CHAPTER 3

SORPTION ELUTION

3.1 INTRODUCTION

A chromatographic process is characterized as moving a discrete zone of a substance in the stream of the mobile phase through a column of adsorbent. It is related to the multiple repetition of adsorption-desorption cycles. In the chromatographic process, the components to be separated are distributed between two phases, one of these phases constituting a stationary bed of large surface area, the other being a fluid that percolates through or along the stationary bed. This definition extends the term chromatographic process to physiochemical measurements in which only a single substance is adsorbed-desorbed on column (238). The separation of the components depends upon the differential migration resulting from a resistive action, namely selective sorption of the components of the mixture. Chromatography (1-15,239-265) is the most variable and in many respects the most adaptable technique in all branches of science, because it may be used for the examination of a variety of chemical substances.

The two major subdivisions of chromatography, based on the mobile phase used, are gas chromatography and liquid chromatography, of which the former has extraordinary success. However, only about 15% of organic compounds are amenable to gas chromatographic analysis. Insufficient volatillity and thermal instability of many organic compounds are mainly responsible for this unfortunate limitation imposed on gas chromatography.

Liquid chromatography was in limited use even from ancient times though the principles underlying this remained unrecognised, for example, the utility of some earths for the purification of sea water was known even to Aristotle. The tremendous advances in researches in biochemistry, diagnostic medicine and pharmaceutical materials are mainly responsible for triggering the explosive growth of liquid chromatography, as many of the substances failing under these heads are nonvolatile.

In liquid chromatography, the stationary phase may be solid or liquid. Liquid chromatography using solid as the stationary phase is potentially more useful branch, since it possesses certain advantages such as greater speed and separation efficiency, ease of automation and uncontrolled operation, easier quantitation and possibility of achieving preparative separations. Liquid-solid chromatography can be classified, based on the way in which the solid stationary phase is used, as column chromatography, thin layer chromatography and paper chromatography.

Liquid-solid chromatography in columns was the first form of chromatography. It was introduced by the Russian botanist Tswett (1905) during the investigation of plant pigments. However, the technique remained practically ignored for a number of years and it is only when Kuhn, Winterstein and Leaderer (1931) reported the separation of Carotenes and Xanthophylls on the columns of alumina and calcium carbonate, that it has attracted attention of investigators who have shown that the chromatographic analysis can render greater service in many areas of enquiry.

Soon after this " rediscovery of chromatography ", Adams and Holmes found that ion exchange could be performed on finely ground gramophone records. This led to the development of synthetic ion exchange resins. An enormous development of different applications of ion exchange emerged, the most important among these being, ion exchange chromatography. Systematic study of the phenomena of ion exchange revealed the great potential of ion exchangers in quantitative analysis and the real breakthrough of ion exchange was the release of information about the separation of rare earths demonstrating the possiblities of ion exchange chromatography in the separation of species with almost identical properties.

Ion exclusion, reported by Wheaton and Bauman (114,115), is one of the several new developments involving ion exchange resins. It is a molecular process whereby a nonionic solute is removed from the solution into the resin phase by sorption and the ionic solutes are excluded by the Donnan effect, the nonionic solutes are then can be physically displaced from the resin by washing with the proper developing agent. This process appears to have its utility in the deionization of aqueous solution of nonpolar or slightly polar solutes such as alcohols, glycols, weak organic acids, ketones and amino acids.

The technique of ion exclusion has been extended to the separation of two or more nonionic compounds. Most ion exchange resins show pronounced differences in their affinities for various nonelectrolytes and can then be used as stationary

phase for the separation of many organic compounds (114,115, 266-312). The scope of this separation method can be broadened by altering conditions in one of the phases. The replacement of water with concentrated electrolyte solution as developer has the effect of salting different solutes into the internal phase to various degrees and thus offering separations that are not possible in water. This technique is known as ' salting out chromatography '. Similarly, the relative distribution of some pairs of compounds can be altered by using a mixture of water and organic solvent as the developer, and the technique is called ' solubilization chromatography '.

Thus the term ' ion exchange chromatography ', in a broader sense, covers all chromatographic separations, ionic as well as nonionic substances carried on with ion exchange resins.

