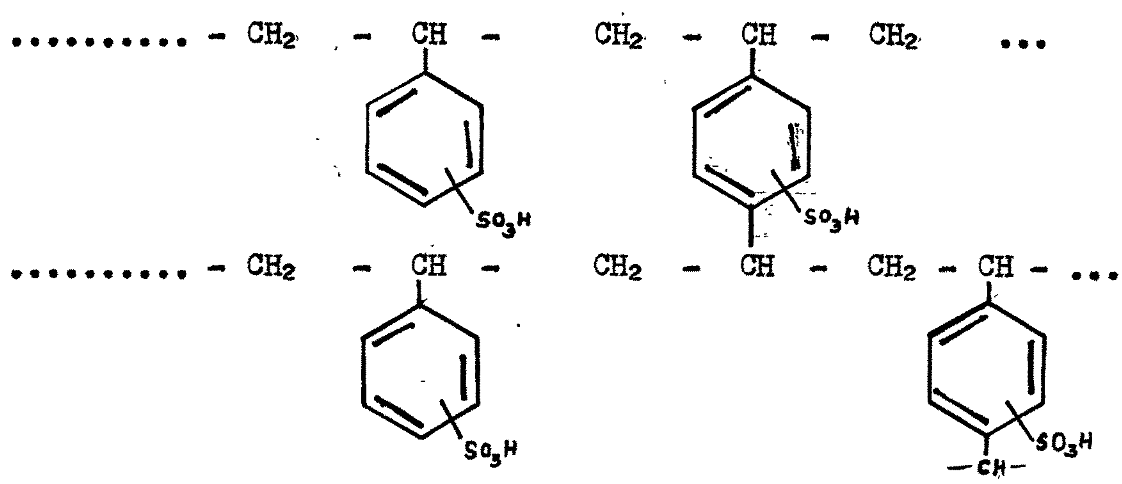
Commercial ion exchangers are insoluble solids. Recently liquid ion exchangers, such as long chain aliphatic amines and fatty acids or alkyl phosphates have become of interest.

Synthetic resins in general, have superior chemical and mechanical stability, exchange capacity, exchange rates and versatility. Inorganic materials possess better thermal stability and resistance to radiation.

A wide variety of ion exchange resins have been prepared and some are available commercially under various trade names.

The synthesis of ion exchange resins should yield a three dimensional, crosslinked matrix of hydrocarbon chains carrying ionic groups. The resins can be prepared by condensation polymerisation or addition polymerisation and the ionogenic groups can be introduced, before, during or after the polymerisation. These groups may be of one or more types giving monofunctional or multifunctional cation exchange or anion exchange or amphoteric resins. Most of the earlier cation exchange resins were condensation products of phenol derivatives and aldehydes. Most of the present commercial resins are addition polymers prepared from vinyl monomers. These resins have a better chemical and thermal stability than the condensation polymers and their degree of crosslinking and particle size can be more easily controlled.

The monofunctional sulfonic acid cation exchange resins available are crosslinked polystyrenes with sulfonic acid groups, introduced by sulfonation of the polymer. The crosslinking agent used is divinylbenzene. Amberlite IR-120, Dowex 50, Nalcite HCR, Permutit Q, Duolite C-20 and C-25 and Lewatit S-100 are resins of this type. The structure may be imagined as :



Pure divinylbenzene is not readily available, hence the resins are prepared with a commercial product consisting of a mixture of the different divinylbenzene isomers (about 40 to 55 %) and ethylstyrene (about 60 to 45 %). Ethylstyrene is also incorporated into the matrix.

By varying the divinylbenzene content, the degree of crosslinking can be adjusted. The nominal DVB content is used to indicate the degree of crosslinking. It refers to the mole per cent of pure divinylbenzene (not of the commercial product) in the polymerisation mixture. Resins with low degree of crosslinking swell strongly and resins with high DVB content swell much less.

The copolymer beads are prepared by the pearl polymerisation technique. The monomers, from which stabilisers have been removed, are mixed and a polymerisation catalyst, such as benzoyl peroxide is added. The mixture is then added to a thoroughly agitated aqueous solution at a required temperature (usually 85° to 100°C.). The mixture forms small droplets, which remain suspended. A suspension stabiliser (gelatin, polyvinyl alcohol etc.) in the aqueous phase prevents agglomeration of the droplets. The size of the droplets depends mainly on the nature of the stabiliser, the viscosity of the solution and the agitation and can be varied within wide limits. The polymer is obtained in the form of fairly uniform beads.

The sulfonation of the beads is simple, if proper precautions are taken. The cracking of beads may be avoided by first swelling the beads in an organic solvent such as toluene, nitrobenzene etc. It is advisable to transfer the sulfonated beads first to a highly concentrated electrolyte solution, which causes less swelling and then to dilute the solution stepwise. Sulfonation with concentrated sulfuric acid or chlorosulfonic acid results in practically complete monosulfonation of all the benzene rings.

