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CHAPTER 3

SORPTION EQUILIBRIUM

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3.1 INTRODUCTION

Following the observation[1] of Sheel and Fontana (1773) on the adsorption of gases and of Lowitz (1785) on the adsorption of coloured organic solutes by charcoal, there have been attempts to evolve a theoretical bases for the phenomena. While significant theoretical work has been done on the adsorption of gases, relatively less progress has been achieved on the treatment of solutions.

Sorption is a generalized term used by McBain to describe the penetration and dispersal of molecules of an ambient gas, vapour or liquid on and throughout a polymeric solid to form a mixture. The process can be described phenomenologically as the distribution of the mobile component between two (or more) phases to include adsorption, absorption, distribution, incorporation into the microcavities and other modes of mixing.

Ion exchangers can sorb a great variety of substances. This can occur both from the gas phase and from the liquid phase.[2-7] Molecular sorption on synthetic ion exchange resins was first carried out by Bhatnagar and coworkers,[8-10] and later applied by Wheaton and Bauman[11,12] for the separation of nonionic materials. Further studies[13-110] have enlarged our knowledge regarding sorption on ion exchange resins.

The synthetic ion exchange resin consists of an irregular, macromolecular, three dimensional network of hydrocarbon chains to which ionogenic groups are attached and the surplus electric charge is balanced by mobile counterions. When the resin particle is placed in a polar solvent, it imbibes the solvent and swells to a limited extent. If the external solvent contains a weak or nonelectrolyte, the molal distribution coefficient (ratio of the molal concentration of the solute in the internal solution of the resin to the molal concentration of the solute in the external solution) should be unity; actually it is rarely so and sorption of the solute is observed. The sorption is influenced by the different variables in the resin-solvent-solute system. For the resin, the variables include the matrix structure, the relative degree of crosslinking, the type and acid or base strength of the ionogenic group and the charge, shape and solvation of counterions. The solvent may be aqueous, mixed or organic, it may be polar or nonpolar and may have different dielectric constants, solvation of ionogenic groups and solute molecules. For the solute, the variables include the shape, size, polarity and the relative solubility in the medium inside and outside the resin particle. The factors which are responsible for the sorption of a solute may include the following :

(i) London and dipole interactions : London interaction between the hydrocarbon part of the solute molecules and the resin matrices, although very weak, favours sorption. A stronger contribution may come from dipole-dipole interaction. The result of this interaction 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 dipole interactions favour local adsorption of the hydrocarbon groups of the solute on the resin matrix and thus enhance the sorption of the nonelectrolytes. London forces are specific interactions and depend on the molecular structure of the solute and matrix.

(ii) Ionic solvation and salting out : The fixed ionic groups and the counterions in the resin form solvation shells, and hence only a section of the total internal solvent is free, in which the nonelectrolyte is dissolved. In the absence of any other interactions, the nonelectrolyte concentration in the free water in the ion exchanger should be the same as the nonelectrolyte concentration in the external solution. Thus the molality of the nonelectrolyte in the ion exchanger is less than that in the external solution. The nonelectrolyte is then salted out. The salting out effect should be more pronounced when the resin is highly crosslinked and the counter ions are strongly solvated. However, the salting out in the ion exchanger could be counterbalanced by adding an electrolyte to the external solution.

(iii) Complex formation and salting in : 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. Interactions between nonelectrolyte and the counterions become more pronounced when inorganic counterions are replaced by organic counterions. The most striking effects are noted when the solute forms complexes with counterions.

(iv) 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. Interior of the swollen resin is under rather high swelling pressure which tends to squeeze the solvent and solute molecules out of the resin. The effect is more pronounced with the larger solute molecules and highly crosslinked resins. With the smaller solute molecules and the resin of moderate crosslinking, the swelling pressure effect is rather small and is often overshadowed by other interactions which favour the sorption of nonelectrolytes.

The sorption of larger molecules is further restricted by purely mechanical sieve action of the matrix. The molecules which are too large for passing through meshes of the matrix, are excluded by the resin. Of course, 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 effect 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 the large molecule under ordinary experimental conditions may be low, because sorption equilibrium, no matter how favourable, is not attained.

(v) 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 solvents 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 the positive curvature are observed. Usually a Langmuir or Freundlich isotherm can be fitted reasonably to the experimental results.

(vi) Dependence on pressure and temperature : The effect of pressure on the 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 volume of the total system.

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.

3.2 EXPERIMENTAL

The solvents used were water (distilled), 0.01N aqueous hydrochloric acid and 10% dioxan in 0.01N aqueous hydrochloric acid (by volume). The solutions of benzoic acids were prepared as described in the Section 2.2.

The sorption equilibrium study was carried out with the resin Dowex 50W-X4 (100/200), a styrene divinylbenzene copolymer type cation exchange resin in the hydrogen form. Before use, the resin was washed, cycled between sodium chloride and hydrochloric acid, regenerated with a large excess of hydrochloric acid, washed free of acid, filtered, air dried and stored in a well stoppered bottle.

The moisture content was determined by heating weighed samples (∽ 0.5 g) of the air dried resin in clean, dry weighing bottles, in an oven (at 101 ± 1°C) to a constant weight and per cent moisture content was then calculated.

For the estimation of capacity, weighed samples of the air dried resin (∽ 0.5 g) were contacted with 50 ml of 1.0N barium chloride solution in well stoppered flasks with frequent shaking. Next day, the liberated acid was estimated by titrating the aliquots with the standard sodium hydroxide solution and the capacity was then calculated. Preliminary work had suggested that increase in contact time did not increase the amount of acid liberated. The capacity of the oven dry resin was 4.87 meq/g.

