CHAPTER 2

SORPTION EQUILIBRIUM

2.1 INTRODUCTION

Following the observation (109) 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 in to the microcavities and other modes of mixing.

Ion exchanger can sorb a great variety of substances. This can occur both from the gas phase and from the liquid phase (1-4,97,110). Molecular sorption on synthetic ion exchange resins was first carried out by Bhatnagar and coworkers (111-113) and later applied by Wheaton and Bauman (114,115) for the separation of nonionic materials. Further studies (116-228) 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. The hydrocarbon network is hydrophobic but the ionegic groups are hydrophilic. Hence, when the resin particle is placed into a polar solvent e.g. Water, it imbibes the solvent and swells to a limited extent. The amount of solute sorbed and the extent of swelling depend on the degree of crosslinking, X, and the counterions. If the external solvent contains a weak or nonelectrolyte it is also sorbed to a certain extent and after sometime a state of equilibrium is reached. At equilibrium, 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. Besides these, there may be specific interactions responsible for the sorption of a solute which may include the following :

(1) 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 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.

(2) 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 non-electrolyte 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 counterions are strongly solvated. However, the salting out in the ion exchanger could be counterbalanced by adding an electrolyte to the external solution.

(3) 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.

(4) 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, isnot attained.

(5) 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.

(6) 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 of 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.

2.2 EXPERIMENTAL

The resins used were Dowex 50W, styrene-divinylbenzene copolymer based sulfonic acid cation exchange resins of nominal degree of crosslinking, X, as 1, 2, 4, 8, 12 and 16. Where X denotes the mole percent of combined pure DVB in the styrene copolymer used as resin matrix for preparing the sulfonate. These are further referred to as indicated in Table 2.3-1. The resins of group I to IV were of Dowex 50W grade. Those given in group V were of Dowex 50 grade and were obtained from Dow Chemical Company, U.S.A. as gift samples for research work at various time as follows :

Time of receipt	Batch
June 1961	I
January 1966	II
September 1970	III
September 1970	IV
September 1976	V

Group VI contains macroreticular resin Amberlite-200 supplied by Rohm and Haas Company, U.S.A.

Before use, these resins were washed, cycled between sodium chloride and hydrochloric acid (229) and finally regenerated with a large excess of hydrochloric acid, washed free of acid, filtered, air dried, sieved and stored in a well stoppered glass bottles.

The moisture content (27) was determined by heating weighed samples ($\sim$0.5 g) of the air dried resin in clean, dry weighing bottles in an oven at 101 ± 2°C to a constant weight and per cent moisture content was then calculated.

For the estimation of capacity (27), weighed samples of the air dried resin ($\sim$0.5 g) were contacted with 50 cc of $\sim$ 1.0 N barium chloride solution in well stoppered reagent bottles 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. Earlier work has suggested that increasing contact time did not show any measurable change in the amount of acid liberated. The capacities of the air dried and oven dried resins are given in Table 2.3-1.

The solvents used were distilled water, Wa, 0.01 N aqueous hydrochloric acid WH and 10 % dioxan in 0.01 N aqueous hydrochloric acid DWH. Dioxan was purified (230) as follows :

A mixture of dioxan (1 liter), concentrated hydrochloric acid (14 ml) and water (100 ml) was refluxed for 10-12 hours during which time a slow stream of nitrogen was bubbled through the solution. The solution was cooled and potassium hydroxide pellets were added slowly with shaking until they no longer dissolved and a second layer had separated. The dioxan was decanted and transferred over potassium hydroxide pellets. If any water separated, it was removed and the dioxan was allowed to stand over fresh potassium hydroxide pellets for a longer time. It was next refluxed with sodium for 10-12 hours till reaction ceased, leaving a part of sodium unreacted. The solvent was then distilled from sodium and stored out of contact with air (B.P. 101-102°C).

Acidic aqueous dioxan was prepared by volume, for example, 10 % acidic aqueous dioxan was prepared by diluting 100 ml of dioxan to 1 liter with aqueous hydrochloric acid so that the final solution was 0.01 N in hydrochloric acid.

All the organic acids studied (Table 1.3-1) were of C.P. (Chemically Pure) or A.R. (Analytical Reagent) grade. They were recrystallized/distilled and their m.p./b.p. were checked with the literature values (107,108). Solutions of these acids were prepared by dissolving weighed amount of samples in the particular solvent in volumertic flasks and then suitably diluting.

The sorption equilibrium study was carried out by contacting the organic acid solutions of different concentrations and known volume (50 ml) with the weighed amounts (~1.0 g) (except for the resins Dowex 50W-X1 and X_2 where it was 0.25 and 0.5 g respectively depending on the degree of swelling of the resin) of the air dried resin, in well stoppered flasks, with frequent shaking at room temperature (~30°C) for about 24 hours. After equilibrium was reached, the initial concentration C_o (moles per liter) and the final equilibrium concentration C_o (moles per liter) were estimated by ultraviolet absorption (231-236) (at λinv or λmax for the particular solute) or by titrating aliquots with standard sodium hydroxide solution (whichever is applicable). A correction for blank was applied for the change in absorption or titration if any of the solvent caused when contacted with the ion exchange resin and the corrected values of C_e were used in further calculations. Preliminary studies revealed that the increase in contact time or a small variation in temperature in the vicinity of room temperature has no significant effect on the sorption.

2.3 RESULTS

Table 2.3-1 : Data for cation exchange resinsused

Group	No.	Resin	Mesh range	X	Further referred to as	Moisture Percentage	Capacity(meqs/gm)	
							Air dry	Oven dry
I	1	Dowex 50W-X1	50-100	1	X1	20.3	4.18	5.24
	2	Dowex 50W-X2	100-200	2	X2	20.4	4.14	5.20
	3	Dowex 50W-X4	100-200	4	X4	24.0	3.70	4.87
	4	Dowex 50W-X8	100-200	8	X8	27.0	3.50	4.79
	5	Dowex 50W-X12	100-200	12	X12	26.0	3.55	4.80
	6	Dowex 50W-X16	20-50	16	X16	24.7	3.54	4.70
II	1	Dowex 50W-X4	20-50	4	$X4_a$	24.6	3.66	4.86
	2	Dowex 50W-X4	50-100	4	$X4_b$	25.0	3.63	4.84
	3	Dowex 50W-X4	100-200	4	X4	24.0	3.70	4.87
	4	Dowex 50W-X4	200-400	4	X4d	25.6	3.65	4.90
III	1	Dowex 50W-X8	20-50	8	$X8_a$	26.6	3.50	4.77
	2	Dowex 50W-X8	50-100	8	$X8_b$	26.0	3.57	4.82
	3	Dowex 50W-X8	100-200	8	X8	27.0	3.50	4.79
	4	Dowex 50W-X8	200-400	8	$X8_d$	27.8	3.45	4.78

cont...

IV	1	Dowex 50W-X12	50-100	12	$X12_b$	25.5	3.56	4.78
	2	Dowex 50W-X12	100-200	12	X12	26.0	3.55	4.80
	3	Dowex 50W-X12	200-400	12	$X12_d$	26.3	3.56	4.83
V	1	Dowex 50 -X4	100-200	4	$X4_A$	26.4	3.68	5.00
	2	Dowex 50 -X4	100-200	4	$X4_B$	25.8	3.56	4.80
	3	Dowex 50 -X4	100-200	4	$X4_C$	29.3	3.55	5.02
	4	Dowex 50 -X4	100-200	4	$X4_D$	28.5	3.61	5.05
VI	1	Amberlite-200	20-50	~20	Amb-200	25.5	3.56	4.78

Table 2.3-2 : Illustrative calculation of sorption coefficient B for pimelic acid with the resin Dowex 50W-X1 (50-100).