Highly porous, macromolecular ion exchange resins are prepared by a variation in the conventional pearl polymerisation technique. An organic solvent, which is a good solvent for the monomers, but a poor solvent for the polymer is added to the polymerisation mixture. As polymerisation progresses, the solvent is squeezed out by the growing copolymer regions. In this way, spherical beads are obtained with wide pores which permit access to the interior of the beads even when nonpolar solvents are used.

The recent Amberlyst ion exchange resins are of this type.

Cation exchangers with specific preference for certain cation can be made by introducing groups which form strong complexes, preferably chelates with these cations. Resins with chelating iminodiacetic acid groups are now commercially available.

Most of the earlier anion exchange resins were condensation products of aromatic or aliphatic amines and aldehydes, dihaloparaffins or haloepoxides. Most of these contains weakly basic groups.

The more important anion exchangers are crosslinked polystyrenes, into which strongly or weakly basic groups are introduced by chloromethylation and subsequent amination. Reaction with tertiary alkyl amines gives strong base quarternary ammonium groups and reaction with primary or secondary alkylamines or ammonia gives weak base amino groups. Anion exchangers with strong base quarternary phosphonium and tertiary sulfonium groups have also been prepared.

Amphoteric ion exchangers contain both acidic and basic groups. Snake cage polyelectrolytes are a novel variety of amphoteric resins. These are prepared from conventional ion exchangers by polymerisation of monomeric counter ions within the resins.

For specific purposes ion exchangers in the form of pellets, rods, belts etc. have been prepared by cementing ion exchange particles together with an inert binder or by impregnating suitable supporting carriers.

Ion exchange membranes have been prepared by various methods. The membranes may be homogeneous or heterogeneous and have become of significant interest particularly for desalination of water.

1.3 Sorption of weak and nonelectrolytes : (17-133)

Sorption of nonelectrolytes :

A quantitative theory for nonelectrolyte sorption on ion exchangers has not yet been developed. However, general rules have emerged, which may explain qualitatively in terms of physical forces and interactions and with due caution, qualitative prediction of sorption equilibria can be made.

In the absence of interactions of any kind, the molal distribution coefficient should be unity; actually it is rarely so and the various interactions which cause deviations from ideality are discussed below.

Ionic solvation and salting out :

The fixed ionic groups and the counter ions in the ion exchangers form solvation shells and hence, only a section of the total internal solvent is free, in which the nonelectrolyte is dissolved. Hence, in the absence of any other interactions, the nonelectrolyte concentration in free water in the ion exchangers should be same as the nonelectrolyte concentration in the external solution. Thus the molality of the nonelectrolyte in the ion exchanger, which refers to the total solvent in the ion exchanger is less than that in the external solution. The nonelectrolyte is then "salted out".

"Salting out" effects should be more pronounced when the fraction of solvent in the ion exchanger, which is free, is smaller. This is the case when the resin is highly crosslinked and the counter ions are strongly solvated. Hence, with salting out as predominant effect, the molal distribution coefficient decreases with increasing degree of crosslinking and increasing solvation number of the counter ion.

If salting out effect is the prominent effect sorption of the nonelectrolyte solute can be increased by adding an electrolyte to the external solution. Addition of electrolytes results in salting out in the solvation also and thus counteracts salting out in the ion exchangers.

<u>Interactions with counter ions : Salting in and complex formation</u> :

In certain systems, exactly the opposite of salting out is observed. The mechanism, which is responsible for such "salting in" effect is not quite clear. Analogous effects are observed with ion exchange resins.

Interactions between nonelectrolyte and the counter ions become more pronounced when inorganic counter ions are replaced by organic ions. The most striking effects are noted when the solute forms complexes with counter ions.

London and dipole interactions :

Sorption of organic nonelectrolytes with hydrocarbon groups by ion exchange resins with hydrocarbon matrices is likely to be affected by two kinds of interactions. First, sorption is favoured by London interactions between the solute and the matrix. These forces are rather weak. A second and stronger contribution may come from dipole-dipole interactions of the polar solvent molecules with one another and with polar groups of the solute. The result of such interactions is that the hydrocarbon groups tend to coagulate or to be squeezed out of the polar solvent into a phase boundary. Both the London and the dipole interactions favour local adsorption of the hydrocarbon groups of the solute on the matrix and this enhance the sorption of the nonelectrolyte. Both interactions are more pronounced when the hydrocarbon group of the solute is larger, provided that the polar group remains the same. Hence, in a homologous series, the distribution coefficient usually increases with increasing molecular weight of the solute, atleast as long as sorption is not limited by molecular size effects.

London forces are specific interactions and depend on the molecular structure of the solute and the matrix. Different types of resins may widely differ in their sorption behaviour. Strong sorption may be expected when the chemical configuration of the solute and the matrix are similar. Large molecules with very strong affinity may even be sorbed irreversibly.