The sorption equilibrium study was carried out by contacting the benzoic acid solutions of different concentrations and known volume (50 ml) with the weighed amounts (1 g) of the air dried resin, in well stoppered flasks, with frequent shaking at room temperature (∽ 30°C) for ∽ 24 hours. After equilibrium was reached, the initial concentration Co (moles/liter) and the final equilibrium concentration Ce (moles/liter) were determined by ultraviolet absorption (at λinv or λmax for the particular solute). A correction for blank was applied for the change in absorbance, if any, of the solvent caused when contacted with the ion exchange resin and the corrected values of Ce were used in further calculations. Preliminary studies revealed that increase in contact time does not change the amount of sorption measurably. Also, a small variation in temperature in the vicinity of room temperature has no significant effect on the sorption.

The amount of the solute sorbed, S, in moles/liter per equivalent of the resin, was calculated according to the equation

$$S = \frac{Co - Ce}{Cr}$$

where Cr is the number of equivalents of the air dried resin per liter of the solution.

The plots of S against Ce were linear in the concentration range of about 0.5×10^{-4} to 15.0×10^{-4} moles/liter, depending on the solubility of the solute in the particular solvent system. The slope of these plots is defined as the 'sorption coefficient' and denoted by B ; it is independent of concentration (Fig 3.3-1).

3.3 RESULTS

Table 3.3-1 : Sorption of benzoic, p-hydroxybenzoic and o-methoxybenzoic acids in water and 2,6-dihydroxybenzoic acid in 0.1N aqueous hydrochloric acid.

Benzoic acid	Solvent	10^4Ce	10^4S
H	Water	1.28	3.44
		2.57	6.87
		3.84	10.30
		5.13	13.70
p-OH	Water	2.79	4.49
		5.55	10.73
		8.24	18.71
		10.87	24.23
o-OMe	Water	3.57	10.60
		7.14	21.10
		10.70	31.70
		14.30	42.30
2,6-diOH	0.1N HCl	1.88	3.96
		3.77	7.92
		5.65	11.85
		7.55	15.85

Table 3.3-2 : Sorption of benzoic acid and monohydroxybenzoic acids in 0.01N aqueous hydrochloric acid and 10% dioxan in 0.01N aqueous hydrochloric acid.

Solvent	0.01N HCl		10% dioxan in 0.01N HCl	
Benzoic acid	10^4Ce	10^4S	10^4Ce	10^4S
H	2.03	6.35	1.19	1.79
	3.99	13.17	2.45	3.53
	6.22	16.82	3.66	5.34
	8.22	22.94	4.74	7.04
o-OH	1.80	5.50	1.99	3.78
	3.53	11.80	3.97	6.92
	5.29	18.12	5.97	10.45
	7.09	24.15	7.95	14.24
m-OH	3.89	8.05	7.79	7.80
	7.79	15.34	15.64	15.16
	11.46	25.02	23.52	25.01
	15.11	32.92	31.18	35.62
p-OH	2.16	6.17	3.73	4.68
	4.37	11.09	7.36	9.29
	6.55	17.30	11.05	14.19
	8.75	23.89	14.66	18.76

Fig 3.3-1 Plot of S versus Ce for (1) o-OH benzoic acid in 0.01N aqueous hydrochloric acid and (2) benzoic acid in 10% dioxan in 0.01N aqueous hydrochloric acid.