$10^3 C_o$	$10^3 C_e$	$10^3 C_r$	$10^3 B$
100	99.01	17.9	558
90	89.04	18.4	589
80	79.11	19.5	578
70	69.25	18.1	602
60	59.37	19.0	557
50	49.45	18.8	594
40	39.58	18.6	568
30	29.67	18.9	581
20	19.77	19.3	590
10	9.89	19.7	573
		Average	579

Table 2.3-3 : Illustrative calculation of sorption coefficient B for pimelic acid with the resin Dowex 50W-X2 (100-200).

10^3Co	10^3Ce	10^3Cr	10^3B
100	97.91	37.1	575
90	87.95	39.2	596
80	78.34	37.3	567
70	68.42	39.4	586
60	58.70	38.4	575
50	49.01	35.9	562
40	39.11	38.7	591
30	29.33	37.8	600
20	19.57	39.0	557
10	9.79	36.6	581
		Average	579

Table 2.3-4 : Illustrative calculation of sorption coefficient B for pimelic acid with the resin Dowex 50W-X4 (100-200).

$10^3 C_o$	$10^3 C_e$	$10^3 C_r$	$10^3 B$
100	96.90	77.2	408
90	87.10	75.9	436
80	77.50	74.8	431
70	67.90	71.5	427
60	58.10	73.7	451
50	48.40	74.5	437
40	38.76	72.3	442
30	29.06	76.6	421
20	19.35	77.9	430
10	9.68	75.1	447
		Average	433

Table 2.3-5 : Illustrative calculation of sorption coefficient B for pimelic acid with the resin Dowex 50W-X8 (100-200).

$10^3 Co$	$10^3 Ce$	$10^3 Cr$	$10^3 B$
100	98.80	76.1	159
90	88.97	73.8	157
80	79.11	74.9	150
70	69.23	75.3	148
60	59.34	72.0	154
50	49.45	76.6	146
40	39.53	74.2	160
30	29.66	75.7	151
20	19.77	77.4	149
10	9.88	78.5	156
		Average	153

Table 2.3-6 : Illustrative calculation of sorption coefficient B for suberic acid with the resin Dowex 50W-X12 (100-200).

10^3Co	10^3Ce	10^3Cr	10^3B
10	9.88	77.9	150
9	8.91	72.1	140
8	7.91	77.4	144
7	6.92	74.4	151
6	5.93	75.0	147
5	4.95	77.0	138
4	3.96	75.2	146
3	2.97	73.3	142
2	1.98	73.9	149
1	0.99	76.1	143
		Average	145

Table 2.3-7 : Illustrative calculation of sorption coefficient B for suberic acid with the resin Dowex 50W-X16 (20-50).

$10^3 Co$	$10^3 Ce$	$10^3 Cr$	$10^3 B$
10	9.83	73.9	230
9	8.84	74.2	239
8	7.87	73.3	225
7	6.88	75.4	234
6	5.90	72.1	241
5	4.91	76.9	228
4	3.93	72.8	236
3	2.95	74.8	244
2	1.96	77.6	235
1	0.98	76.0	238
		Average	235

Table 2.3-8 : Illustrative calculation of sorption coefficient B for azelaic acid with the resin Amberlite-200.

10^3Co	10^3Ce	10^3Cr	10^3B
10	9.91	74.9	114
9	8.92	75.5	118
8	7.93	72.9	115
7	6.94	73.4	116
6	5.95	77.7	115
5	4.96	72.2	117
4	3.96	74.3	120
3	2.97	76.1	116
2	1.98	74.0	122
1	0.99	77.0	117
		Average	117

Table 2.3-9 : Values of sorption coefficient B for dicarboxylic acids studied with different resins

Resin X =		Oxalic	Malonic	Succinic	Glutaric	Adipic	Pimelic	Suberic	Azelaic	Sebacic
1	Exp	-	0.0539	0.0976	0.1761	0.3204	0.6258	0.9424	1.8790	2.8910
	Cal	0.0363	0.0631	0.1096	0.1905	0.3311	0.5754	1.0000	1.7380	3.0200
2	Exp	-	0.0584	0.1000	0.1832	0.3099	0.5807	0.9657	1.9010	2.9200
	Cal	0.0363	0.0630	0.1095	0.1903	0.3308	0.5748	0.9988	1.7360	3.0160
4	Exp	-	0.0471	0.0830	0.1442	0.2510	0.4350	0.7510	1.3020	2.2790
	Cal	0.0273	0.0475	0.0826	0.1435	0.2494	0.4333	0.7530	1.3080	2.2740
8	Exp	-	-	-	0.0510	0.0870	0.1540	0.2680	0.4610	0.8060
	Cal	0.0097	0.0168	0.0292	0.0508	0.0882	0.1532	0.2663	0.4623	0.8042
12	Exp	-	-	-	-	0.0478	0.0837	0.1460	0.2500	0.4390
	Cal	0.0053	0.0092	0.0159	0.0276	0.0480	0.0834	0.1450	0.2520	0.4377
16	Exp	-	-	-	-	0.0638	0.0925	0.2084	0.3749	0.7352
	Cal	0.0085	0.0149	0.0258	0.0448	0.0779	0.1354	0.2354	0.4090	0.7108
Amb-200	Exp	-	-	-	-	-	-	0.0728	0.0946	0.2131
	Cal	0.0024	0.0042	0.0074	0.0128	0.0223	0.0387	0.0672	0.1168	0.2030

Fig. 2.3-1 : Plot of log B versus n_c for aliphatic dicarboxylic acids for resins X1, X4, X16 and Amberlite-200.