Molecular size, swelling pressure and sieve action :

The molecular size of the solute, in combination with the crosslinking of the resin, may considerably influence the sorption of the nonelectrolyte. The interior of the swollen resin is under rather high swelling pressure, which tends to squeeze the solvent and solute molecules out of the resin. Large molecules are strongly affected. This may be expressed by the equation,

$$\pi V_N = - RT \ln \frac{\bar{a}_N}{a_N}$$

A given swelling pressure π reduces the internal activity $\bar{a}_N$ of a species N more strongly, if the partial molar volume V_N of the species is large. The equilibrium swelling pressure, in turn, is high if the resin is highly crosslinked. With resins of moderate crosslinking and smaller nonelectrolyte molecules, this swelling pressure effect is rather small and is often overshadowed by other interactions which favour soeption of larger molecules. However, with increasing size of solute molecule or increasing degree of crosslinking, the effect becomes more important. The distribution coefficient in a homologous series may then have maximum value at medium molecular size.

Sorption of larger molecule is further restricted by the purely mechanical sieve action of the matrix. Molecules, which are too large for passing through the meshes of the matrix are excluded by the resin. Ofcourse, sieve action does not impose a sharp limit on the molecular size of the solute, since the mesh width of the matrix is not uniform. Swelling pressure and sieve effects are hence, difficult to distinguish. Also, the sorption rate becomes very low, when the molecular size of the solute approaches the critical range. Hence, uptake of large molecules under ordinary experimental conditions may be low, because sorption equilibrium, no matter how favourable, is not attained.

Dependence on solution concentration :

The uptake of the solute by the resin increases with increase in the concentration of the solution. The sorption isotherm usually has a negative curvature. This is particularly true for solutes which are strongly sorbed even from dilute solutions. Here, the saturation of the resin is fairly complete at relatively low solution concentrations, so that the isotherm flattens out after an initial steep rise. However, in a number of cases, isotherms with positive curvature are observed. Usually, a Langmuir or Freundlich isotherm can be fitted reasonably to the experimental results.

Dependence on temperature and pressure :

The effect of temperature on sorption equilibria is complex and has not yet been studied systematically. Not only the heat of actual sorption process is involved but also the temperature dependence of swelling, solvation and in some cases, of dissociation of ion pairs or complexes in the resin. Usually the temperature dependence of sorption is small. In case of strong specific sorption, the temperature coefficient is likely to be negative.

The effect of pressure on sorption of solutes has so far received little attention. However, one may expect that the pressure dependence is insignificant, since sorption usually occurs without much change in the volume of the total system.

Sorption of weak electrolytes :

Weak electrolytes are little affected by Donnan exclusion and thus are sorbed in essentially the same way as nonelectrolytes. The dissociation of weak electrolytes and hence their uptake by ion exchangers depends on the pH of the solution. The pH dependence can be used for elution. Weak electrolytes can also be sorbed, without simultaneous ion exchange, by resins containing univalent counter ions.

1.4 Chromatography with ion exchange resins : (2,3,8,11)

Chromatography is a technique in which resolution of a mixture is achieved by virtue of difference in migration rates of the components in a packed column.

Ion exchange chromatography has played an important role in the isolation and identification of transuranic elements and separation of rare earth elements. A number of organic substances have been separated by chromatography with ion exchange resins where the mechanism may be sorption or ion exchange.

In conventional chromatography the mechanism is sorption and desorption, the components of the mixture are reversibly sorbed by the solid sorbent and can be eluted with pure solvent. In ion exchange chromatography, the mechanism is stoichiometric exchange of counter ions; the counter ions of the mixture when taken up by the ion exchanger liberate the original counter ion and can only be eluted by an electrolyte since other counter ions are needed to take their place in the resin. It is difficult to make clear distinction between the two types since most of the conventional sorbents are not nonionic and most ion exchange processes are accompanied to certain extent by sorption or hydrolysis.

Chromatographic columns can be operated by various different techniques important amongst them are :

1. Displacement - Development :

In this technique to separate the different counter ions, an ion exchanger is chosen which has some selectivity. The ion exchange bed is converted to, say, the A form, where A is a counter ion which has less affinity for the resin than the counter ions(B, C and D) of the mixture have. The mixture is loaded at the top of the column and the development is carried out with a counter ion 'E' which the resin prefers to the counter ions of the mixture, the selectivity sequence being $A < B < C < D < E$. The development agent E when fed to the column displaces the counter ions of the mixture with a self sharpening boundary. These in turn displace the counter ions A in the zone occupied by the mixture. Amongst the counter ions of the mixture, the ion exchanger retains the ion D more strongly and the ion B less strongly with the result that the ion D accumulates in the upper part and ion B in the lower part of the zone. On its way through the bed the zone separates into individual bands of counter ions in the sequence of selectivity. The bands follow one another without intervals and move at equal rates. The migration rate is determined by the flow rate, the feed concentration and the volume capacity of the ion exchanger and is independent of the nature of the counter ions. The boundaries are not ideally sharp and the small overlap which occurs, can be resolved by repeating the process in a smaller column.

High selectivity, high volume capacity and small particle size of the resin, low flow rate, low feed concentration and elevated temperature are favourable since they give sharp boundaries.