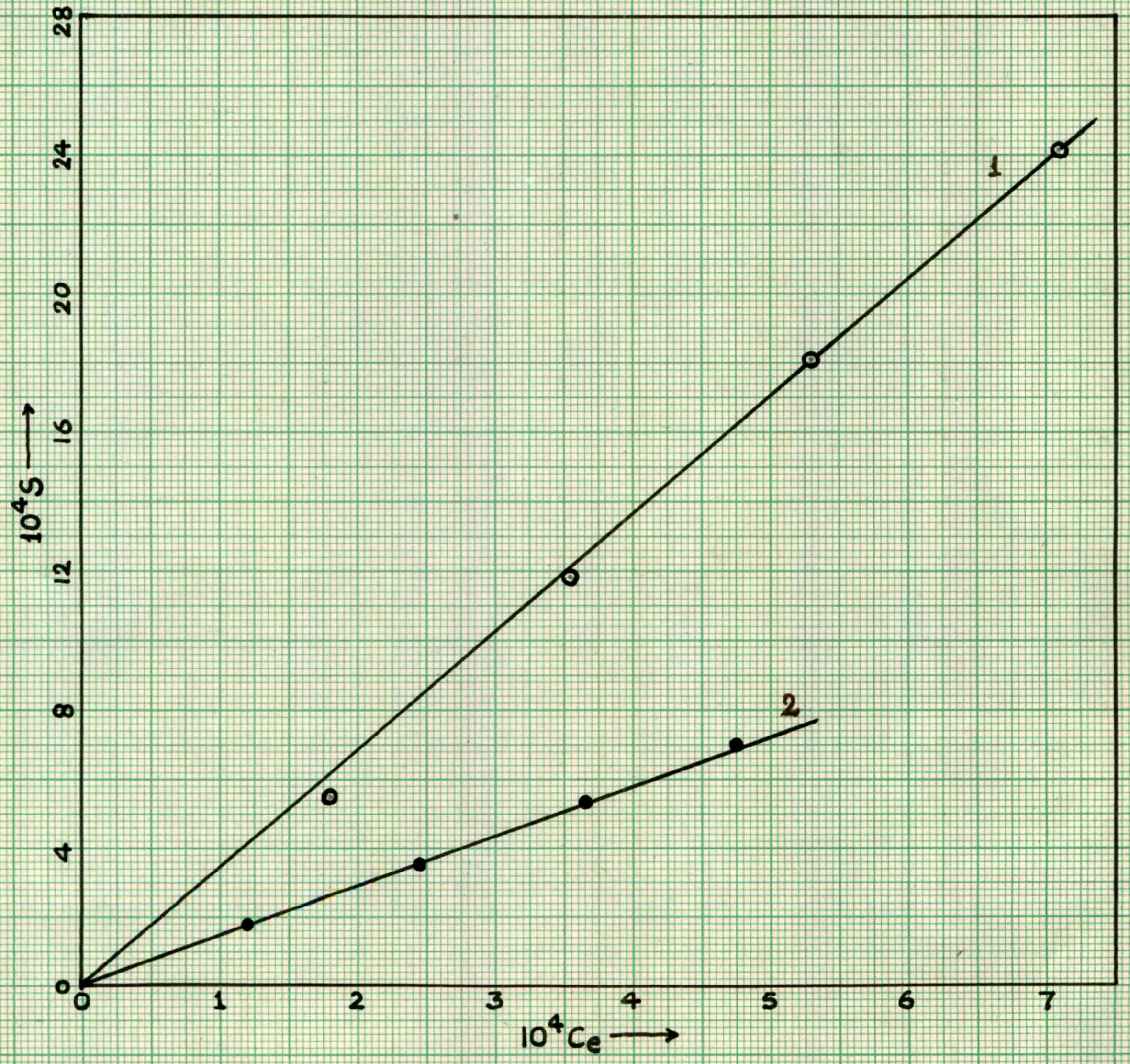


Table 3.3-3 : Sorption of monomethoxybenzoic acids in 0.01N aqueous hydrochloric acid and 10% dioxan in 0.01N aqueous hydrochloric acid.

Solvent	0.01N HCl		10% dioxan in 0.01N HCl	
Benzoic acid	10^4Ce	10^4S	10^4Ce	10^4S
o-OMe	3.83	15.56	8.07	14.51
	7.69	31.46	16.14	28.96
	10.54	46.28	24.31	45.12
	15.38	61.65	32.58	60.31
m-OMe	3.40	21.60	3.62	8.12
	6.69	38.36	7.10	17.09
	9.97	58.48	10.46	25.00
	13.53	79.02	14.14	34.12
p-OMe	0.38	2.42	1.79	4.68
	0.75	4.78	3.40	9.30
	1.13	7.49	5.16	14.10
	1.52	9.46	6.88	18.81

Table 3.3-4 : Sorption of p-alkoxy and p-halobenzoic acids in 10% dioxan in 0.01N aqueous hydrochloric acid.

Benzoic acid	10^4C_e	10^4S
p-OEt	0.56	1.68
	1.01	3.39
	1.48	5.21
	2.09	7.10
p-n-OPr	0.43	2.21
	0.85	4.39
	1.31	6.32
	1.79	9.41
p-iso-OPr	0.42	1.71
	0.86	3.43
	1.24	5.27
	1.76	7.12
p-n-OBu	0.25	1.80
	0.51	3.56
	0.78	5.58
	1.00	7.30
p-Cl	1.10	2.92
	2.12	5.81
	3.25	9.39
	4.27	12.31
p-Br	0.81	3.08
	1.59	6.21
	2.46	8.90
	3.33	13.21
p-I	0.60	3.61
	1.24	7.20
	1.82	11.01
	2.41	14.46

Table 3.3-5 : Sorption of 2,3-dihydroxy, 2,4-dihydroxy and 2,5-dihydroxybenzoic acids in 0.01N aqueous hydrochloric acid and 10% dioxan in 0.01N aqueous hydrochloric acid.

Solvent	0.01N HCl		10% dioxan in 0.01N HCl	
Benzoic acid	10^4Ce	10^4S	10^4Ce	10^4S
2,3-diOH	2.33	5.74	3.36	3.94
	4.70	11.32	6.74	7.81
	6.76	18.55	10.15	11.48
	9.25	23.01	13.53	15.57
2,4-diOH	1.41	5.09	1.51	2.55
	2.85	10.43	3.04	4.80
	4.15	15.40	4.59	7.03
	5.71	20.55	6.05	10.21
2,5-diOH	4.39	8.90	3.93	4.75
	8.61	20.20	7.90	8.89
	13.08	30.00	11.84	13.54
	17.20	41.03	15.85	17.07

Table 3.3-6 : Sorption of 2,6-dihydroxy, 3,4-dihydroxy and 3,5-dihydroxybenzoic acids in 0.01N aqueous hydrochloric acid and 10% dioxan in 0.01N aqueous hydrochloric acid.

Solvent	0.01N HCl		10% dioxan in 0.01N HCl	
Benzoic acid	10^4Ce	10^4S	10^4Ce	10^4S
2,6-diOH	4.07	2.77	2.74	1.01
	8.20	4.18	5.37	2.25
	12.22	6.46	8.07	3.37
	16.44	8.46	10.66	4.72
3,4-diOH	2.35	4.06	2.37	2.00
	4.63	8.67	4.72	4.02
	7.07	11.10	7.11	6.00
	9.32	16.66	9.46	8.05
3,5-diOH	2.28	3.69	2.89	2.89
	4.50	7.60	5.92	4.80
	6.74	11.32	8.88	7.36
	9.07	15.18	11.89	9.54

Table 3.3-7 : Sorption of dimethoxybenzoic acids in 10% dioxan in 0.01N aqueous hydrochloric acid

Benzoic acid	10^4Ce	10^4S
2,3-diOMe	4.42	7.93
	8.93	14.62
	13.34	23.16
	18.07	29.82
2,4-diOMe	1.24	4.31
	2.49	8.47
	3.76	12.62
	5.04	16.40
2,5-diOMe	1.35	4.44
	2.66	9.28
	3.98	13.02
	5.34	17.26
2,6-diOMe	2.31	2.88
	4.79	6.27
	6.94	9.56
	9.26	11.60
3,4-diOMe	1.12	3.38
	2.23	6.90
	3.32	10.49
	4.47	14.11
3,5-diOMe	0.31	1.63
	0.60	3.19

Table 3.3-8 : Sorption of 2-hydroxy-3-methoxy, 2-hydroxy-4-methoxy, 2-hydroxy-5-methoxy, 4-hydroxy-3-methoxy and 2-hydroxy-4-ethoxybenzoic acids in 10% dioxan in 0.01N aqueous hydrochloric acid.