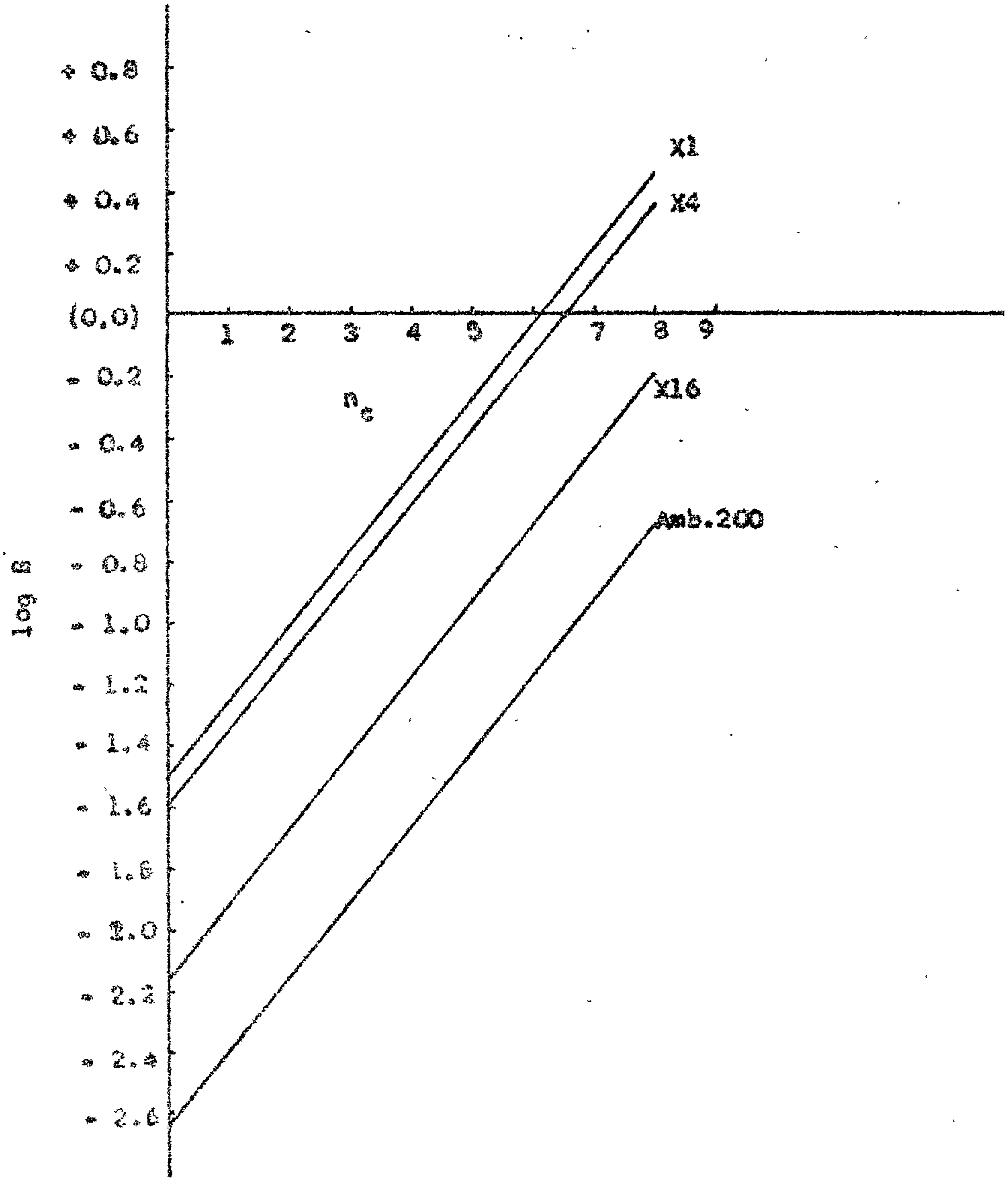

Table 2.3-10 : Values of m for the resins studied.

Group	Resin	m	log m
I	Dowex 50W-X1 (50-100)	15.850	1.2000
	Dowex 50w-X2 (100-200)	5.610	0.7490
	Dowex 50W-X4 (100-200)	2.630	0.4200
	Dowex 50W-X8 (100-200)	2.630	0.4200
	Dowex 50W-X12 (100-200)	2.630	0.4200
	Dowex 50W-X16 (20-50)	1.052	0.0221
V	Dowex 50-$X4_A$ (100-200)	2.995	0.4765
	Dowex 50-$X4_B$ (100-200)	3.296	0.5180
	Dowex 50-$X4_C$ (100-200)	2.995	0.4765
	Dowex 50-$X4_D$ (100-200)	3.296	0.5180
VI	Amberlite-200 (20-50)	2.636	0.4210

The values of m and log m for resins of groups II,III and IV (Table 2,3-1) were practically same as those given for corresponding resins in group I.

Table 2.3-11 : Values of n_c and calculated values of log $mBX^{1.5}$ (equation:12)

Acid	n_c	log $mBX^{1.5}$
Oxalic	0	-
Malonic	1	0.00
Succinic	2	0.24
Glutaric	3	0.48
Adipic	4	0.72
Pimelic	5	0.96
Suberic	6	1.20
Azelaic	7	1.44
Sebacic	8	1.68

Table 2.3-12 : Values of sorption coefficient B for dicarboxylic acids with different batches of resin X4.

Resin batch		Oxalic	Malonic	Succinic	Glutaric	Adipic	Pimelic	Suberic	Azelaic	Sebacic
$X4_A$	Exp	-	-	0.0732	0.1259	0.2005	0.4198	0.6557	1.1551	2.0100
	Cal	0.0240	0.0417	0.0725	0.1260	0.2190	0.3806	0.6613	1.1490	1.9970
$X4_B$	Exp	-	-	0.0702	0.1155	0.2112	0.3501	0.5857	1.1002	1.8506
	Cal	0.0218	0.0379	0.0659	0.1145	0.1990	0.3458	0.6010	1.0440	1.8150
$X4_C$	Exp	-	-	0.0751	0.1283	0.2302	0.3769	0.6852	1.1406	1.9504
	Cal	0.0240	0.0417	0.0725	0.1260	0.2190	0.3806	0.6613	1.1490	1.9970
$X4_D$	Exp	-	-	0.0623	0.1167	0.1810	0.3203	0.6250	1.0040	1.8095
	Cal	0.0218	0.0379	0.0659	0.1145	0.1990	0.3458	0.6010	1.0440	1.8150

Fig. 2.3-2 : Plot of log D versus n_c for dicarbonylic acids studied with resin XA_2.