2. Elution development :

In this technique a small amount of the mixture containing, say counter ions B, C and D introduced at the top of the column with the resin in A form and developed with a solution of the counter ion A, the order of selectivity being $A < B < C < D$. The mixture separates into different bands which migrate at unequal rates and come farther apart while moving down the column. The bands are not sharp and flatten out while coming down. High selectivity of the exchanger gives greater difference in the migration rates and this helps in the separation. With high ion exchange rates and low migration rates sharp peaks are obtained.

Clear separations may be obtained with small particle size, high volume capacity of resin, low flow rate, low eluant concentration and elevated temperature. With increasing column length the separation efficiency is improved but the bands get flattened.

3. Frontal analysis :

In this technique a solution containing the ions B, C and D to be separated is passed continuously through an ion exchange column containing exchangeable ion A which are less strongly held than any of those in the mixture. The ions initially in the resin are therefore displaced down the column in front of the ions in the mixture, under these conditions, the more strongly an ion is held by the resin the less rapidly will it move down the column. The least strongly held ions therefore accumulate in an absorption band which moves down the column in front of the other ions in the mixture.

In frontal analysis only one of the constituents of the mixture which is least strongly held is separated from the other. This method, therefore, is not often employed, but is useful occasionally for the removal of strongly absorbed impurities from a solution containing a solute which is only weakly sorbed.

4. Partition chromatography :

In partition chromatography, a granular solid is used as the carrier for a stationary liquid phase. Chromatographic separations are achieved by virtue of differences in the distribution coefficients of the components of a mixture between the stationary liquid and the percolating solution. Upon development with a suitable solvent or agent the components emerge in the sequence of increasing distribution coefficients. As a rule, the elution development technique is used.

Ion exchangers can be used as the stationary phase in partition chromatography of weak and nonelectrolyte and even electrolytes. In such operations, the ion exchangers acts nearly as a sorbent and no ion exchange takes place. The use of ion exchangers is advantageous if they can distinguish more sharply than non-ionic sorbents between the components of the mixture, i.e. if the differences between the distribution coefficients of the components are greater. Ion exclusion, which is based on the pronounced dependence of the sorption strength on the degree of dissociation of the sorbate, is an extreme example of partition chromatography with ion exchangers.

The sorption characteristic of ion exchangers depend on the ionic form of the resin and the composition of the external solution. The resolution can often be enhanced by the use of particular development agents. Particular effects can be achieved by addition of water miscible organic solvents which may profoundly affect the distribution of both electrolytes and non-electrolytes. More recently, ion exchangers have also been used for partition chromatography with a stationary and a moving solvent that are immiscible with one another. For example, metals have been separated with partially or completely water swollen ion exchangers as the stationary sphase and kerosene solutions of alkylphosphoric acids or phosphin oxides as the moving phase. Such 'gel-liquid extraction' can be carried out with a wide variety of combinations of immiscible solvent pairs and with stationary solid as well as moving liquid ion exchangers.

Application of Plate theory :

The Plate theory was introduced to chromatography by Martin and Synge (136) and to ion exchange chromatography by Mayer and Tompkins (134) and was refined by Glueckauf (135).

According to this theory the column can be considered as consisting of number of theoretical plates (N) in each of which the average concentration (c) of solution in the pores can be considered as effectively in equilibrium with the average amount of solute sorbed by the resin. The effectiveness of the column can be judged by the number of theoretical plates it appears to contain and if N is known the elution curve can be predicted.

The rate of movement of the band down the column is inversely proportional to the equilibrium distribution coefficient Kd, defined by

$$Kd = \frac{\text{Concentration of the ion in the resin(meq.per g.)}}{\text{Concentration of the ion in solution (meq.per ml.)}}$$

and hence, the rate of separation of two species say, A and B depends on the ratio of their distribution coefficients which can be determined by simple batch equilibrium experiment.

The effective number of theoretical plates N , in the column can be determined by a study of the elution curve for a suitable species say, A. According to theory the shape of the elution curve is given approximately by

$$C = C_{max} \left[-\frac{N}{2} \quad \frac{(V_{max} - V)^2}{V\,V_{max}} \right]$$

where C concentration of the species in the effluent flowing from the column. V the volume of eluant passed through column. C_{max} and V_{max} are the co-ordinates of the centre of the band. The position of the maximum is given by

$$C_{max} = \frac{m}{V_{max}} \sqrt{\frac{N}{2\pi}}$$

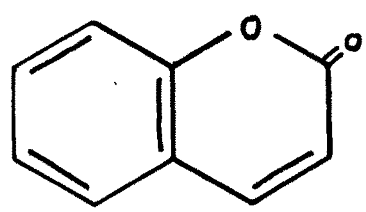
m is total quantity of the given solute in the band is equal to the area under the elution curve and the band width β at the concentration C_{max}/e making use of the relationship:

$$N = 8 \left(\frac{V_{max}}{\beta} \right)^2$$

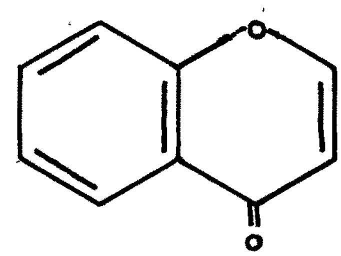
N can be determined. Since N is proportional to the length of the column, the improvement of separation obtainable by increasing the length can be calculated.

