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 class of substances ubiquitous in plant and animal kingdom. This has led bio-organic chemist to extensive studies in phytochemical and zoochemical, especially those directed towards their role in various matabolism and other vital processes. They are also used in almost all synthetic organic products, either as part of the final composition or in one or more of the processing stages.

Recognition of the presence of organic acids and related compounds in many biological systems has naturally triggered the explosive growth of numerous chromatographic methods for their separation and identification. Molecular sorption on synthetic ion exchange resins is one of the most efficient methods which 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 process.

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 closely related acids, such as members of the homologous series,

position isomers and geometrical isomers, depending upon their sorption behaviour, have been explored. Also, attempts have been made to make the study useful both industrially and academically by postulating equations for the sorption and resolution.

1. SORPTION EQUILIBRIUM STUDY

In chromatography the distribution coefficient, here expressed as ' sorption coefficient B ', is a primary parameter and plays an important role in deciding the chromatographic behaviour of the solute. The sorption equilibria of some aliphatic and aromatic acids have been carried out with resin Dowex 50W ; a styrene-divinylbenzene copolymer based sulfonic acid cation exchange resin of nominal degree of crosslinking X, as 1, 2, 4, 8, 12 and 16, in hydrogen form, in suitable media ; such as distilled water, 0.01 N aqueous hydrochloric acid and 10 % dioxan in 0.01 N aqueous hydrochloric acid. A recently developed macroreticular ion exchange resin Amberlite-200, has also been tried to see its behaviour to the sorption and application to separation.

The observed sorption depends on solute-resin, solvent-resin and solute-solvent interactions and these include London dispersion forces, dipole-dipole interactions, steric interactions and hydrogen bonding. Thus, a complex behaviour is to be expected whose exact mechanism has still remained unknown. However in the present work, efforts have been made to reveal this phenomenon for closely related compounds by proposing the overall sorption as a product of two terms, a group term ; which is a summation of the increments contributed by each additional group and and a ground term ; which is function of the sorptive system, provided the molecular size is not too large to be excluded from the resin phase by seive action. This has made possible the study of nature of substituents and the effects due to their positions and various interactions. From the study following general conclusions could be drawn :

(A) Sorption of homologous series of dicarboxylic acids is found to follow the following equation,

$$-\frac{\Delta F}{2.303\ RT} = \log B = 0.24n_c - 0.12n_x - \log mX^{\gamma}$$

where n_c is the number of $-CH_2$ groups in the straight hydrocarbon chain, n_x is the number of terminal carboxylic groups, X is the degree of crosslinking of the resin used and m and γ are constants determined by the resin-solute-solvent system. Above equation indicates that :

1) the sorption of dicarboxylic acids increases with increase in chain length among the series.
2) the sorption equilibrium constant B could be related with free energy change and other thermodynamic properties.
3) the equation is equally valid for a series of monocarboxylic acids, as indicated by the involvement of n_x term in the equation.

4) the sorption decreases with increase in degree of crosslinking.

(B) Oxalic acid is an exception, indicating that the equation is valid from $n_c = 1$ and not from $n_c = 0$. This means that homology may not be operative untill the first $-CH_2$ group is introduced in the unique environment of ground molecule. i.e. second member (Malonic acid) of the series.

(C) Sorption is not measurably affected by the particle size of the resin.

(D) Sorption observed with macroreticular ion exchange resin is relatively less, therefore such resins are not desirable for chromatographic work where sorption is involved.

(E) Lesser the solubility of a compound in the solvent, the higher will be its sorption.

(F) Some of the benzoic acids in dilute aqueous solution undergo partial ionization and may be excluded from the resin phase because of the Donnan membrane effect. Hence, acidic solvents should be used to suppress the ionization.

(G) Sorption of disubstituted benzoic acid (B_{xy}) can be predicted from the sorption of corresponding mono substituted benzoic acids (B_x and B_y) and unsubstituted benzoic acid (B_u) by the following formula :

$$B_{xy} = \frac{B_x \cdot B_y}{B_u}$$

(H) Polar substituents generally decrease the sorption of benzoic acid, while the substituents which increase the organic nature, increase it.

(I) Acids in which the carboxyl group is sterically hindered, show lower sorption.