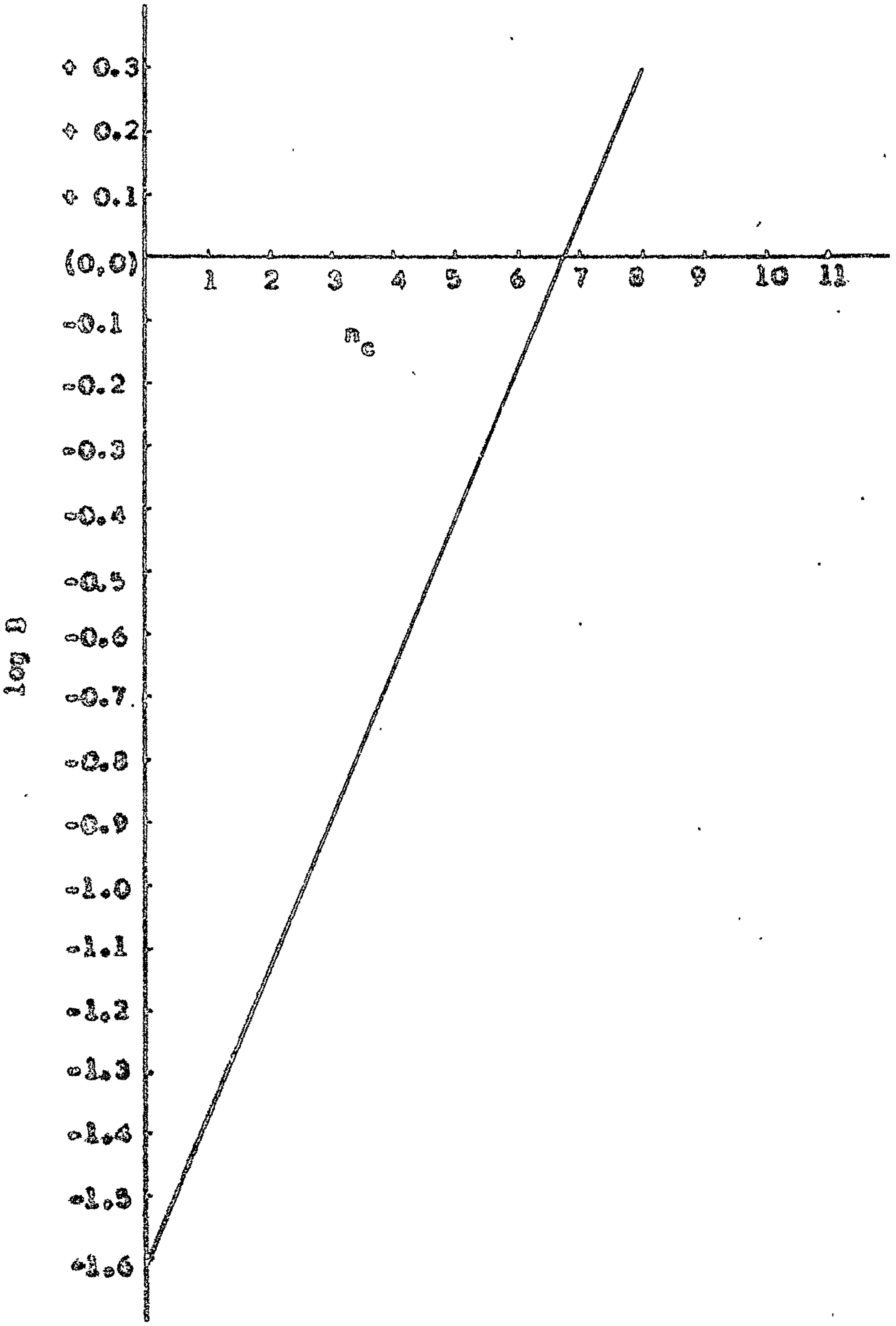

Table 2.3-13 : Illustrative calculation of sorption coefficient B

Acid : Benzoic acid.

Solvent : WH

Resin : Dowex 50W-X12 (100-200).

$10^4 C_o$	$10^4 C_e$	$10^4 C_r$	$10^4 S$
9.98	9.32	740.9	8.85
14.65	13.67	751.2	12.99
20.04	18.72	742.3	17.78
24.57	22.93	753.2	21.78
30.16	28.15	750.8	26.74
33.71	31.45	757.4	29.88
38.00	35.49	743.7	33.72
43.33	40.43	755.9	38.41
46.59	43.50	747.7	41.33
48.68	45.40	760.5	43.13

Table 2.3-14 : Illustrative calculation of sorption coefficient B

Acid : 2,6-dihydroxybenzoic acid

Solvent : WH

Resin : Dowex 50W-X4 (100-200).

10^4 Co	10^4 Ce	10^4 Cr	10^4 S
4.53	4.40	753.8	1.76
5.46	5.30	751.0	2.12
7.00	6.80	745.4	2.72
7.93	7.70	744.8	3.08
9.58	9.30	751.9	3.72
10.92	10.60	752.5	4.24
11.54	11.20	750.4	4.48
13.49	13.10	749.2	5.24
15.96	15.50	748.1	6.20
16.50	16.02	747.7	6.41

Table 2.3-15 : Illustrative calculation of sorption coefficient B

Acid : 2,4-dihydroxybenzoic acid

Solvent : DWH

Resin : Dowex 50W-X4 (100-200).

10^4Co	10^4Ce	10^4Cr	10^4S
1.70	1.50	751.2	2.61
2.16	1.90	772.9	3.31
2.72	2.40	766.2	4.18
3.16	2.80	739.0	4.87
3.73	3.30	745.8	5.74
4.52	4.00	740.7	6.96
5.09	4.50	748.3	7.83
5.66	5.00	759.6	8.70
6.33	5.60	747.2	9.74
6.81	6.02	755.4	10.47

Table 2.3-16 : Illustrative calculation of sorption coefficient B

Acid : 2,4-dihydroxybenzoic acid

Solvent : WH

Resin : Dowex 50W-X8 (100-200).

$10^4 Co$	$10^4 Ce$	$10^4 Cr$	$10^4 S$
4.07	3.4	757.0	8.84
4.77	4.0	745.1	10.40
6.13	5.1	774.4	13.26
8.05	6.7	775.2	17.42
9.44	7.9	750.3	20.54
11.12	9.3	753.2	24.18
14.10	11.8	749.8	30.68
17.18	14.4	742.4	37.44
19.41	16.2	762.4	42.12
20.46	17.1	755.6	44.46

Table 2.3-17 : Illustrative calculation of sorption coefficient B

Acid : 2,6-dihydroxy benzoic acid

Solvent : DWH

Resin : Dowex 50W-X4 (100-200).

10^4Co	10^4Ce	10^4Cr	10^4S
2.76	2.72	745.3	0.52
3.14	3.10	755.9	0.59
4.36	4.30	753.2	0.82
5.27	5.20	747.8	0.99
5.99	5.90	765.5	1.12
7.51	7.40	750.2	1.41
8.32	8.20	748.6	1.56
8.92	8.80	739.3	1.67
10.04	9.90	751.8	1.88
10.65	10.50	752.7	2.00

Table 2.3-18 : Illustrative calculation of sorption coefficient B

Acid : 3,5-dimethoxybenzoic acid

Solvent : DWH

Resin : Dowex 50W-X4 (100-200).

10^4Co	10^4Ce	10^4Cr	10^4S
0.434	0.31	755.8	1.65
0.475	0.34	750.2	1.81
0.548	0.39	760.7	2.08
0.615	0.44	747.9	2.35
0.686	0.49	753.8	2.61
0.739	0.53	742.3	2.82
0.788	0.56	764.6	2.98
0.836	0.60	740.5	3.20

Table 2.3-19 : Illustrative calculation of sorption coefficient B

Acid : 2,4-dimethoxybenzoic acid

Solvent : DWH

Resin : Dowex 50W-X4 (100-200).

$10^4 Co$	$10^4 Ce$	$10^4 Cr$	$10^4 S$
1.55	1.23	741.7	4.31
2.19	1.74	746.8	6.09
2.85	2.26	749.2	7.91
3.41	2.71	740.1	9.49
4.19	3.32	752.3	11.62
4.80	3.80	750.2	13.30
5.34	4.22	760.6	14.77
5.77	4.54	773.9	15.89
6.20	4.90	755.5	17.15
6.47	5.10	767.8	17.85

Fig. 2.3-3 : Plot of S versus Ce for (i) 2,4-dimethoxybenzoic acid in solvent DWH and (ii) 2,6-dihydroxybenzoic acid in solvent WH with resin Dowex 50W-X4 (100-200).

