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MOLECULAR SORPTION OF BENZOIC ACIDS ON ION-EXCHANGE RESINS: SORPTION EQUILIBRIUM STUDIES

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SUMMARY

The sorption equilibrium behaviour of benzoic acid and 41 substituted benzoic acids has been studied with styrene–divinylbenzene copolymer-based sulphonic acid cation exchange resins. The variables studied included the nature and position of the substituent, the degree of cross-linking of the resin and the solvent medium.

INTRODUCTION

The study of molecular sorption on ion-exchange resins is of interest for the separation of organic and bio-organic compounds. Earlier, the sorption and separation of aliphatic mono- and dicarboxylic acids on cation-exchange resins were studied[1]. This paper describes a study of the sorption behaviour of benzoic acid and 41 substituted benzoic acids on cation-exchange resins. The variables studied included the nature and position of the substituent, the degree of cross-linking of the resin and solvent medium.

EXPERIMENTAL

The resins used were styrene–divinylbenzene copolymer-based sulphonic acid cation exchangers (Dow Chemical, Midland, MI, U.S.A.) with degrees of cross-linking (X) of X4, X8 and X12. These resins were from the batches used in the earlier work[1] and the capacities of X4, X8 and X12 were 4.87, 4.79 and 4.80 mequiv. per gram of the oven-dry resin, respectively.

The benzoic acids used in this study were from earlier stock[2].

The solvents used were 0.01 *N* hydrochloric acid and 10% dioxan in 0.01 *N* hydrochloric acid. Acidic aqueous dioxan (10%) was prepared by diluting 100 ml of purified dioxan[3] to 1 l with dilute hydrochloric acid. The final hydrochloric acid concentration was 0.01 *N*.

The sorption equilibrium studies were carried out at room temperature (about 30°C) by contacting the organic acid solutions of different concentrations and known volumes (50 ml) with weighed amounts (*ca.* 1.0 g) of the air-dried resin in well-stoppered flasks with frequent shaking to attain equilibrium (about 24 h). The organic acids were determined by ultraviolet absorption[2]. Preliminary work indicated

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that an increase in the contact time or small variations in room temperature did not measurably alter the amount sorbed.

RESULTS AND DISCUSSION

Ion-exchange resins tend to sorb organic solutes from solutions and the extent of sorption should be determined by the combined effects of various interactions. The hydrophilic nature of the substituent, steric interactions and ion exclusion would tend to decrease sorption whereas the hydrophobic nature of the substituents, hydrogen bonding and dispersion interactions would tend to increase sorption. The effect of dispersion interactions would increase with increasing size of the substituents[4-6]. These interactions in turn would depend on the variables of the resin–solute–solvent system[7-10].

In this study, the amount of the solute sorbed, S, in moles per litre per equivalent of the resin was calculated according to the equation

$$S = \frac{C_0 - C_e}{C_r}$$

where C_0 and C_e are initial and equilibrium concentrations of the solute in moles per litre, respectively, and C_r is the number of equivalents of the air-dried resin added per litre of the solution. A graph of S against C_e was linear and the slope of this plot is defined as the sorption coefficient, B. The values of B for various benzoic acids obtained in this way are given in Tables I and II.

The results indicate that the order of sorption is as follows: for methyl-, alkoxy- and halobenzoic acids H $<$ *o*- $<$ *p*- $\leqslant$ *m*-, where H denotes the unsubstituted benzoic acid, for nitrobenzoic acids, *o*- $<$ H $<$ *p*- $<$ *m*-, and for hydroxybenzoic acids *m*- $<$ *p*- $<$ H $<$ *o*-.

In the *p*-alkoxybenzoic acid series the sorption increases with increase in the number of straight-chain carbon atoms, n, in the alkoxy group[1,10-13], and log B is given by the equation

$$\log B = 0.15n + 0.26$$

The experimental and the calculated values of B for the basic molecule, *p*-hydroxybenzoic acid (*i.e.* when $n = 0$) differ. This is because homology may not be operative until the second member of the series and the first CH_2 unit (*i.e.*, when $n = 1$) is substituted into a unique molecular environment.

The value of B for *p*-isopropoxybenzoic acid is less than that of its straight-chain isomer, possibly because of the smaller contribution of the branched-chain carbon atom compared with that of the straight-chain carbon atom[1]. For the *p*-halobenzoic acid series log B is a linear function of the atomic radius[14] of the halogen.

With disubstituted benzoic acids, the contribution of the two substituents to the overall log B value seems to be partly additive and partly constitutive. The additive component of the sorption coefficient for the disubstituted benzoic acids may be calculated as the product of the sorption coefficients of the two corresponding monosubstituted benzoic acids divided by the sorption coefficient of the unsubstituted benzoic acid[1]. We may regard the sorption coefficient of unsubstituted benzoic acid as the

TABLE I

SORPTION COEFFICIENTS (*B*) OF BENZOIC ACIDS IN 0.01 *N* AQUEOUS HYDROCHLORIC ACID AND 10% DIOXAN IN 0.01 *N* AQUEOUS HYDROCHLORIC ACID ON RESINS X4, X8 AND X12