1.5 Coumarins (137, 138)

The fusion of a pyrone ring with a benzene nucleus gives rise to a class of heterocyclic compounds known as benzopyrones, of which two distinct types are recognized ; (1) benzo-α-pyrones commonly called coumarins and (2) benzo-γ-pyrones, called chromones, the latter differing from the former only in position of the carbonyl group in the heterocyclic ring.



Benzo-α-pyrone



Benzo-γ-pyrone

Representatives of these groups of compounds are found to occur in the vegetable kingdom, either in free or in the combined state. Coumarin, the parent substance of the benzo-α-pyrone group, was first isolated from tonkbeans in 1820. Several coumarin derivatives have been found to be widely distributed in the plant kingdom. Particularly the plants belonging to the natural orders of Orchidaceae, Leguminoceae, Rutaceae, Umbellifereae and Labiatae are rich in sources of naturally occuring coumarins. Coumarins and its derivatives are substances of potential value for synthetic purposes. Their easy accessibility opens the way through suitable reactions to the synthetic preparation of other heterocyclic compounds.

Coumarins have been found to be physiologically active for animals as well as men. It has been observed that coumarin acts as a narcotic for rabbits, frogs, earthworms and many other animals. It is a sedative and hypnotic for mice. It has toxic effect on man as well as dog.

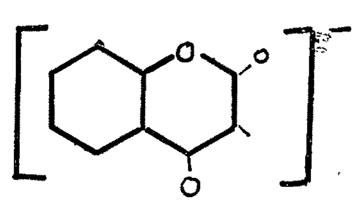
Some hydroxycoumarins possessing the power of absorbing ultraviolet light are used as medicinals in skin deseases. Some coumarins in the plant play the important role of protecting the plant from harmful effects of the short wave radiation.

1.6 Ultraviolet absorption spectra of coumarins :

Tasaki (139) studied the absorption spectra of the substituted coumarins in alcoholic solution. Coumarin, hydroxy and methoxycoumarins, dihydroxycoumarin, esculin, esculetin, acetylcoumarin, diacetylesculetin and methylene dihydroxyphenylcoumarin were studied. Coumarin showed two absorption maxima.

Mangini and Passerini (140) have reported the ultraviolet absorption maxima and log ϵ for coumarin (I), its 3-, 4-, 5-, 6-, 8-Me, 3-, 4-, 6-, 7-Cl and 3-, 4-, 6-, 7-MeO derivatives in ethanol, C_6H_{14}, 60 % $HClO_4$ or H_2SO_4 (1:10^5).

Examination of ultraviolet spectra by Chemielewska and Ciecierska (141) showed that the three substituted derivatives of 4-hydroxycoumarin in 96 % ethanol were completely ionised with formation of an



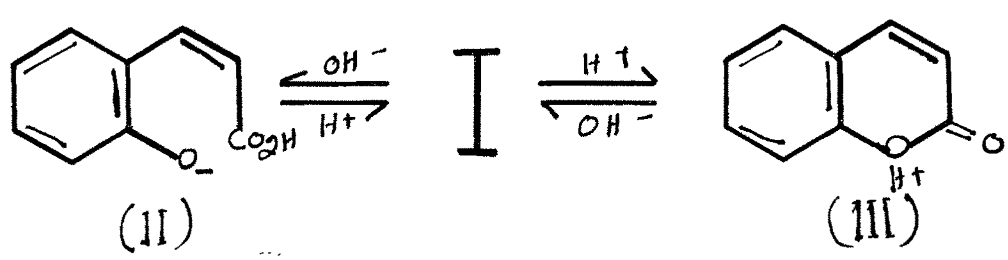
ion

5-, 6- and 7-hydroxy(I), methoxy(II), methyl(III) and acetoxycoumarins(IV) and 5,7-, 6,7- and 7,8-dihydroxy(V), dimethoxy(VI), dimethyl(VII) and diacetoxy(VIII) coumarins were prepared by Nakabayashi, Tokoroyama, Miyazaki and Isono (142) and the ultraviolet absorption spectra were studied in 95 % ethanol. (III), (IV), (VII) and (VIII) showed spectra similar to that of coumarin, irrespective of the position or number of the substituents; (I), (II), (V) and (VI) on the other hand showed complicated spectra according to the position and number of substituents present. On the assumption that the two absorption bands of coumarin at 270 and 312 mμ were those of benzene around 200 and 240-260 mμ which had shifted to these regions, the ultraviolet absorption spectra of these coumarin derivatives were qualitatively explained according to the theory regarding light absorption.

Jacobson and Amstutz (143) recorded ultraviolet absorption spectra of a series of thirteen new coumarins and concluded that neither addition of 4-methyl group nor of 6-alkyl groups have significant effect on the spectra.

Goodwin and Pollock (144) studied the ultraviolet absorption spectra of a series of coumarin derivatives to identify unknown fractions isolated from roots. They concluded that saturation of the double bond at the 3,4-position in the coumarin nucleus greatly reduces absorption at wavelengths larger than 300 mμ, secondly, 4-Me substitution has very little effect upon the absorption and thirdly, there is a great similarity between absorption spectra of hydroxy derivatives and their ethers.