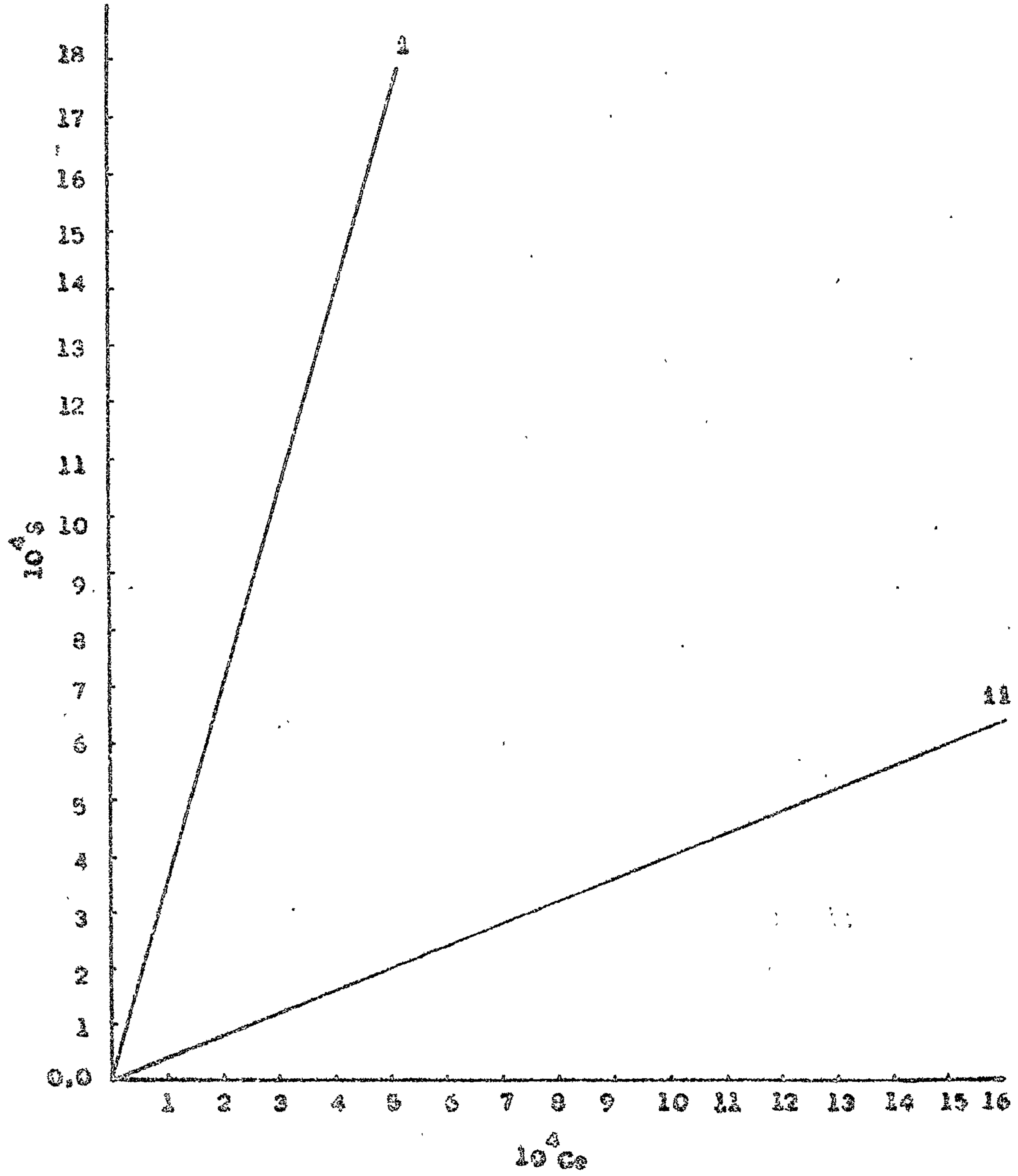

Table 2.3-20 : Illustrative calculation of sorption coefficient B

Acid : 2,6-dimethoxybenzoic acid
Solvent : DWH
Resin : Dowex 50W-X4 (100-200).

10^4 Co	10^4 Ce	10^4 Cr	10^4 S
2.53	2.30	754.2	2.99
3.13	2.85	752.0	3.71
3.75	3.42	746.4	4.45
4.29	3.91	744.3	5.08
5.13	4.67	753.8	6.07
5.93	5.40	749.9	7.02
7.43	6.76	757.7	8.79
8.62	7.86	748.5	10.22
9.30	8.48	742.6	11.02
10.16	9.25	756.1	12.03

Table 2.3-21 : Experimental and calculated values of sorption coefficient B for benzoic acids studied with resin Dowex 50W-X4.

I = Benzoic acid ; $\Delta B = B_{exp} - B_{cal}$; $R = B_{exp}$ in WH/B_{exp} in DWH

Acid	Solvent									
	Wa			WH			DWH			R
	Exp	Cal	Δ B	Exp	Cal	Δ B	Exp	Cal	Δ B	
I	2.68			2.82			1.41			
2-OHI	2.12			3.40			1.70			
3-OHI	1.22			2.15			1.07			
4-OHI	2.20			2.62			1.31			
2-OMeI	2.96			4.00			1.80			
3-OMeI	4.30			6.00			2.70			
4-OMeI	4.30			6.00			2.70			
3,5-diOHI	0.96	0.56	+0.40	1.68	1.64	+0.04	0.80	0.81	-0.01	2.10
2,4-diOHI	1.62	1.74	-0.12	3.65	3.16	+0.49	1.74	1.58	+0.16	2.10
2,6-diOHI	0.31	1.68	-1.37	0.40	4.10	-3.70	0.19	2.06	-1.86	2.11
3,5-diOMeI	-	-	-	-	-	-	5.33	5.17	+0.16	-
2,4-diOMeI	-	-	-	-	-	-	3.50	3.45	+0.05	-
2,6-diOMeI	-	-	-	-	-	-	1.30	2.30	-1.00	-

Table 2.3-22 : Experimental and calculated values of sorption coefficient B for benzoic acids studied with resin Dowex 50W-X8

I = Benzoic acid ; $\Delta B = B_{exp} - B_{cal}$

Acid	Solvent					
	Wa			WH		
	Exp	Cal	Δ B	Exp	Cal	Δ B
I	1.34			1.40		
2-OHI	1.06			2.35		
3-OHI	0.62			1.10		
4-OHI	1.12			1.30		
2-OMeI	2.20			2.70		
3-OMeI	3.10			4.20		
4-OMeI	3.10			4.20		
3,5-diOHI	0.50	0.29	+0.21	0.85	0.86	-0.01
2,4-diOHI	1.14	0.89	+0.25	2.60	2.18	+0.42
2,6-diOHI	-	-	-	-	-	-

Table 2.3-23 : Experimental and calculated values of sorption coefficient B for benzoic acids studied with resin Dowex 50W-X12

I = Benzoic acid ; $\Delta B = B_{exp} - B_{cal}$

Acid	Solvent					
	Wa			WH		
	Exp	Cal	ΔB	Exp	Cal	ΔB
I	0.85			0.95		
2-OHI	0.70			2.00		
3-OHI	0.40			0.70		
4-OHI	0.72			0.90		
2-OMeI	1.70			2.30		
3-OMeI	2.50			3.40		
4-OMeI	2.50			3.40		
3,5-diOHI	0.30	0.19	+0.11	0.55	0.52	+0.03
2,4-diOHI	0.90	0.59	+1.30	1.30	1.89	-0.59
2,6-diOHI	-	-	-	-	-	-

2.4 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 non-electrolyte 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.

(1) 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.

(2) 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.

(3) 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.

2.4.1 Aliphatic Dicarboxylic Acids

In the present work eight straight chain aliphatic dicarboxylic acids (malonic to sebacic) have been studied with six resins of different degree of crosslinking, X, as 1, 2, 4, 8, 12 and 16 (group I Table 2.3-1) in aqueous medium. Resins of different crosslinkage such as 4, 8 and 12 of various mesh size (group II, III and IV Table 2.3-1) were studied to investigate the effect of particle size on sorption equilibrium. Resin of crosslinking 4 was studied with four batches (group V Table 2.3-1) obtained at different times of ordinary (Dowex 50) grade to study the variation of sorption on resins of supposedly same degree of crosslinking. Studies were also carried out with a macroreticular cation exchange resin Amberlite-200, to study the behaviour of such resin (group VI Table 2.3-1) on sorption equilibria.

