SUMMARY

6. Summary :

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

The present study includes, ultraviolet absorption spectra, sorption equilibrium study and column study of (A) coumarins and (B) nitrotoluenes.

A.1 Ultraviolet absorption spectra :

Ultraviolet absorption spectra of substituted coumarins were studied in aqueous, aqueous methanols, methanol and 10 % methanol over the pH range 7-1.

The substitution of a hydroxy group in coumarin nucleus markedly changes the ultraviolet absorption values. The substitution of a methyl group causes a small change in the value of λm and $\log \epsilon$. When a hydroxy group is converted to a methoxy group the value of λm is decreased by a small amount and the value of $\log \epsilon$ is altered by a small amount only.

The change of solvent from methanol to 10 % aqueous methanol does not make substantial difference in ultraviolet absorption. It appears that the change in solvent-solute interaction accompanying the change in dielectric constant of the medium when the solvent is changed from methanol to 10 % aqueous methanol has relatively small effect on ultraviolet absorption of the coumarins studied.

The change of pH from 7 to 1 has no measurable effect on the ultraviolet absorption of coumarins except for 4-hydroxy coumarin and coumarin-carboxylic acids.

The observation that change of pH from 0.5 to 7 has relatively little effect on the ultraviolet absorption of 7-hydroxy-4-methylcoumarin-6-carboxylic acid and 7-hydroxy-4-methylcoumarin-8-carboxylic acid implies that the ultraviolet absorption of the acid molecule and acid anion may not differ significantly.

For 4-hydroxycoumarins in 10 % methanol at low pH, the values of λm are either same or are increased by small amount as compared to those in methanol solution. When the pH is reduced from 7 to 1, the values of λ and logϵ for maxima for ultraviolet absorption may vary measurably. At the invarient wave length the value of log ϵ is not affected by pH in the range from 7 to 1.

A.2 Sorption equilibrium study :

The sorption equilibria of coumarins have been studied with the resin Dowex 50W styrene divinylbenzene copolymer based sulfonic acid cation exchanger in hydrogen form of degree of crosslinking from 4 to 16 in aqueous and aqueous methanol solution in absence or presence of hydrochloric acid.

The data indicate that in most cases the sorption of the solute as well as the slope of the plot of B against X decreases as the degree of crosslinking increases. This may be attributed to the decrease in the water sorption in the resin with increase in degree of crosslinking. The extent of decrease in the value of B with increase in degree of crosslinking may be considered to depend mainly on relative contribution of two effects : the decrease in the water sorption of the resin and an increase in the interaction of the hydrocarbon net work of the resin and the organic solute with increase in degree of crosslinking of the resin. It appears that the first effect is relatively more pronounced than the second, leading to overall decrease in the sorption of the coumarins with increase in degree of crosslinking. The actual extent however may vary in some cases.

It is indicated that the value of B for the sorption decreases with increase in per cent content (by volume) of methanol in the solute. This may be attributed to the decrease in dipole-dipole interactions with decrease in the dielectric constant of the solvent medium.

In case of some of 4-hydroxycoumarins and coumarin-carboxylic acids the value of B increases as the pH of the solvent is reduced by the presence of hydrochloric acid.

In general, it is also observed that the conversion of the hydroxycoumarin to the corresponding methoxycoumarin increases the value of B about 2 to 1½ times, which implies that the separation of the mixtures of hydroxycoumarins and corresponding methoxycoumarins may be feasible.

The sorption equilibria of some coumarins on ion exchange resin of degree of crosslinking 4 with different organic counter ions in 10 % aqueous methanol solutions were studied. The sorption is significantly increased in some cases as compared to that for resin in H^+ form. The order of sorption is :

5-OH-4-MeI $\geqslant$ 7-OH-4-MeI $\geqslant$ 6-OH-4-MeI

The extent of increase in the sorption depends on both, the organic solute in solution and organic counter ion of the resin. In some cases a difference in the sorption of the isomers as indicated by B values is significant and is of interest.

The relative variation in sorption as indicated by value of B for the coumarins in different conditions suggest that separation of mixtures should be feasible by suitable choice of experimental conditions. In particular the separation of position isomers should be of interest.

A.3 Column study :

Column elution runs on resin Dowex 50W X4 in hydrogen form in water, aqueous N/100 HCl, aqueous N/10 HCl as well as in aqueous methanol of different pH with two column lengths have been studied.

The results are in general, as expected from the values of B. The results indicate that as the value of B for a compound increases, in general, the break-through volume increases and the elution bands becomes broader and reduced in height. The increase in column length increases the break-through volume and the number of samples containing the solute, but the relative separation is improved. The results with aqueous methanol as solvent indicate that with increase in per cent content of methanol the break-through volume and the number of samples containing solute is reduced.

In the study of column elution of 4-hydroxycoumarins it is observed that some of the 4-hydroxycoumarins show two elution bands. This indicates that some of the 4-hydroxycoumarins resolved into two components.

It appears that 4-hydroxycoumarins exists in solution as a mobile equilibrium between coumarin and chromone. The relative amounts of coumarin and corresponding chromone determining the equilibrium constant may vary with the composition and pH of the solvent as well as the nature and position of the substituents in the 4-hydroxycoumarin nucleus.

The column study indicates that separation of the mixtures including those of some position isomers is possible. The separation of some mixtures has been carried out to illustrate the application of this technique.

B.1 Ultraviolet absorption spectra :

Ultraviolet absorption spectra of o-, m- and p-nitrotoluenes were studied in aqueous, aqueous methanols and methanol.

For mono nitrotoluene the value of λm is in the order :

$$\text{ortho} < \text{meta} < \text{para}$$

At relatively higher methanol content the value of λm is decreased and that of log ϵ is somewhat increased. The decrease in the value of λm may be attributed to the decrease in the dielectric constant of the solvent and hence, decrease in solvent-solute interaction.

The ultraviolet absorption measurements provide a convenient method for the estimation of nitrotoluenes in dilute solution and was used in sorption studies.

B.2 Sorption equilibrium and column study :

The sorption of three mono nitrotoluenes was studied with resin X4 in H^+ form in aqueous and aqueous methanol solution.

The sorption of ortho and para isomers is practically same and that of meta only somewhat higher, indicating that the sorption of the three isomers id not significantly different. The sorption in aqueous methanol was almost same with or without the presence of hydrochloric acid.

Mono nitrotoluenes can be sorbed from aqueous or aqueous alcoholic solution by the resin, but the relative sorption is not substantially different and extent of sorption decreases with decrease in dielectric constant of the solvent, implying that alcoholic or aqueous alcoholic medium should give fast elution.