Cingolani (145) studied the ultraviolet absorption spectra in ethanol, 0.1N NaOH and 60 % $HClO_4$ solution of coumarin(I) and its following derivatives; 3-Me, 3-Me-6-MeO, 3-Me-7-MeO, 3-Me-8-MeO, 3-Me-6,7-diMeO, 3-Me-6,8-diMeO, 4-Me, 4-Me-6-MeO, 7-MeO, 4-Me-5,7-diMeO, 4-Me-6,7-diMeO and 4-Me-7,8-diMeO and has given interpretation in terms of electronic structures. Variation of spectra in acid and alkaline solutions agree with the possibility that coumarins could ionize as bases or acids (by ring opening). Spectra in alcoholic solution were attributed to (I), in 0.1N NaOH to (II) and in 60 % $HClO_4$ to (III). The position of MeO



in the ring influences the spectra. 6-MeO derivative caused bathochromic shifts in the first band below 250 mμ; 8-MeO derivatives caused hypsochromic shifts. The maxima bands of all 3-MeI derivatives were shifted to greater wavelength in contrast with 4-Me derivatives. The position of the -Me caused a shift to greater wavelength. This was evident with the lactone form of 3-MeI derivatives and explained by admitting that the equilibrium for 3-MeI is shifted towards quinoid form, whereas with 4-MeI it was shifted to non-quinoid form.

Nakabayashi (146) has shown that the absorption band of coumarin(I) or Me(I) in the shorter wavelength range shifted towards the visible range by the increase of the dipolar character of the solvent, while the absorption band in the larger wavelength range shifted towards the ultraviolet region. These characteristics agree with the regularity of the solvent effect observed in α, β unsaturated ketone and so it is known that there is some ketonic property in I.

Ganguli and Bagchi (147) studied the ultraviolet absorption maxima and log ϵ for coumarin(I), 3-MeI, 3,4-diMeI, 4,8-diMeI and 4,6-diMeI in 95 % ethanol solution. Absorption measurements in region 220-340 mμ showed that it is possible to distinguish between them on the basis of absorption characteristics.

Cingolani (148) examined the ultraviolet absorption spectra in ethanol, in 0.1N NaOH and after acidification of alkaline solution for coumarin and following derivatives : 4-Me-8-OH, 8-OH, 4-Me-5,8-$(OH)_2$, 3-Me, 4-Me, 4-Me-6-OH-5,7-$(MeO)_2$ and 4-Me-5-OH. The curves are characteristic enough for any of these compounds to be identified in an unknown solution, especially if the behaviour in alkaline solution is examined, since the lactone ring opens and the hydroxy cinnamic acid formed isomerizes at different rates according to structures. After isomerization the original lactone can only be recovered by acidification if a 5-OH group is present.

In comparative studies of 4-OHI by Böhme and Severin (149), the long wave absorption bands were found to be moved bathochromically by introduction of a -OH group in 6 or 7 position, while the corresponding maximum of -5 and -8-OHI lies at shorter wavelengths. As with coumarin itself 3 bands appear with 5-, 6-, and 8-OH coumarin. 7-OHI does not produce the medial bands with an inflection at 240 mμ DiOH-trans-cinnamic acids are optically very similar to their methylated derivatives, but big differences were noted between -OHI and diMeO-cis-trans-cinnamic acids.

Cingolani and Gaudiano (150) studied that all the coumarin derivatives in alcoholic solution absorbed strongly between 250-350 mμ, because of their lactone structure coumarin (and its Me-derivatives) has its sharpest maximum at 275 mμ and another at 310 mμ. 6-substitution by -OH and -MeO has a bathochromic effect and a maximum below 250 mμ appears. 7-substitution increases absorption near 310 mμ 8- or 5-substitution has a hypsochromic effect in 250-280 mμ region and causes another maximum to appear there. Disubstituted derivatives show typical curves combining the characteristics of the monosubstituted compounds. In alkaline solutions, a bathochromic effect is evident and this may go quickly or slowly, but is reversed upon acidification in some cases, whereas is not reversible in some cases. This irreversible change confirms the transition from a cis-O-hydroxycinnamic to a trans-O-hydroxycinnamic system.

Sen and Bagchi (151) studied the ultraviolet absorption spectra of coumarin(I), 7-OHI, 7-OH-4-MeI, 6-OH-4-MeI, 4-OHI, 4-OH-3-MeI, 3-OH- and 5-OH-4-MeI in ethanol. Absorption spectra of coumarin substituted by hydroxy group in the aromatic as well as heterocyclic nucleus in different positions showed bathochromic shift in the position of one or more of the principal bands.

Shah and Bafna (152) studied the ultraviolet absorption spectra of methyl-, methoxy-, and hydroxy-coumarins in methanol in the range 250-350 mμ. It was concluded that the absorption maxima were almost same for hydroxy and methoxycoumarins, if the substituents were 5, 6, 7 or 8 position; however the substituents position (5 or 8),(6 or 7) could be distinguished. It should be possible to distinguish isomeric monomethyl and dimethyl-coumarins from a study of their ultraviolet absorption data.