In chromatography, the sorption coefficient of a solute is a basic parameter and related to the behaviour of the solute in the column and its appearance in the effluent. This implies that the first step should be to study the sorption coefficient of solutes. The extent of the sorption of the solute per unit capacity of the resin at a given temperature would be determined by the interplay of various interactions such as London dispersion, dipole-dipole, steric and hydrogen bonding. These in turn would be influenced by several variables of the resin-solute-solvent system (Section 2.1,2.4). Thus a complex behaviour is to be expected. However, a systematic study of one variable at a time should lead towards a better understanding of the phenomena.

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

$$S = \frac{Co - Ce}{Cr} \qquad \text{------(1)}$$

where Co and Ce are initial and final equilibrium concentrations of the solute in moles per liter and Cr is the number of equivalents of the air dried resin added per liter of the solution.

But, for a linear sorption isotherm of solute-resin system, we have,

$$\frac{Co - Ce}{Cr} = B.Ce \qquad \text{-----(2)}$$

where B is the sorption coefficient of the solute (liter per equivalent of the resin) at a given temperature. Hence from equations (1) and (2) we have,

$$S = B.Ce \qquad \text{-----(3)}$$

$$\text{and} \qquad B = \frac{Co - Ce}{Cr.\,Ce} \qquad \text{-----(4)}$$

Alternatively, one may consider that the solute is partitioned between the two immiscible phases, the solvent phase and the resin phase and the value of B may be regarded as a measure of partition coefficient.

Alternatively, we may consider the sorption equilibrium as

$$R + S \overset{B}{\rightleftharpoons} RS \qquad \text{-----(5)}$$

where R and S denote resin and solute respectively. The sorption equilibrium constant B is then given by equation (4).

The sorption coefficients were determined at room temperature (~30^0C) for eight aliphatic dicarboxylic acids with resins X1, X2, X4, X8, X12, X16 and Amberlite-200 in hydrogen form in aqueous medium. In hydrogen form of the resin, as there is high concentration of H^+ ions in the resin phase, ion exchange of dicarboxylic acids is superseded by molecular sorption.

Table 2.3-2 to Table 2.3-5 give an illustrative calculations of the sorption coefficient B for pimelic acid with resins X1, X2, X4 and X8 and Tables 2.3-6 to 2.3-8 give the same for suberic acid with resins X12 and X16 and Azelaic acid with resin Amberlite-200. The experimental values of sorption coefficient obtained in this way are summarized in Table 2.3-9 and are in agreement with the values obtained earlier for some of these acids (222).

These results can be formulated by postulating that the sorption coefficient B for a resin-solute-solvent system is given by the product of two terms, the group term φ ; a summation of the increments contributed by each additional group and the ground term Φ; a function of the sorptive system. Here, oxalic acid ($n_c = o$) may be considered as the ground molecule and increment in the aliphatic chain can be made by sequential addition of a $-CH_2$ unit between two head groups of the ground molecule, provided resulting molecule is not so large that the steric effects become effective. Hence we have,

$$B = \varphi \cdot \Phi \qquad \text{-----(6)}$$

If, there are n_1 groups of type 1 and the group constant for each is a_1, n_2 groups of type 2 and the group constant for each is a_2--------and n_r groups of type r and group constant for each is a_r then the group term ρ is given by

$$\rho = a_1^{n_1} \cdot a_2^{n_2} \text{-----} a_r^{n_r} \qquad \text{-----(7)}$$

It is suggested that the ground term Φ may be given by

$$\Phi = \frac{1}{m} \cdot X^{-\gamma} \qquad \text{-----(8)}$$

Where X is the degree of crosslinking of the resin and m and γ are constants (Table 2.3-10). Combining the equations (6), (7) and (8) and taking logarithm on both the sides, we have

$$\text{Log } B = n_1 \log a_1 + n_2 \log a_2 + \text{---------} + n_r \log a_r - \log(m\,X^{\gamma}) \qquad \text{-----(9)}$$

Logarithm of the experimental values of B (Table 2.3-9) were plotted against the values of n_c (the number of straight chain carbon atoms in the molecule, Table 2.3-11) for each homologous series. The plots were linear and the slope of each plot is 0.24 (Fig. 2.3-1). From the values of their slopes and intercepts, the logarithm of the groups constants and the numerical values of log m and γ (Table 2.3-10) were computed.

The B value of ground molecule is too low to be measured precisely and found to be acting exceptionally. This means that 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 environment which in fact, makes the molecule more organic in nature. Further, similar linear relations have been reported for monocarboxylic acids, alcohols and coumarins (176, 168, 193, 226). Combining the results of similar study of aliphatic monocarboxylic acids, we have the equation,

$$\log B = 0.24n_c - 0.12n_x - \log(m X^{\gamma}) \qquad \text{-----(10)}$$

where n_x denotes the number of terminal carboxylic groups. For dicarboxylic acids $n_x = 2$ and $\gamma = 1.5$. Hence equation (10) becomes

$$\log B = 0.24n_c - 0.24 - \log m - 1.5 \log X \text{ -----(11)}$$

Values of sorption coefficient B derived from this equation are given in Table 2.3-9. Agreement between experimental and calculated values of B is fair. Rearranging the equation (11) we have,

$$\begin{aligned} \log mBX^{1.5} &= 0.24n_c - 0.24 \\ &= 0.24\,(n_c - 1) \qquad \text{-----(12)} \end{aligned}$$

The calculated values of $\log mBX^{1.5}$ according to this equation are mentioned in Table 2.3-11. These are too in good agreement with the values of $\log mBX^{1.5}$ obtained experimentally.

It is evident from B values (Table 2.3-9) that the sorption increases with increase in chain length among the homologous series. This may be attributed to the decrease in the solubility of the solute in the solvent and the increase in the two types of dispersion interactions ; (i) the London interactions between the dicarboxylic acid molecules and the resin matrix and (ii) the dipole-dipole interactions of the polar solvent molecules between one another and with the polar groups of the dicarboxylic acid molecules (which account for a major part of the total attractive forces in the cases of organic compounds particularly hydrocarbons). The sorption of dicarboxylic acid is lower than that of corresponding monocarboxylic acid (220). This is because of the increased steric hindrance due to the presence of two carboxylic groups and the increased effect of ion exclusion due to the lower pK values of these acids. Morevoer, hydrophilic nature of the carboxylic group also diminishes the sorption of dicarboxylic acids.

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,

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

$$\therefore -\Delta F = RT \cdot \ln B$$

$$\therefore \frac{-\Delta F}{2.303RT} = \log B = 0.24n_c - 0.24 - \log m - 1.5 \log X \text{ ---(13)}$$

where R is molar gas constant and T is the absolute temperature. 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 of homologous acids, the only change made is the increase in the number of carbon atoms in the aliphatic chain length. 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 hydrocarbon chain and it should be directly proportional to n_c. It follows therefore that log B 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. These conclusions are also supported by the observations of Tanaka, N. and Thornton, E.R. (237).