Benzoic acid	10^4Ce	10^4S
2-OH-3-OMe	4.16	11.43
	8.37	22.13
	12.47	33.79
	16.85	43.51
2-OH-4-OMe	1.23	4.80
	2.46	9.06
	3.67	13.72
	4.94	18.63
2-OH-5-OMe	1.10	3.24
	2.15	7.17
	3.26	10.99
	4.27	13.98
4-OH-3-OMe	1.31	2.00
	2.65	3.94
	3.95	6.05
	5.30	8.39
2-OH-4-OEt	0.87	4.75
	1.76	9.58
	2.68	13.36
	3.57	17.63

Table 3.3-9 : Sorption of 2-hydroxy-3-methoxy, 4-hydroxy-3-methoxy, 2,3-dimethoxy and 2,6-dimethoxybenzoic acids in 0.01N aqueous hydrochloric acid and 2-hydroxy-5-bromo and 2-methoxy-5-bromobenzoic acids in 10% dioxan in 0.01N aqueous hydrochloric acid.

Benzoic acid	Solvent	$10^4 Ce$	$10^4 S$
2-OH-3-OMe	0.01N HCl	0.69	4.52
		1.34	9.46
		2.05	13.67
		2.81	17.29
4-OH-3-OMe	0.01N HCl	0.53	2.10
		1.05	4.14
		1.57	6.34
		2.06	8.38
2,3-diOMe	0.01N HCl	0.51	1.69
		1.04	3.18
		1.64	5.38
		2.12	7.88
2-OH-5-Br	10% dioxan in 0.01N HCl	0.55	3.71
		1.14	7.93
		1.75	11.80
		2.24	16.03
2-OMe-5-Br	10% dioxan in 0.01N HCl	0.37	2.61
		0.76	5.56
		1.10	8.32
		1.52	11.09

Table 3.3-10 : Values of B for substituted benzoic acids in
(a) 0.01N aqueous hydrochloric acid and
(b) 10% dioxan in 0.01N aqueous hydrochloric acid.
B = Slope of the plot of Ce against S

Solvent Benzoic acid	(a) B	(b) B	Solvent Benzoic acid	(a) B	(b) B
H *	2.82	1.45	2,6-diOH**	0.51	0.42
o-OH	3.40	1.75	3,4-diOH	1.74	0.85
m-OH	2.15	1.00	3,5-diOH	1.68	0.82
p-OH *	2.62	1.28	2-OH-3-OMe	6.66	2.65
o-OMe *	4.00	1.75	2-OH-4-OMe	-	3.76
m-OMe	6.00	2.40	2-OH-5-OMe	-	3.24
p-OMe	6.44	2.65	4-OH-3-OMe	4.00	1.53
p-OEt	-	3.48	2-OH-4-OEt	-	5.15
p-n-OPr	-	5.05	2-OH-5-Br	-	6.90
p-iso-OPr	-	4.10	2-OMe-5-Br	-	7.20
p-n-OBu	-	7.40	2,3-diOMe	3.45	1.70
p-Cl	-	2.82	2,4-diOMe	-	3.36
p-Br	-	3.87	2,5-diOMe	-	3.24
p-I	-	6.00	2,6-diOMe	-	1.30
2,3-diOH	2.45	1.15	3,4-diOMe	-	3.14
2,4-diOH	3.70	1.64	3,5-diOMe	-	5.33
2,5-diOH	2.35	1.12	-	-	-

* B values in water : H = 2.68; p-OH = 2.20; o-OMe = 2.96

** B value in 0.1N HCl : 2,6-diOH = 2.10.

3.4 DISCUSSION

The ion exchange resins tend to sorb organic solutes from solutions. This could be explained by considering the swollen resin system consisting of two parts : the resin phase and the interstitial liquid between the resin beads (the external phase). The resin phase may have some characteristics of an organic solvent imparted to it by the hydrocarbon matrix and thus can act as a solid 'solvent' for organic compounds, particularly containing benzene rings. The resin phase also contains the occluded liquid which differs from the interstitial liquid because of high ionic concentration within the resin and the organic nature of the resin. If the conditions are such that no ion exchange is possible, ionized materials are excluded from the resin phase because of the Donnan effect. However, a nonelectrolyte or a nonionized material is not restricted by electrostatic forces and should distribute equally between the two phases. This is true only as a first approximation and usually, there exists an unequal distribution of the solute between the two phases because of the operation of various interactions within the solvent-resin-solute system.

(i) Solvent-Resin interaction : Usually a dry exchanger swells when brought into contact with a solvent. The extent of swelling depends on the type and nature of the ionogenic groups and the degree of crosslinking of the resin. Higher solvation of the counterions and lower degree of crosslinking would generally enhance the swelling - a situation which should favour the sorption. However, when a mixed solvent is used the situation becomes more complicated because the resin may have unequal affinity for the components of the solvent mixture.

(ii) Solute-Resin interaction : This includes London dispersion, dipole-dipole and steric interactions and hydrogen bonding between the solute molecules and the resin, which would depend on the size, structure and polarity of the solute molecules and the type of the resin matrix, ionogenic groups and counterions.

(iii) Solute-Solvent interaction : This includes London dispersion interaction, dipole-dipole interaction and hydrogen bonding between the solute and solvent molecules, which would govern the relative solubility of the solute in the given solvent. These interactions depend on the structure and polarity of the solute molecules and the type of the solvent.