Dezelic, Trkovnik and Zovoko (153) found that the absorption after 300 mμ is caused by double bond at 3-4 position. It was found that stabilization or aromatization of lactone ring in the coumarin system, the absorption after 300 mμ disappears owing to a partial or complete localization of π electrons in the 3-4 position. The benzene ring in the 4-OHcoumarin plays an important role in the stabilization or aromatization of the lactone ring.

Mehta, Hegde, Bhatt, Patel and Bafna (154) studied the ultraviolet absorption spectra of 4-OHI and derivatives of 4-OHI. In methanol coumarin has two maxima, at 274 mμ and 311 mμ. In 4-OHI these are replaced by three maxima at 270, 280 and 302 mμ, 4,7-diOHI gives two maxima and when 3-Me group is introduced in 4-OHI it gives a single maximum.

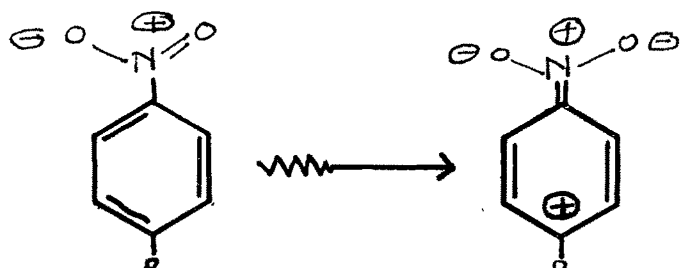
In 10 % aqueous methanol, the values of λ and ϵ for maxima are practically unaffected by pH over the range 7-1, but for 4-OHI and substituted 4-OHI the λ and/or ϵ values for maxima significantly changed except below pH $\sim$2. This may be attributed to a decrease in the dissociation of the 4-OHI with decrease in pH.

1.7 Ultraviolet absorption spectra of nitro toluenes :

Doub and Vandenbelt (168) have studied a number of m- and o- disubstituted benzene derivatives. The trend established separately in each type are similar and consist of three families of points corresponding to secondary, first primary and second primary bands. m- and o- disubstituted compounds containing nitro group occupy an exceptional position among the simple benzene derivatives. The unique feature of the plot of these nitro compounds is the appearance of an additional family of bands at short wavelength. It may arise from the nitro group itself, which is known to absorb strongly in this region or it may represent the displacement of a band of benzene occuring in the spectrum of that compound at shorter wavelength than the 183.5 mμ band.

A study of the ultraviolet absorption spectra of a number of derivatives of toluene by Francisco Poggio Mesorana and Francisca Marquet (171) has shown that ortho substituted toluene tend to displace the absorption spectrum into the ultraviolet region, while the para substitution tend to displace it towards longer waves. In case of nitro toluenes wide absorption bands were found, which occupied a good part of spectrum.

Schubert, Robins and Haun (172) have studied the influence of solvent on the principal ultraviolet band of p-nitro toluene. The principal band in the ultraviolet spectrum which occurs at 210 $m\mu$ for alkyl nitrobenzene is due to a $\pi \longrightarrow \pi^*$ transition to a dipolar excited state and is represented by the valence bond structure I and II for ground and excited states respectively.



(I) (II)

The general band width and shape did not change as the solvent was changed, although there was some flattening at the very peak in polar solvents.

The solvent has a considerable influence on the apparent relative effect of alkyl group in the system.

Over the wide range of solvents used, the decrease in ν_{max} (maximum frequency) for nitro toluene in proceeding from heptane to 70 % perchloric acid amounts to 13,900 cal/mole. It is granted that the linearity of the ν plot for nitro toluene is a result of a linearity between the response of the excitation energies of the methyl and unsubstituted compounds to solvent change, then it follows that the methyl substituent is releasing electrons in a linear proportion to changing electron demand (ρ changing with solvent) over a very considerable change in medium. Thus it would appear that either (1) the methyl group is releasing electrons by a single mechanism or (2) if more than one mechanism are operative, these are acting in constant proportion with changing solvent. Therefore, the concept of solvent enhancement of C-H hyperconjugation does not satisfactorily explain the results for this system. It follows also that steric hinderence to solvation is negligible with the methyl substituent.

Pivovarav and Ordyntseva (174) investigated the ultraviolet absorption spectra of P-nitro toluene in varied concentration in a number of solvent and found that the absorption bands shifted to smaller wavelengths on transition from a polar to a non-polar medium. The influence of concentration on absorption spectra is very small.

Conduit (176) has reported that the absorption curves of nitrobenzene and nitro toluene in the ultraviolet consisted mainly of a single intense maximum in the 210-80 mμ range with one or more inflections on the long wavelength side. The λ_{max} is 269 mμ for nitrobenzene, but < 210 mμ for o-dinitrobenzene, 242 for m-dinitrobenzene and 265 mμ for p-dinitrobenzene.