2.4.1.1 Effect of Particle Size of the Resin

Sorption equilibrium of eight straight chain aliphatic dicarboxylic acids was studied with resins of nominal degree of crosslinking 4, 8 and 12 of different particle size viz. 20-50, 50-100, 100-200, 200-400 (group II, III and IV Table 2.3-1). Particle size 100-200 means, on sieving the resin, particles of resin can pass through a mesh of 100 and are retained by a mesh of 200.

It was observed that the sorption coefficient B was not measurably affected by the particle size in each case. This implies that, in the cation exchange resins studied, sorption occurs on and through the entire particle provided sufficient time is permitted for sorption. Thus the diffusion of the organic acid molecule is possible through the entire resin particle and is not limited to certain portion of the particle.

2.4.1.2 Effect of Crosslinking of the Resin

Sorption of eight straight chain aliphatic dicarboxylic acids has been studied with the conventional gel-type resin of nominal degree of crosslinking, X, as 1, 2, 4, 8, 12 and 16.

For each acid the sorption coefficient was practically same, when X increased from 1 to 2, then decreased, when X increased up to 12 and again increased, when X increased up to 16 (Table 2.3-9). When log B was plotted against n_c for each resin, the plots were parallel and the slope in each case was 0.24 (Fig. 2.3-1) and independent of the degree of crosslinking X. This observation indicates the significant conclusion that the contribution of methylene group is independent of the degree of crosslinking of the resin for a given solvent. In orther words, the group term in equation (6) is independent of the value of X. The variation of sorption therefore is given by the variation of the ground term ϕ(Equation : 8), which is reflected in the variation of the value of log m or m with increase in X. Table 2.3-10 indicates that the value of log m or m decreases as the value of nominal degree of crosslinking X increases from 1 to 4, then becomes constant as X increases from 4 to 12 and again decreases as X increases to 16. With increase in X, the sorption should decrease due to the decrease in the uptake of the solvent by the resin and the increase in the salting out effect and it should increase due to the increase in the dispersion interactions between the solute molecules and the resin matrix. Hence the overall effect may be decrease or increase in the sorption depending on the relative contribution of the interactions.

2.4.1.3 Effect of the Resin Batch

Sorption equilibrium studies of eight aliphatic dicarboxylic acids were carried out with the resin of nominal degree of crosslinking X as 4 of four batches (group V Table 2.3-1) of Dowex 50 grade. The Dowex 50 resins are considered to be of less pure grade than those of Dowex 50W grade. Although Dowex 50 grade are much cheaper than Dowex 50W grade, the object here was to study the behaviour of less expensive resin and the variation in sorption from batch to batch of resin of supposedly same degree of crosslinking.

It is observed that the sorption for resins of Dowex 50 grade (Table 2.3-12) vary to a small extent from batch to batch and is lower than those of resins Dowex 50W grade in which variation observed is negligible as indicated by the fair agreement with the earlier results (222). This may be attributed to the variation in the relative amounts of the isomers of the crosslinking monomers (DVB, ethylstyrene) in the monomer mixture used for commercial resin preparation (Section 1.2.2). Since, pure DVB is too expensive to be used for manufacturing commercial resin, a mixture of about equal weights of DVB and ethylstyrene is used industrially. The presence of ethylstyrene results in the ethyl substituent in some of the benzene rings. The variation in composition of the commercial DVB should account in part for the differences observed among different batches of supposedly identical resins. However it is observed that when log B is ploted against n_c, the slope for each batch is again 0.24 (Fig. 2.3-2). In other words, the contribution of the group term to the overall sorption is unaffected by the grade or batch of the resin. The variation in sorption, hence, should be attributed to the change in the contribution of the ground term Φ (Equation : 8) which is reflected in the values of log m (Table 2.3-10).

2.4.1.4 Effect of Structure of the Resin

The resins of Dowex 50 and Dowex 50W grade are conventional gel-type exchangers. On the other hand, resin Amberlite-200 (group VI Table 2.3-1) is a macroreticular type resin. The degree of crosslinking of this resin is not exactly known but as has been mentioned in ' Amber-hi-lites ' issue (19), it is approximately 20.

The sorption of eight straight chain aliphatic dicarboxylic acids with Amberlite-200 in aqueous medium was studied. The plot of log B versus n_c is linear and the slope is here too 0.24 (Fig. 2.3-1). Taking the value of X = 20, the value of B calculated according to the equation (11) are in good agreement with experimental values (Table 2.3-9). From this observation it follows that the contribution of group term for both gel-type and macro-reticular-type is same, and the differences in sorption is again to be attributed to the change in the ground term Φ . This is reflected in the value of log m or m (Table 2.3-10). The sorption for Amberlite-200 is relatively much lower than the conventional gel-type resins. However, due to the open high-internal-surface structure of the macroreticular resin, diffusion rate through the resin particle and hence the attainment of the sorption equilibrium should be faster than the gel-type resin of degree of crosslinking X = 20. Actually, the value of m is same for Amberlite-200 and for resins X4, X8 and X12, while for that of X16, the value of m is lower. This should be due to the open structure of macroreticular resin. Also, for a gel-type resin of X = 20, the sorption should be higher than that for a resin of X = 12 but for the resin Amberlite-200, the reverse is the case. This implies that due to the open structure of the resin, sorption is reduced if comparision could be made with the gel-type resin of degree of crosslinking X=20. From the practical point of view, this behaviour should be of advantage in industrial process where sorption is not desirable. However, for chromatographic work, such resin of macroreticular structure should be relatively less suitable.

2.4.2 Disubstituted Benzoic Acids

The sorption behaviour of three m-dihydroxybenzoic acids and three m-dimethoxybenzoic acids was studied with resins of nominal degree of crosslinking, X, as 4, 8 and 12 (group I Table 2.3-1). The solvents used were distilled water, Wa ; 0.01N aqueous hydrochloric acid, WH ; and 10% dioxan in 0.01 N aqueous hydrochloric acid ; DWH. The values of S in equation (1) were calculated for the values of Co and Ce. The range of Co studied was about 0.5×10^{-4} to 15×10^{-4} moles per liter depending on the solubility of solute in the particular solvent system. The values of Co and Ce were determined by ultraviolet absorption with the

Beckman model Du-2 spectrophotometer, using 10 mm matched quartz cells. The plots of S versus Ce were linear. Figure 2.3-2 gives an illustrative plot. The slope of this plot is defined as the sorption coefficient B. Tables 2.3-13 to 2.3-20 give the illustrative values of S and Ce for some of the experiments carried out. The values of B obtained in this way are summarized in Tables 2.3-21 to 2.3-23 which also include the values of B for benzoic acid, monohydroxy and monomethoxybenzoic acids from the work of other colleagues of this laboratory.

2.4.2.1 Effect of Substitution

Substitution changes the sorption of benzoic acid. One of the important factors which contributes towards overall sorption is the nature of the substituents. The benzoic acids with hydrophobic (non polar or less polar) substituents e.g. methoxy, 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. hydroxyl, 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 positions of the substituents in the aromatic nucleus. It seems in the case of disubstituted benzoic acids that the contribution of the two substituents towards overall log B is partly additive and partly constitutive. The constitutive contribution may include an addition due to the enhanced contribution of the second substituent and a 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 (Tables2.3-21 to 2.3-23).