A quantitative description of the complex interplay of these interactions on sorption is probably difficult. However, the study of one variable at a time should lead to a better understanding of the phenomena. In the present work the variation of sorption with changes in the structure of the solute has been investigated by studying the sorption behaviour of substituted benzoic acids with the resin Dowex 50W-X4 (100/200). Earlier work has shown that this resin is suitable for the sorption and chromatographic studies.[109] The hydrogen form of the resin is used to avoid ion exchange.

Benzoic acids are weak organic acids. In aqueous solutions these acids undergo ionization and may be partially excluded from the resin phase because of electrostatic repulsion, as indicated by relatively lower sorption of these acids from aqueous solutions (Table 3.3-1). Under this condition the sorption depends, apart from other factors, on the dissociation constant of the acids also. In 0.01N aqueous hydrochloric acid, however, the sorption is relatively higher and almost independent of dissociation constant because in this solvent most of the acids studied will remain practically undissociated and the exclusion from the resin phase is prevented. For this reason the sorption behaviour of benzoic acids was studied in 0.01N aqueous hydrochloric acid and/or 10% dioxan in 0.01N aqueous hydrochloric acid.

3.4-1 : Effect of Substitution :

Monosubstituted benzoic acids : Substitution changes the sorption of benzoic acid. One of the important factors which contributes towards overall sorption is the nature of the substituent. The benzoic acids with hydrophobic (nonpolar or less polar) substituents e.g. methoxy and halo, which are relatively more soluble in organic solvents should favour the resin phase because of the 'solvent' action of the hydrocarbon matrix leading to higher sorption whereas the acids with hydrophilic (polar) groups, e.g. hydroxy, which are relatively more water soluble should favour the external phase leading to lower sorption.

Another factor which contributes significantly towards sorption is the relative position of the substituent in the aromatic nucleus. It is seen that ortho substituted benzoic acids generally show lower sorption than the corresponding meta and para isomers. Actually, the change in sorption caused by the introduction of a group into any molecule should be constant provided its introduction does not cause intramolecular interactions with the other parts of the molecule that might themselves affect the sorption. In the case of the meta and para isomers, the substituent can interact electronically (intramolecularly) with the carboxyl group with resulting changes in the sorption behaviour. In the case of the ortho isomers, intramolecular steric effects come into play along with electronic effects. The size and proximity of the substituent in the ortho position may result in the interference with the normal interactions of the carboxyl group with the solvent and its close approach to an adsorbant site. Therefore, although electronic effects in the ortho and para positions are probably comparable in affecting sorption, the ortho isomer is less strongly sorbed.

Table 1 gives the sorption coefficient values for benzoic acid and methoxy and hydroxybenzoic acids. The methoxy isomers show the following order in their B values :

$$\mathrm{H} < \text{o-OMe} < \text{m-OMe} < \text{p-OMe}$$

which is in consistence with the above explanation. The methyl substituted benzoic acids also show the same order.[109] However, the hydroxy isomers show a different trend in their B values which is as follows :

$$\text{m-OH} < \text{p-OH} < \mathrm{H} < \text{o-OH}$$

The lower sorption of the meta and para isomers than benzoic acid is understandable. If the steric effect were the sorption determining factor, the ortho isomer should have shown lower sorption than the meta and para isomers. On the contrary, it shows higher sorption, which may be attributed to the intramolecular hydrogen bond formation between the ortho hydroxy group and the carboxyl group. When the hydroxy group is involved in hydrogen bonding its hydrophilic nature is reduced which in turn would remove its sorption decreasing tendency. In the para isomer also, hydrogen bonding of the intermolecular type may, to some extent, reduce the sorption decreasing tendency of the hydroxy group for there is only a small difference in the B values of benzoic acid and p-hydroxybenzoic acid.

Table 1 : Values of B for benzoic acid and monomethoxy and monohydroxybenzoic acids in 0.01N aqueous hydrochloric acid.

Benzoic acid	Position of the substituent		
	ortho	meta	para
H	2.82	2.82	2.82
OH	3.40	2.15	2.62
OMe	4.00	6.00	6.44

Within a related group- e.g. a homologous series - it should be possible to correlate the sorption behaviour with the two parameters, a ground constant which is a function of the sorptive system and a summation of the increments contributed by each additional group. p-n-Alkoxybenzoic acids form one such series. p-Hydroxybenzoic acid may be considered as the ground molecule and the hydrogen of the hydroxy group can be replaced by $-CH_3$, $-C_2H_5$ etc which amounts to the sequential addition of a $-CH_2$ unit to the ground molecule. It is evident from the B values (Table 2) that the sorption increases with the increase in the length of the alkoxy group. This may be attributed to the decrease in the solubility of the solute in the solvent and the increase in the dispersion forces (which account for a major part of the total attractive forces in the case of organic compounds particularly hydrocarbons) between the resin matrix and the solute molecules. The plot of log B versus n_c (the number of carbon atoms in the alkoxy group) is linear (Fig. 1). Hence, one may put

$$\log B = m.n_c + C$$

where m (slope, 0.15) and C (intercept, 0.26) are the group and ground constants respectively. From Fig. 1 it is seen that the value for the ground molecule does not fall on the line. This may be because homology may not be operative until the second member of the series and the first $-CH_2$ unit (n_c=1) is substituted into a unique molecular enviornment which, in fact, changes the hydrophilic nature of the hydroxy group into hydrophobic. Similar relationships have been observed for the sorption of series of aliphatic mono and dicarboxylic acids, alcohols and coumarins.[65,90,110]

The branched chain acid is found to show lower sorption than its straight-chain isomer (Table 2). The reasons for this may include, shorter straight-chain length and steric effects.

This type of relation between B and n_c may also be expected from thermodynamic point of view because the sorption coefficient B may be compared with the equilibrium constant, K, which is related to the change in free energy ΔF by the equation

$$-\ \Delta F = RT.\ln K$$

Now, in a given system, the change in free energy, ΔF, should be due to the change in intra and intermolecular forces. In the present system the only change made is the increase in the number of carbon atoms in the p-alkoxy chain. Therefore, the change in intra and intermolecular forces and hence the change in the free energy is due to the increase in the length of the alkoxy group and it should be directly proportional to n_c. It follows therefore that logB should increase with increase in n_c provided the molecular size is not too large to be excluded from the resin phase by sieve action.