3.1.1 Techniques

There are essentially three methods of performing column liquid chromatography. These are :

(1) Frontal analysis : In this technique the solution of the mixture of substances is introduced continuously into the column. Only a part of the least sorbed component is obtained in the pure form. The method is not attractive for preparative requirements as well as for analytical purposes.

(2) Displacement analysis : In this technique the components of the mixture, initially sorbed in the column, are successively displaced (depending on the affinity for the stationary

phase) by continuously passing the solution of substance which is more strongly sorbed than the components present in the mixture. In this case also the separation of the components is not complete.

(3) Elution analysis : In this technique the sample, initially sorbed on the top of the column, is washed down with an appropriate developer (eluent or solvent). The components often leave the column in pure form. One of its disadvantages is much smaller capacity of the column and much higher consumption of the solvent. Simple elution - using a single solvent, stepwise elution - using several solvents successively with increasing elution capacity and gradient elution - varying the nature of the solvent gradually and continuously, but not in steps, so that a mixture of uniformly changing composition is introduced into the column, are the three methods of carrying out the elution analysis.

3.1.2 Theory of Chromatography (1-15, 114,115,220,221,225, 228,239-392)

The ultimate goal of theories of chromatography is to provide means for predicting from known, or independently measurable fundamental properties, performance of columns under given conditions and optimum conditions for given separations. However, the general theories of column performance are too complex to be solved by mathematical analysis unless very drastic simplifications are introduced and numerous simplifying assumptions are made. Inspite of these limitations, fundamental data can be used to derive simple useful relationships which serve as helpful guides in obtaining optimum operating conditions.

In general, three quantities of the chromatogram are of interest, the time necessary to elute a given component from the column, the width of the peak and the completeness of the separation (resolution).

The elution curve in chromatography represents the distribution of concentration with time and is therefore a probability density curve. Although these curves are generally asymmetric, for ease of interpretation they are usually considered symmetric and described mathematically by a Gaussian curve. Under these conditions it is possible to relate the rate of movement of the zone expressed in terms of the volume of eluent, from the start to the emergence from the column of the midpoint of the peak, to the distribution coefficient (Section 3.4.1).

Two parameters can be used to describe peak widths, the variance σ^2 and the number of theoretical plates, N or the plate height, H. σ is the half of the width measured at the ordinate of $Cm/\sqrt{e}$, where Cm is the peak height of the elution curve. In the literature euqations are given correlating σ^2 with the distribution coefficient and the column parameters (313-339).

The theoretical plate concept was introduced by Martin and Synge, who recognized the similarity in the chromatographic process to that taking place in distillation columns. The concept was applied to ion exchange columns by Mayer and Tompkins and later modified by Glueckauf, who based his analysis on a continous flow model. The theory brings out effects arising from the operating parameters,

such as flow rate, feed concentration, particle size etc., It also includes the distribution coefficient of a component being separated and all possible diffusion effects. Despite the value of this approach in characterizing the efficiency of distillation columns and extractors, its physical significance in chromatography is questionable. Nevertheless the measured quantities N and H are useful for characterizing band spreading and the efficiency of a chromatographic system. Other factors being equal, for a given size of the column, its efficiency will be greater, the larger the number of theoretical plates or smaller the plate height. Also, in using it to compare the performance of different columns, one finds that their ability to separate substances does not increase in parallel with a decrease in plate height. This is obviously a practical disadvantage.

Thus it can be seen that the size, shape and position of the peaks on the chromatogram can be calculated with some success from fundamental data and the various compromises necessary in striving for optimal column performance.

Another important parameter used as a quantitative measure of the ability of a column to separate two given components is resolution. In mathematical terms it is a measure of the degree of separation of zones, represented as

$$R_n = \frac{\Delta Vm}{n(\sigma_1 + \sigma_2)}$$

where ΔVm is the gap between the centres of the peaks of the two neighbouring zones, σ_1 and σ_2, the standard deviations

of the two zones, n is an intiger greater than zero. The magnitude of n indicates the degree to which the gap between the two zones is filled and the crosscontamination by zone spreading. The value of n depends on the type of problem and chromatography and the degree of separation required. In liquid chromatography the generally accepted criterion of minimum resolution is to select the value of n as 3. This means that after having devided the effluent into fraction at a point $Ve = Vm_1 + 3\sigma_1$ at least 99.86 % of each of the components is in its appropriate fraction and the impurity amounts to at the most 0.14 % of the peak of the contagious component.