In calculation of the values of B for disubstituted benzoic acids, it is postulated as stated earlier that the sorption coefficient B for a resin-solute-solvent system is given by the product of two terms, the group term ϱ and the ground term Φ , provided molecular size is not too large to be excluded from the resin phase by sieve action, hence we have,

$$B = \varrho \cdot \Phi$$

For this study, we may consider the unsubstituted benzoic acid molecule as the ground state and the sorption coefficient B_u for unsubstituted benzoic acid as ground term Φ . The total group term ϱ is the product of the group terms for each substituent. Hence, if B_x denotes the sorption coefficient for benzoic acid with substituent X, B_y the sorption coefficient for benzoic acid with substituent Y, B_{xy} the sorption coefficient for benzoic acid with substituents X and Y and ϱ_x is the group term for substituent X and ϱ_y is the group term for substituent Y, then we have,

$$\varrho_{xy} = \varrho_x \varrho_y \qquad \text{-----(14)}$$

Also, $$\rho_x = \frac{B_x}{B_u}$$

$$\rho_y = \frac{B_y}{B_u}$$

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

or, $$B_{xy} = \frac{B_x \cdot B_y}{B_u} \qquad \text{-----(15)}$$

Thus the sorption coefficient for disubstituted benzoic acid is given by the product of sorption coefficients of the two corresponding monosubstituted benzoic acids divided by the sorption coefficient of unsubstituted benzoic acid.

As an illustration we may consider 2,4-dihydroxybenzoic acid in solvent WH. The sorption coefficients for unsubstituted benzoic acid, 2-hydroxybenzoic acid and 4-hydroxybenzoic acid are 2.82, 3.40 and 2.62 respectively. So, calculated value of sorption coefficient for 2,4-dihydroxybenzoic acid is $\frac{3.4 \times 2.62}{2.82} = 3.16$

The values of the sorption coefficient calculated in this way for m-disubstituted benzoic acids are cited in Tables 2.3-21 to 2.3-23 alongwith the values of Δ B where Δ B denotes $B_{exp} - B_{cal}$.

It is indicated that in 3,5-disubstituted benzoic acids where all the three groups are apart and no steric factor is operative, the experimental values are slightly higher than calculated as expected. On the other hand, in 2,6-disubstituted benzoic acids the experimental values are less than those of calculated.

In solvent WH and DWH the values of B for the m-dihydroxybenzoic acids (Tables 2.3-21 to 2.3-23) are in the order :

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

which shows that the isomer having one of the hydroxyl groups in the ortho position shows higher sorption than the other 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 solvent WH, 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 counterbalanced by the decrease in sorption due to steric interaction and ion exclusion. This explanation gets support from the fact that in 0.1 N aqueous hydrochloric acid the 2,6-isomer shows the significant increase in sorption ($B = 2.1$) while, the other isomers do not show any substantial increase.

In the case of m-dimethoxybenzoic acids steric factor should play a prominent role in determining the sorption (Table 2.3-21). The order of sorption is :

2,6-diOMe $<$ -H $<$ 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 steric interaction is minimum, whereas in the case of 2,6-isomer, carboxyl groups is hindered from both the sides by the bulky methoxy groups leading to the lowest sorption. In 2,4-isomer only two of the three groups are adjacent, hence, this isomer exhibits relatively higher sorption.

2.4.2.2 Effects of Crosslinking of the Resin

The values of B for the sorption of some dihydroxybenzoic acids on the resins of nominal degree of crosslinking X, as 4, 8 and12 are given in solvents Wa and WH (Tables 2.3-21 to 2.3-23). The sorption decreases with the increase in the degree of crosslinking of the resin. The relationship of the sorption coefficient, B and degree of crosslinking, X may be expressed by the equation.

$$BX^{\gamma} = \beta \qquad \text{------}(16)$$

where γ and β are constants. The value of γ may be considered to indicate the rate of change of the sorption with increase in X. If $\gamma = 1$, we have $B = \beta/X$ i.e. B is inversely proportional to X ; if $\gamma = 0.5$, then $B = \beta/\sqrt{X}$ i.e. B is inversely proportional to square root of X. Tables 2.3-21 to 2.3-23 indicate that for solvents Wa and WH, $\gamma = 0.5$ for acids containing 2-hydroxyl group and $\gamma = 1$ for benzoic and other dihydroxybenzoic acids. It appears that in general, for substituted benzoic acids having relatively higher sorption $\gamma = 0.5$ and for acids having relatively lower sorption $\gamma = 1$.

With increase in X, the sorption should decrease due to the decrease in the uptake of the solvent by the resin and the increase in the salting out effect, and it should increase due to the increase in the dispersion interactions between the solute molecule and the resin matrix. The overall effect is a decrease in the sorption.

2.4.2.3 Effect of Solvent

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

The sorption behaviour of disubstituted benzoic acids have been studied in solvents Wa, WH and DWH (Tables 2.3-21 to 2.3-23). The disubstituted benzoic acids show comparatively lower sorption from water solutions. One of the possible reasons should be the operation of ion exclusion effect for acids having relatively lower pK values. In acidic solvent, this is overcome because the ionization is suppressed and it is also likely that the solubility of the acids is decreased to some extent. In the mixed solvent all the acids show lower sorption by a factor of about 2 to 2.22 as indicated by the values of R in Table 2.3-21. This may be attributed to :

(1) the decrease in the dielectric constant of the solvent medium. It should be reasonable to consider that the dielectric constant of the solvent medium should be

one of the primary parameters determining the extent of sorption.

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

(3) For this solvent composition, the resin prefers water to dioxan. Therefore, the ratio water to dioxan 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.

(4) Interaction forces between the resin matrix and the hydrocarbon portion of dioxan would block some of the sorption active sites for the solute molecules. This would mean that the enviornment inside the resin phase is less favourable for the retention of disubstituted benzoic acids.

It is seen that the decrease in sorption caused due to change in solvents from aqueous to mixed, is relatively higher for the solutes having methoxy groups than for the hydroxyl groups. This may be attributed 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.

2.4.3. Geometrical Isomeric Acids

The sorption equilibrium study of three unsaturated acids : crotonic, maleic and fumaric was carried out with resin Dowex 50WX4 (group I Table 2.3-1) in hydrogen form in aqueous medium at room temperature.

The sorption coefficient B for crotonic acid is 0.22 which is practically same as that for propionic acid (i.e. 0.22). Hence it appears that the contribution of -HC=CH- (vinyl) group to the sorption constant B for unsaturated aliphatic monocarboxylic acids is same as that of -CH2- (methylene) group of saturated aliphatic monocarboxylic acids.

The sorption constant of maleic acid is found to be ~0.05 which is almost equal to the sorption constant of malonic acid (~0.05), (however, sorption of these two acids is too low to be measured precisely). Here again the contribution of vinyl group to the sorption for unsaturated dicarboxylic acids seems same as that of methylene group of saturated dicarboxylic acids. Above conclusions are interesting and it should be worthwhile to verify them by taking suitable pairs of acids.

However for fumaric acid which is a dicarboxylic acid having trans configuration, the B value is 0.1 which is almost double the value of maleic acid and half the value of crotonic acid. From this fact, following conclusions may be drawn.

(1) In cis isomer, due to steric hindrance the sorption is decreased.

(2) Under the same molecular environment, contribution of $-CH_3$ group to the sorption is higher than that of -COOH group. This may be attributed to the hydrophobic nature of $-CH_3$ group.

The present study of the sorption behaviour of the organic 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 or selectivity of members of homologous series of the resin, which may be considered as a particular case of resin 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.