Table 2 : Values of B and n_c for p-alkoxybenzoic acids in 10% dioxan in 0.01N aqueous hydrochloric acid.

Benzoic acid	n_c	B	logB
p-OH	0	1.28	0.11
p-OMe	1	2.65	0.42
p-OEt	2	3.48	0.54
p-n-OPr	3	5.05	0.70
p-iso-OPr	3	4.10	-
p-n-OBu	4	7.40	0.87

A similar relationship should be expected for the p-halobenzoic acid series also, because the only variable in this series is the size of the halogen substituent. Therefore, the change in free energy and hence logB should be

Fig 1 Variation of log B with n_c for (1) p-alkoxybenzoic acid series and (2) 2-OH-p-alkoxybenzoic acid series in 10% dioxan in 0.01N aqueous hydrochloric acid.

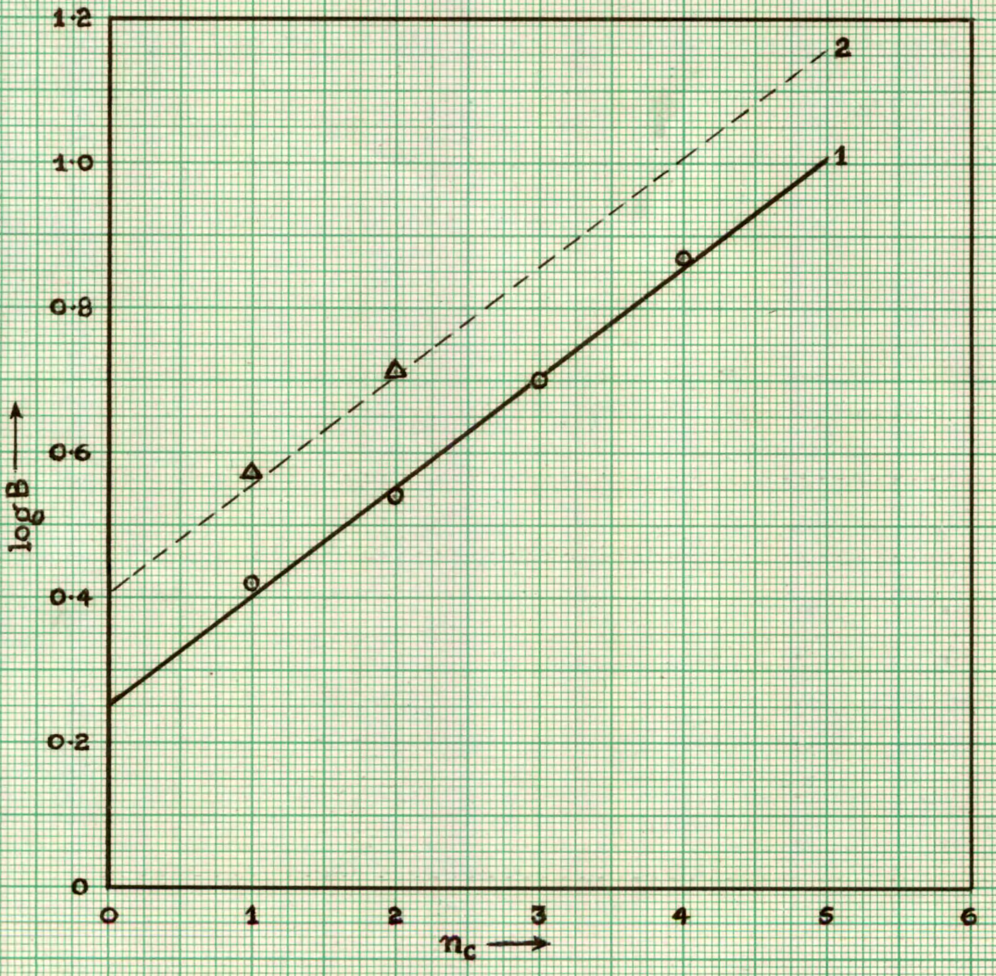
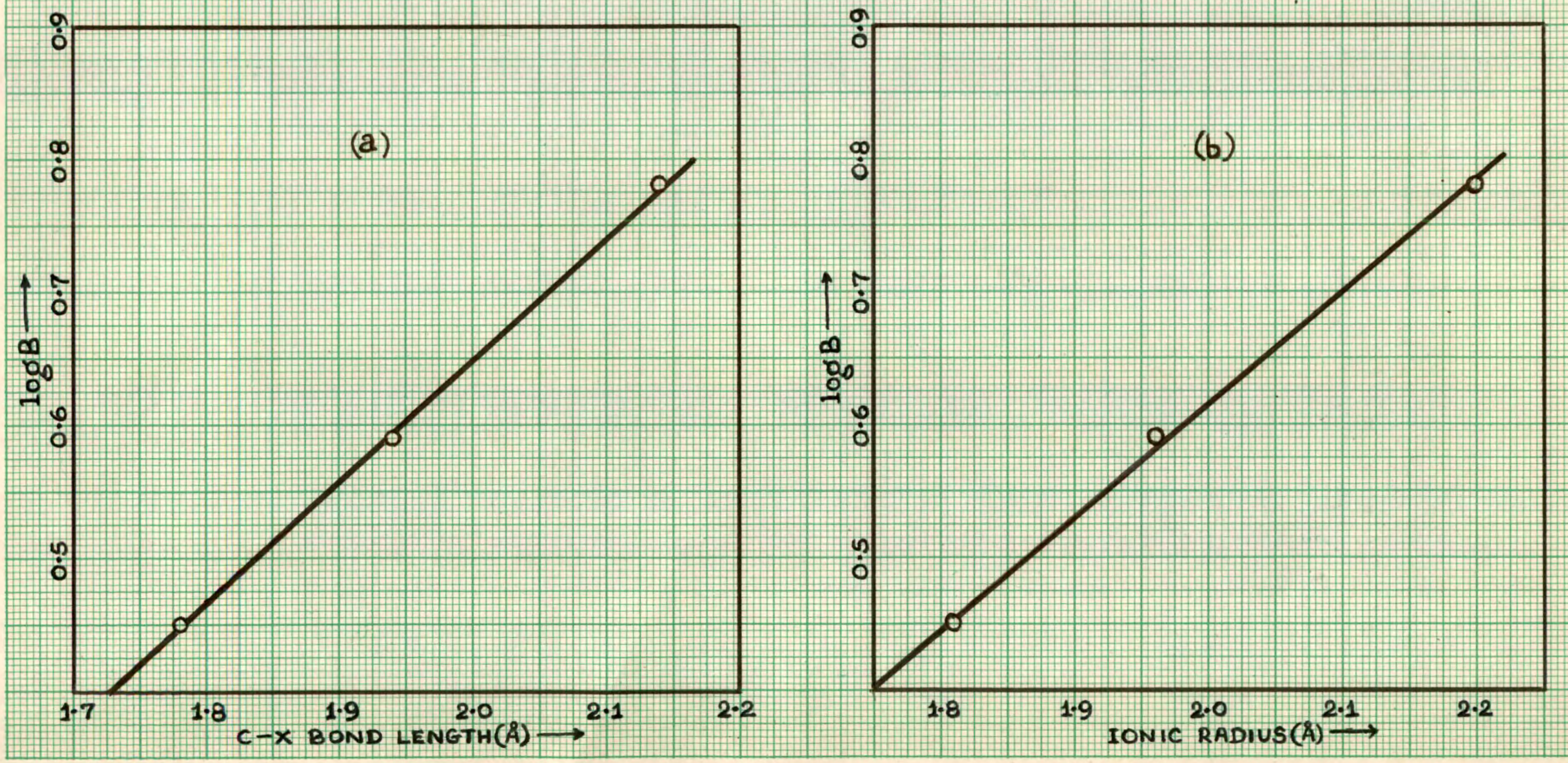