(J) Intramolecular hydrogen bonding between the carboxyl group and the ortho substituents may increase sorption.

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

(L) Sorption of trans-isomer is higher than that of cis-isomer.

(M) In case of unsaturated aliphatic mono carboxylic acids, the contribution to sorption for vinyl group may be taken as that of methylene group of the saturated monocarboxylic acids. This is equally true for dicarboxylic acids too.

2. SORPTION ELUTION STUDY

The sorption elution of dicarboxylic acids and mineral acids have been studied on the column of resin X1, X2, X4, X8, X12, X16 and Amberlite-200 in hydrogen form in aqueous medium. The same study has been carried out for disubstituted benzoic acids with resin X4 in 0.01 N aqueous hydrochloric acid and/or 10 % dioxan in 0.01 N aqueous hydrochloric acid solution. Studies were carried out for geometrical isomeric acids with resin X4 using distilled water and N/100 aqueous hydrochloric acid as solvent and eluent.

The results are used to correlate sorption coefficient B, which determines the rate of movement of the solute down the column, with various chromatographic quantities, viz, (i) peak elution volume Vm, (ii) peak width σ or β, (iii) peak height Cm, (iv) number of theoretical plates N, for the given column and (v) resolution Rn, by the following equations :

$$Vm = Vd + 0.4\ Vb + 0.5\ Vf + C\ (\alpha_1 + \alpha_2 B + \alpha_3 B^2) \qquad \text{----(1)}$$

For disubstituted benzoic acids
$\alpha_3 B^2$ term vanishes.

$$\sigma = \frac{Vf}{6} + \sqrt{C}\ (f_1\alpha_1 + f_2\alpha_2 B) \qquad \text{----(2)}$$

$$\beta = 2\sqrt{2}\left[\frac{Vf}{6} + \sqrt{C}\ (f_1\alpha_1 + f_2\alpha_2 B)\right] \qquad \text{----(2a)}$$

$$Cm = \frac{W}{\sqrt{2\pi}\left[\frac{Vf}{6} + \sqrt{C}\ (f_1\alpha_1 + f_2\alpha_2 B)\right]} \qquad \text{----(3)}$$

$$N = \frac{0.5\ Vf + C\ (\alpha_1 + \alpha_2 B + \alpha_3 B^2)}{\frac{Vf}{6} + \sqrt{C}\ (f_1\alpha_1 + f_2\alpha_2 B)} \qquad \text{----(4)}$$

$$Rn = \frac{Vm_2 - Vm_1}{3(\sigma_1 + \sigma_2)} \qquad \text{----(5)}$$

where, Vd is disc volume (ml), Vb is bed volume (ml), Vf is feed volume (ml), C is total capacity of the resin in column (milliequivalents), W is total amount of solute (millimoles)in the feed volume and αs and fs are constants determined by the resin-solute-solvent system and particle size of the resin respectively.

Equation (5) indicates that Rn is proportional to $\sqrt{C}$ provided Vf is negligible and reaches unity - a condition required for a satisfactory separation - if suitable column length 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 alternate members of the homologous series of aliphatic dicarboxylic acids is easier than the separation of adjacent members. In the later, elution curves overlap to some extent which can be overcome by decreasing the feed volume or by increasing the column length to improve the separation.

(B) Mineral acids can not be separated from their mixtures using sorption-elution technique because of their poor and similar sorption.

(C) The separation of benzoic acids with different substituents in the same positions would be easier, e.g. separation of 2,4-dihydroxybenzoic acid and 2,4-dimethoxybenzoic acid.

(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.

(E) Quantitative separation could be easily achieved for any mixture whose difference of B values of components under isolation is substantial.

(F) Separation of maleic and fumaric acid in aqueous medium is relatively poor. However, a quantitative separation could be achieved using N/100 aqueous hydrochloric acid as solvent and eluent on the column of resin Dowex 50W-X4 of 100/200 mesh.

(G) Since the elution behaviour of each component is independent of the presence of other, separation of binary, ternary or multicomponent mixtures is feasible.

(H) Resin Dowex 50W-X4 shows the excellent chromatographic performance out of all the resins studied.

Thus the present study throws light on structure sorption relationship and provides a technique of interest for qualitative as well as quantitative analysis of mixtures of the acids studied with suitable column parameters and experimental conditions.