Substituent	*pK**	*B*			
		X4		*X8* *(HCl)*	*X12* *(HCl)*
		HCl	*Dioxan–HCl*		
H	4.20	2.82	1.41	1.40	0.95
2-CH_3	3.91	4.10	–	–	–
3-CH_3	4.27	6.10	–	–	–
4-CH_3	4.37	5.95	–	–	–
2-OCH_3	4.09	4.00	1.80	2.70	2.30
3-OCH_3	3.09	6.00	2.70	4.20	3.40
4-OCH_3	4.47	6.00	2.70	4.20	3.40
2-Cl	2.92	3.10	–	–	–
3-Cl	3.82	6.50	–	–	–
4-Cl	3.98	4.72	–	–	–
2-Br	2.85	4.30	–	–	–
2-NO_2	2.17	2.20	–	–	–
3-NO_2	3.49	4.90	–	–	–
4-NO_2	3.42	3.90	–	–	–
2-OH	2.97	3.40	1.70	2.35	2.00
3-OH	4.08	2.15	1.07	1.10	0.70
4-OH	4.48	2.62	1.31	1.30	0.90
2,3-Di-OH	2.94	2.50	1.19	1.75	1.40
2,4-Di-OH	3.29	3.65	1.75	2.60	1.30
2,5-Di-OH	2.89	2.35	1.12	1.72	1.40
2,6-Di-OH	1.22	0.40	0.19	–	–
3,4-Di-OH	4.48	1.75	0.83	0.86	0.54
3,5-Di-OH	4.05	1.68	0.80	0.85	0.55

* Literature values.

basic term. The constitutive contribution may include an addition due to the enhanced contribution of the second constituent and a negative contribution due to steric factors. The extent of these contributions would depend on the nature and position of the substituents.

The values of *B* for dihydroxybenzoic acids (Table I) increase in the order 2,6-di-OH < 3,5-di-OH < 3,4-di-OH < 2,5-di-OH < 2,3-di-OH < H < 2,4-di-OH, which indicates that the isomers with one of the hydroxy groups in the *ortho* position show higher sorption than the others because of the intramolecular hydrogen bonding. However, the 2,6-isomer shows the least sorption. For this isomer, the p*K* value indicates that in 0.01 *N* hydrochloric acid the ionization of the carboxyl group is not completely suppressed. The increase in sorption caused by intramolecular hydrogen bonding is more than counterbalanced by the decrease in sorption due to steric interaction and ion exclusion. This explanation is supported by the fact that in 0.1 *N* hydrochloric acid, the 2,6-isomer shows a significant increase in sorption ($B = 2.10$) whereas the other isomers do not show any substantial increase.

For dimethoxybenzoic acids steric factor should play a prominent role in de-

TABLE II

SORPTION COEFFICIENTS (*B*) OF BENZOIC ACIDS IN 10% DIOXAN IN 0.01 *N* HYDROCHLORIC ACID ON RESIN X4

Benzoic acid	*pK**	*B*
4-OCH_3	4.47	2.70
4-OC_2H_5	4.44	3.48
4-*n*-C_3H_7	4.45	5.05
4-iso-C_3H_7	4.65	4.10
4-*n*-C_4H_9	4.52	7.40
4-Cl	3.98	2.82
4-Br	3.97	3.87
4-I	3.90	6.00
2,3-di-OCH_3	3.98	1.70
2,4-di-OCH_3	4.36	3.50
2,5-di-CH_3	–	3.36
2,6-di-OCH_3	–	1.30
3,4-di-OCH_3	4.45	3.14
3,5-di-OCH_3	–	5.33
2-OH-3-OCH_3	–	2.65
2-OH-4-OCH_3	–	3.36
2-OH-5-OCH_3	–	3.24
4-OH-3-OCH_3	–	1.53
2-OH-4-OC_2H_5	–	5.15
2-OH-5-Br	2.62	6.90
2-OCH_3-5-Br	–	7.20

* Literature values.

termining the sorption, as indicated by the following order of their *B* values (Table II): 2,6-di-OCH_3 < H < 2,3-di-OCH_3 < 3,4-di-OCH_3 < 2,5-di-OCH_3 < 2,4-di-OCH_3 < 3,5-di-OCH_3. The sorption coefficients of hydroxymethoxybenzoic acids increase in the order 4-OH-3-OCH_3 < 2-OH-3-OCH_3 < 2-OH-5-OCH_3 < 2-OH-4-OCH_3.

2,4-Dihydroxy-, 2-hydroxy-4-methoxy- and 2-hydroxy-4-ethoxybenzoic acids are the first three members of another series of *p*-alkoxybenzoic acids. The experimental data may be expressed by the equation

$$\log B = 0.14n + 0.43$$

The values of *B* for the sorption of some hydroxy- and methoxybenzoic acids on resins X4, X8 and X12 in 0.01 *N* hydrochloric acid are given in Table I. The sorption decreases with increase in the degree of cross-linking of the resin. The relationship of the sorption coefficient and degree of cross-linking may be expressed by the equation

$$BX^{\gamma} = \beta$$

where β and γ are constants. In general, it appears that for substituted benzoic acids having a relatively higher sorption $\gamma = 0.5$ and for acids having a relatively lower sorption $\gamma = 1$.

Effect of the solvent

The sorption behaviour of some substituted benzoic acids was studied in 0.01 *N* hydrochloric acid and 10% dioxan in 0.01 *N* hydrochloric acid (Tables I and II). In the mixed solvent these acids show about a 2–2.2-fold lower sorption.

It is interesting to note the similarity in the influence of intramolecular hydrogen bonding and steric interaction on the sorption of the solute on the resin and its ultraviolet absorption[2,4]. Intramolecular hydrogen bonding, which tends to increase the sorption of the solute molecule, shifts the UV absorption maxima, λ_{max} towards longer wavelengths with enhanced intensity. On the other hand, when the carboxyl group is sterically hindered, the sorption is decreased and λ_{max} is also shifted to a shorter wavelength or the band appears only as an inflection.

CONCLUSION

This study of the sorption behaviour of benzoic acids has revealed that the resin is selective with respect to the functional group. Isomer selectivity of the resin is also fairly good. This suggests that the separation of some closely related acids should be feasible by proper selection of the experimental conditions.

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