Fig 2 Variation of logB with (a) C-X bond length and
(b) ionic radius of the halo atom for the
p-halobenzoic acid series.



proportional to the molar volume or the C-X bond length (X = Cl, Br or I) or the ionic radius of the halo atom. It is seen that the sorption increases with the size of the halo atom, i.e. Cl < Br < I, and plots of logB versus C-X bond length and ionic radius of the halo atom are both linear (Fig. 2),

Table 3 : Values of B and logB for p-halobenzoic acids in 10% dioxan in 0.01N aqueous hydrochloric acid.

Benzoic acid	B	logB
p-Cl	2.82	0.45
p-Br	3.87	0.59
p-I	6.00	0.78

Disubstituted benzoic acids : In the case of disubstituted benzoic acids the contribution of the two substituents towards overall sorption seems to be partly additive and partly constitutive. The constitutive contribution may include an addition due to the enhanced contribution of the second substituent and a small negative contribution due to steric factor. The extent of these contributions would depend on the nature and position of the substituents. The differences in the experimental and calculated values of B support the above explanation.

The values of B for disubstituted benzoic acids can be calculated as follows : From the B values of benzoic acid and monosubstituted benzoic acids, the δB values for the particular substituents are determined.

Table 4 : δB values for benzoic acid substitution.
(Solvent : 10% dioxan in 0.01N aqueous HCl)

Parent value = B_0 = 1.45

Substituent	Position	B	δB
-OH	o-	1.75	+ 0.30
	m-	1.00	- 0.45
	p-	1.28	- 0.17
-OMe	o-	1.75	+ 0.30
	m-	2.40	+ 0.95
	p-	2.65	+ 1.20
-OEt	p-	3.48	+ 2.03

The algebraic addition of the parent value (benzoic acid) B_0 and δB for each substituent gives the values of B for the disubstituted benzoic acids. e.g.

Benzoic acid : 2-OH-3-OMe

$$B_{cal} = B_0 + \delta B_{o\text{-}OH} + \delta B_{m\text{-}OMe}$$
$$= 1.45 + 0.30 + 0.95$$
$$= \underline{2.70}$$

The values of B thus calculated for different acids are given in Table 5 and 6, alongwith the experimental values. The tables also give the differences between the two values, which indicate that in 3,5-disubstituted benzoic acids, where all the three groups are apart and no steric factor is operative the experimental values are higher than calculated, as expected. On the other hand, in 2,3- and 2,6-disubstituted benzoic acids the experimental values are less than calculated values.

In 0.01N aqueous hydrochloric acid, the values of B for the dihydroxybenzoic acids (Table 5) are in the order :

2,6-diOH < 3,5-diOH < 3,4-diOH < 2,5-diOH ⩽ 2,3-diOH < H < 2,4-diOH

which shows that the isomers having one of the hydroxy groups in the ortho position show higher sorption than the others because of intramolecular hydrogen bonding. However, 2,6-dihydroxybenzoic acid seems to be an exception as this isomer shows the least sorption. This can be explained as follows : In 2,6-dihydroxybenzoic acid two opposing factors are operative; first, the steric crowding of the carboxyl group with a tendency to decrease the sorption and second, intramolecular hydrogen bonding with a tendency to increase the sorption. Further, the pK value indicates that in 0.01N aqueous hydrochloric acid the dissociation of the carboxyl group is only partially suppressed which will result in the partial exclusion of the acid from the resin phase. The increase in sorption caused by intramolecular hydrogen bonding is more than counter balanced by the decrease in sorption due to steric interaction and ion exclusion. This explanation gets support from the fact that in 0.1N aqueous hydrochloric acid the 2,6-isomer shows a significant increase($B=2.10$) in sorption while the other isomers do not show any substantial increase.