In nitro toluene the Me group enhances the conjugation of nitro group. This shifts λ_{max}, p-nitro toluene 283.5 mμ. In the ortho position some steric hinderence is met,

λ_{max}, o-nitro toluene is 265 $m\mu$.

Kiss and Horvath (181) have reported that the electronic spectra of C_6H_6 derivatives, containing the NO_2 group as an electron acceptor and Me as electron donar, consist of B, K and E bands ($\pi \rightarrow \pi^*$ transitions); further they contain the band corresponding to $n \rightarrow \pi^*$ transition of a lone pair electron of NO_2 group.

Jatkar and Phansalkar (180) have studied ultraviolet absorption spectra of nitro toluenes in ethanol and dioxane. They showed that the absorption maxima shifted towards shorter wavelengths in dioxane than in ethanol. The wavelength of maximum absorption in each solvent varied linearly with the dipole moments of the compounds.

Table 1.1

Values of λm and $\log \epsilon$ for ortho-, meta- and para-nitrotoluenes

Ref.No.	Compound :	o-nitro		m-nitro		p-nitro	
	solvent	λm	$\log \epsilon$	λm	$\log \epsilon$	λm	$\log \epsilon$
165	iso-octane	250	3.78	256.5	3.91	264	4.01
166	dil.methanol	266	3.72	273.0	3.86	-	-
174	5 % ethanol-water mixture	265	3.74	274.0	3.86	283.5	3.97
176	Methanol	-	-	265.0	3.89	273.5	3.99
177	Methanol	255	3.69	264.0	3.89	274.5	4.00
177	2-Propanol	-	-	263.5	3.90	273.5	4.01
177	Dioxane	254	3.73	264.5	3.91	274.5	3.99
177	Cyclohexane	250	3.84	257.0	3.85	266.0	4.02
180	Water	-	-	-	-	285.0	3.96
180	ter-butanol	-	-	-	-	271.5	3.97

1.8 Summary of the earlier work done in this laboratory :

Ultraviolet absorption spectra of some substituted (hydroxy, methoxy and/or methyl) coumarins were studied in methanol and aqueous methanols. The ultraviolet absorption provided a convenient method for their estimation in dilute solutions.

Sorption equilibria of coumarin in water and aqueous methanols on sulfonic acid and carboxylic acid cation exchange resins of different degree of crosslinking and counter ions were studied (113).

Sorption isotherms of substituted coumarins in resin Dowex 50X4 (sulfonic acid cation exchange resin further referred to as X4) in aqueous methanol have been studied. The sorption of hydroxycoumarins was lower than that of corresponding methoxy or methylcoumarins. It was also observed that sorption decreased as the per cent content of methanol of the solvent was increased or dielectric constant of the solvent was decreased. The sorption equilibria of the 4-hydroxycoumarins have been studied on sulfonic acid cation exchange resin X4, in aqueous methanols and in 10 % aqueous methanol at low pH. The sorption for some 4-hydroxycoumarins increases at low pH (158).

The sorption equilibria on sulfonic acid resin X4 in 16 ionic forms in 10 % aqueous methanol and on ammonium form of the resin in aqueous methanols have been studied.

Column study of substituted coumarins was carried out on a column of sulfonic acid cation exchange resin X4, using 10 % aqueous methanol as solvent and eluant. The elution band became broader and reduced in height and break through volume increased as the value of B increased. Based on these elution studies, two and three component mixtures were separated.

What is B,

Column sorption-desorption of some coumarins in 10 % aqueous methanol was studied on a chloride form of a strongly basic anion exchange resin Amberlite IRA-400. The sorption was in the order methoxy, methylcoumarin < monohydroxycoumarin < dihydroxycoumarin. On the basis of these observations two and three component mixtures were separated (104).

The column elution behaviour of some coumarins on a column of sulfonic acid resin X4, in ammonium form has been studied in aqueous methanols as solvent and eluant. The break through volume and elution band width decreases with increase in per cent methanol content of the solvent. Fair separation in two component mixtures were obtained.

1.9 Nomenclature :

X = the per cent of combined divinylbenzene in the styrene copolymer used as the resin matrix.

M = methanol.

TM = 10 % aqueous methanol.

v.v. = sample volume equal to void volume.

W_s = the solute content in milli moles in 100 ml. of effluent sample.

W = the solute content in milli moles in 100 ml. of the solution initially sorbed on the column.

U_s = the solute content in milli moles in 25 ml. of effluent sample.

U = the solute content in milli moles in 25 ml. of the solution initially sorbed on the column.

λ = wavelength in millimicron ($m\mu$).

ϵ = extinction coefficient.

Co = initial concentration in gram moles per litre.

Ce = equilibrium concentration in gram moles per litre.

S = the moles of the solute sorbed per equivalent of the resin = (Co - Ce) / Cr.

Cr = the capacity of the air dried resin in equivalents per litre of the solution

B = (Co - Ce)/Ce · Cr.

K = equilibrium constant.

E.R. = elution range.

W_F = amount eluted out in the first band

P_F = per cent of the total amount that eluted out in the first band = 100 W_F / W.

I = coumarin.