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SUMMARY

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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 group of substances ubiquitous in the plant-kingdom and the recognition of this has stimulated the development of numerous chromatographic methods for their separation and identification. The study of molecular sorption on modern synthetic ion exchange resins, particularly styrene based ion exchangers, has provided a technique of potential interest for the chromatographic separation of molecular mixtures and prompted many research workers to try and turn it into economically and industrially feasible and acceptable processes.

The present work includes sorption equilibrium and sorption elution studies of some substituted benzoic acids. The work also includes ultraviolet absorption studies, effect of pH on the absorption spectra and the determination of isosbestic points (invariant wavelengths) as this serves as one of the best analytical methods for the estimation of dilute solutions of benzoic acids of variable pH.

1. Ultraviolet Absorption Study :

The ultraviolet absorption spectra have been taken in water and/or 10% aqueous dioxan (by volume) at different pH and in methanol.

The parent compound, benzoic acid, shows two absorption bands, of which the one near 230 nm is ascribed to an intramolecular charge transfer or electron transfer (E.T.) absorption and the other near 270 nm is the shifted benzene band. The ortho and meta isomers show two E.T. bands each, which exhibit the effect due to steric interaction (direct or indirect) and hydrogen bonding whereas para isomers show only one intense band. The spectra of disubstituted benzoic acids are determined by the nature and position(s) of the substituents and the effects due to steric interaction become more pronounced when the groups are in adjacent position to the carboxyl group.

From the spectral studies at different pH, the following general conclusions could be drawn :

A. Benzoic acid and the substituted benzoic acids carrying electronically complementory groups show a hypsochromic shift in the bands as the pH of the solution is increased, shifts being relatively less for the acids having an ortho hydroxy group. In the case of nitro benzoic acids the bands are shifted bathochromically.

B. At higher pH values the principal E.T. band of the ortho, meta and the disubstituted benzoic acids having an ortho substituent and no para substituent appears only as an inflection or is completely removed from the spectrum.

C. Benzoic acid and the ortho isomers of chloro, bromo and methylbenzoic acids do not exhibit isosbestic points. o-Hydroxy and o-methoxybenzoic acids exhibit two isosbestic points each ($\lambda_{inv.}$).

D. All the meta isomers show two λinv each and the second λinv is in the same order as that of λmax for the second E.T. band.

E. All the para isomers studied exhibit one λinv each.

F. The disubstituted benzoic acids containing a para substituent show two λinv each. The difference between the second λinv and the λmax for the principal E.T. band is almost a constant except for those acids in which the carboxyl group is sterically hindered.

G. The disubstituted benzoic acids which do not contain a para substituent show three λinv each with the exception of acids which contain bulky groups in 2,3- or 2,6-positions, where steric interaction may be responsible.

2. Sorption Equilibrium Study :

The sorption equilibrium studies have been carried out with the resin Dowex 50W-X4 (100/200), a styrene divinylbenzene based sulfonic acid cation exchange resin in the hydrogen form, in 0.01N aqueous hydrochloric acid and/or 10% dioxan in 0.01N aqueous hydrochloric acid (by volume).

The overall sorption depends on solute-resin, solvent-resin and solute-solvent interactions and these include London dispersion forces, dipole-dipole interactions, steric interaction and hydrogen bonding. The sorption of benzoic acids is thus influenced by the nature of the substituent(s) and its position(s) in the aromatic nucleus. From the study following general conclusions could be drawn :

A. In water solutions most of the acids undergo ionization and may be excluded from the resin phase because of Donnan membrane effect. Hence acidic solvents were used to suppress the ionization.

B. Lesser the solubility of a compound in the solvent the higher will be its sorption.

C. Polar substituents generally decrease the sorption of benzoic acid while the substituents which increase the organic nature increase it.

D. Acids in which the carboxyl group is sterically hindered show lower sorption.

E. Intramolecular hydrogen bonding between the carboxyl group and the ortho substituent may increase sorption.

F. Sorption of p-alkoxybenzoic acids increases with the chain length.

G. In p-halobenzoic acid series sorption increases with the size of the halo atom.

H. Sorption of the disubstituted benzoic acids depends on the position of the two groups with respect to each other and to the carboxyl group.

I. The sorption shows a decrease when the solvent is changed from 0.01N aqueous hydrochloric acid to 10% dioxan in 0.01N aqueous hydrochloric acid.

3. Sorption Elution Study :

The sorption elution studies have been carried out on columns of different bedlengths of the resin Dowex 50W-X4 (100/200) using 0.01N aqueous hydrochloric acid and/or 10% dioxan in 0.01N aqueous hydrochloric acid as solvent and eluent.

The results are used to correlate the sorption coefficient, B, with the various chromatographic quantities, viz,

(i) peak elution volume, V_{mo}, (ii) peak width, σ or β, (iii) peak height, Cm, (iv) number of theoretical plates, N, for the given column and (v) resolution, R_n, by the following equations :

$$V_{mo} = V_o + B.C \tag{1}$$

$$\sigma = k_1 \sqrt{BC} \ (1 + k_1\sqrt{B}) \tag{2a}$$

$$\beta = 2k_1 \sqrt{2BC} \ (1 + k_1\sqrt{B}) \tag{2b}$$

$$C_m = \frac{W}{k_1 \sqrt{2\pi BC} \ (1 + k_1 \sqrt{B})} \tag{3}$$

$$N = \frac{B.C}{k_2 \ (1 + k_1 \sqrt{B})^2} \tag{4}$$

$$R_n = \frac{\sqrt{C} \ (\sqrt{B_2} - \sqrt{B_1})}{3k_1 \left[1 + k_1 \dfrac{B_2 + B_1}{\sqrt{B_2} + \sqrt{B_1}} \right]} \tag{5}$$

where, V_o = void volume, C = total capacity of the resin in the column (equivalents) and W = total amount of the solute (millimoles) in the feed volume, $k_1 = \sqrt{V_f} / \pi$, $k_2 = V_f / \pi^2$, V_f = feed volume (liter).

Equation (5) indicates that Rn is proportional to C and reaches unity - a condition required for a satisfactory separation - if a sufficiently long column is used. The minimum value of C required for the separation of a given pair of solutes can be calculated by setting Rn = 1, in equation (5). However, if C_{min} is large, the whole process becomes time consuming and the detection of the zones, when the separation achieved, may become difficult due to dilution.

The study revealed that :

A. The separation of benzoic acids with different substituent(s) in the same position(s) would be easier, e.g. separation of m-hydroxybenzoic acid and m-methoxybenzoic acid.

B. The separation of position isomers of monosubstituted benzoic acids is possible in some cases, e.g. separation of o- and m-hydroxybenzoic acids.

C. The separation of the members of the homologous series can be achieved under suitable conditions.

D. Sterically hindered disubstituted benzoic acids can be separated from other isomers in which the steric effect is lesser or negligible, e.g. separation of 2,6-dihydroxy (γ-resorcylic), 2,4-dihydroxy (β-resorcylic) and 3,5-dihydroxy (α-resorcylic) benzoic acids.

Thus the technique provides a convenient and useful procedure for the separation of substituted benzoic acids and in general, should be applicable for the separation of other molecular families.

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