Table 5 : Values of B, B_{cal} and ΔB for dihydroxybenzoic acids.

Solvent Benzoic acid	0.01N HCl B	10% dioxan in 0.01N HCl B	 B_{cal}	 $(B-B_{cal})=\Delta B$
2,3-diOH	2.45	1.15	1.30	- 0.15
2,4-diOH	3.70	1.64	1.58	+ 0.06
2,5-diOH	2.35	1.12	1.30	- 0.18
2,6-diOH	0.51	0.42	-	-
3,4-diOH	1.74	0.85	0.83	+ 0.02
3,5-diOH	1.68	0.82	0.55	+ 0.27

In the case of dimethoxybenzoic acids steric factor should play a prominent role in determining the sorption (Table 6). The order of sorption is : 2,6-diOMe < H < 2,3-diOMe < 3,4-diOMe < 2,5-diOMe < 2,4-diOMe < 3,5-diOMe. 3,5-dimethoxybenzoic acid shows the highest sorption because in this isomer all the three groups are nonadjacent and hence steric interaction is minimum whereas in the case of 2,6-isomer the carboxyl group is hindered from both the sides by the bulky methoxy groups leading to the lowest sorption. Steric effect is reduced to some extent in the 2,3-isomer as evident from slightly higher sorption of this acid than the 2,6-isomer. In 2,4-, 2,5- and 3,4-isomers only two of the three groups are adjacent. Hence these isomers exhibit relatively higher sorption.

Table 6 : Values of B, B_{cal} and ΔB for dimethoxy and hydroxymethoxybenzoic acids in 10% dioxan in 0.01N aqueous hydrochloric acid.

Benzoic acid	B	B_{cal}	$(B - B_{cal}) = \Delta B$
2,3-diOMe	1.70	2.69	- 0.99
2,4-diOMe	3.36	2.94	+ 0.42
2,5-diOMe	3.24	2.69	+ 0.55
2,6-diOMe	1.30	2.03	- 1.27
3,4-diOMe	3.14	3.60	- 0.46
3,5-diOMe	5.33	3.33	+ 2.00
2-OH-3-OMe	2.65	2.70	- 0.05
2-OH-4-OMe	3.76	2.95	+ 0.81
2-OH-4-OEt	5.15	3.78	+ 1.37
2-OH-5-OMe	3.24	2.70	+ 0.54
4-OH-3-OMe	1.53	2.23	- 1.30

If the ortho methoxy group in 2,3-, 2,4- or 2,5-diOMe benzoic acids is replaced by a hydroxy group, an increase in sorption is observed (Table 6), the gain in sorption being maximum for the 2,3-isomer because steric interaction is considerably reduced in this case. Comparatively lower sorption of 4-hydroxy-3-methoxybenzoic acid when compared to that of 3,4-dimethoxybenzoic acid is as expected.

2,4-Dihydroxy, 2-hydroxy-4-methoxy and 2-hydroxy-4-ethoxybenzoic acids form another series of p-alkoxybenzoic acids with an additional substituent in the ortho position. The sorption behaviour of this series should be similar to that of p-alkoxybenzoic acids with the only change in the ground constant (Fig. 1).

A bromo group when substituted in a molecule may enhance the sorption by virtue of its hydrophobic nature. Thus, 2-hydroxy-5-bromo (B = 6.90) and 2-methoxy-5-bromo (B = 7.20) benzoic acids show very high sorption and the comparison of the B values indicates that the contribution of the bromo group towards the overall sorption is almost the same in both the cases.

3.4-2 Solvent Effect :

The solvent plays an important role in determining the sorption and the one way of varying the relative sorption of the solute is to change the solvent. The sorption studies of difficultly soluble samples may also require a solvent of high solvency.

The sorption behaviour of benzoic acids have been studied in water, 0.01N aqueous hydrochloric acid and 10% dioxan in 0.01N aqueous hydrochloric acid. The mixed solvent was used because of very low solubility of many of the acids in water.

As already mentioned in section 3.4-1, the benzoic acids show comparatively lower sorption from water solutions due to the operation of the ion exclusion mechanism. In acidic solvent this is overcome because the ionization is suppressed and it is also likely that the solubilities of the acids are decreased to some extent. In the mixed solvent all the acids show lower sorption and the reasons for this may include :

(i) In this solvent mixture the organic acids are more soluble than in water and hence will favour the external phase.

(ii) For this solvent composition, the resin prefers water to dioxan. Therefore, the water to dioxan ratio inside the resin phase is higher than in the external solution. Since the solubility of these acids increases with increase in dioxan concentration, these acids will prefer the dioxan rich phase, i.e. the external phase.

(iii) Interaction forces between the resin matrix and the hydrocarbon portion of dioxan would have an influence in the same direction, because such an interaction would block some of the sorption active sites for the solute molecules. This would mean that the envionment inside the resin phase is less favourable for the retention of benzoic acids.

It is seen that the decrease in sorption caused, when the solvent is changed from aqueous to mixed, is relatively higher for the solutes having methoxy groups than for the hydroxybenzoic acids. This may be due to relatively more increase in the solubility of benzoic acids with hydrophobic substituents as the organic nature of the solvent is increased than for hydroxybenzoic acids.

The present study of the sorption behaviour of benzoic acids, on the whole, reveals that the resin is selective with respect to the functional group i.e. the molecules that differ in the type or number of functional groups. Isomer selectivity of the resin, which may be considered as a particular case of functional group selectivity, is also fairly good. This suggests that the separation of some closely related acids would be feasible by the proper selection of experimental conditions.

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