Thus resolution can act as one bridge between theory and practice. However, it does not describe the physical and chemical factors which are the causes of the separation. It must also be emphasized that the resolution is not a complete measure of practical success. It provides no inkling of the time which may be consumed in achieving the separation nor does it gurantee that the zones are readily detectable. Nevertheless, it is a practical measure of some worth, if its limitations are kept in mind.

3.2 EXPERIMENTAL

For preparing a resin column, a definite quantity of air dried resin in hydrogen form was weighed, soaked into distilled water contained in a beaker and then transferred carefully into a pyrex glass column. The length (L), bed volume (Vb), void volume (Vi), and disc volume (Vd) were measured. The column capacity (C) was calculated from the amount of air dried resin taken in the column and its air dried capacity (c) per gram of the resin. All these column data are given in section 3.3 where needed.

The solutions of organic acids and the solvents were prepared as described in Section 2.2.

The resin column was conditioned prior to performing the elution run by washing it with several bed volumes of the solvent to be used as eluent, back washed by passing the solvent upwards with sufficient speed to loosen the resin and to remove air bubbles. The resin was then allowed to settle under gravity to achieve a size classification within the column.

For carrying out the elution run, the liquid level was first brought to the resin bed level, then a known feed volume (Vf) containing W millimoles depending on the solubility of the solute were added carefully from the top of the resin bed so that the surface layer of the resin was disturbed minimum. The solution was allowed to sink into the resin by

opening the pinch cock at the lower end of the column. The effluent was collected in a measuring flask (Vs ml) and it was marked as sample number 1. When the liquid level was again at the resin bed level, 5ml of the eluent were added to rinse the inside of the column above the resin bed and it was allowed to sink into the resin. Then the column was connected to an overhead reservoir of the eluent and the continuous elution was carried out at the rate of 2 ml per minute. The effluent was collected in measuring flasks (Vs ml) and numbered as 2, 3, 4 and so on.

The solute content in each sample was estimated by simple titration or by ultraviolet absorption. W and Ws denotes the solute content in millimoles in the feed solution (Vf) initially sorbed on the resin bed and in the effluent sample (Vs) respectively.

After the run was completed the column was washed with distilled water and conditioned with the solvent to be used for the next run.

The same procedure was followed for the column elution of the mixtures of organic acids.

3.3 RESULTS

Table 3.3-1 : Values of constants (equations : 19 & 23) for dicarboxylic acids studied.

Resin	α_1	α_2	α_3	f_1	f_2
Dowex 50W-X1	0.75	1.6	0.000	1	1
Dowex 50W-X2	0.30	1.6	0.005	1	1
Dowex 50W-X4	0.19	1.6	0.060	1	1
Dowex 50W-X8	0.02	1.6	0.550	-	-
Dowex 50W-X12	0.00	1.6	-	-	-
Dowex 50W-X16	0.00	1.6	-	-	-
Amberlite-200	0.12	1.6	-	-	-

Table 3.3-2 : Elution runs of Glutaric acid on the column of resins X1, X2 and X4 in aqueous medium.

Sample No.		X1	X2	X4
	10^2W =	50	50	50
	Vf =	5	5	5
	Vs =	5	5	5
		10^2Ws		
1-21		-	-	-
22		-	-	0.3
23		0.3	-	0.9
24		0.5	1.2	2.3
25		0.7	4.0	7.9
26		1.3	8.5	15.3
27		2.3	13.7	15.1
28		4.5	13.1	7.5
29		6.7	7.8	2.0
30		9.1	3.4	0.6
31		9.3	1.5	0.3
32		7.2	0.5	-
33		4.9	-	-
34		2.9	-	-
35		1.6	-	-
36		0.9	-	-
37		0.3	-	-
38		-	-	-

Fig. 3.3-1 : Plot of Ws versus sample number for the column elution of glutaric acid on the column of resin Dowex 50W-X1 (50-100) using distilled water as solvent and eluent.

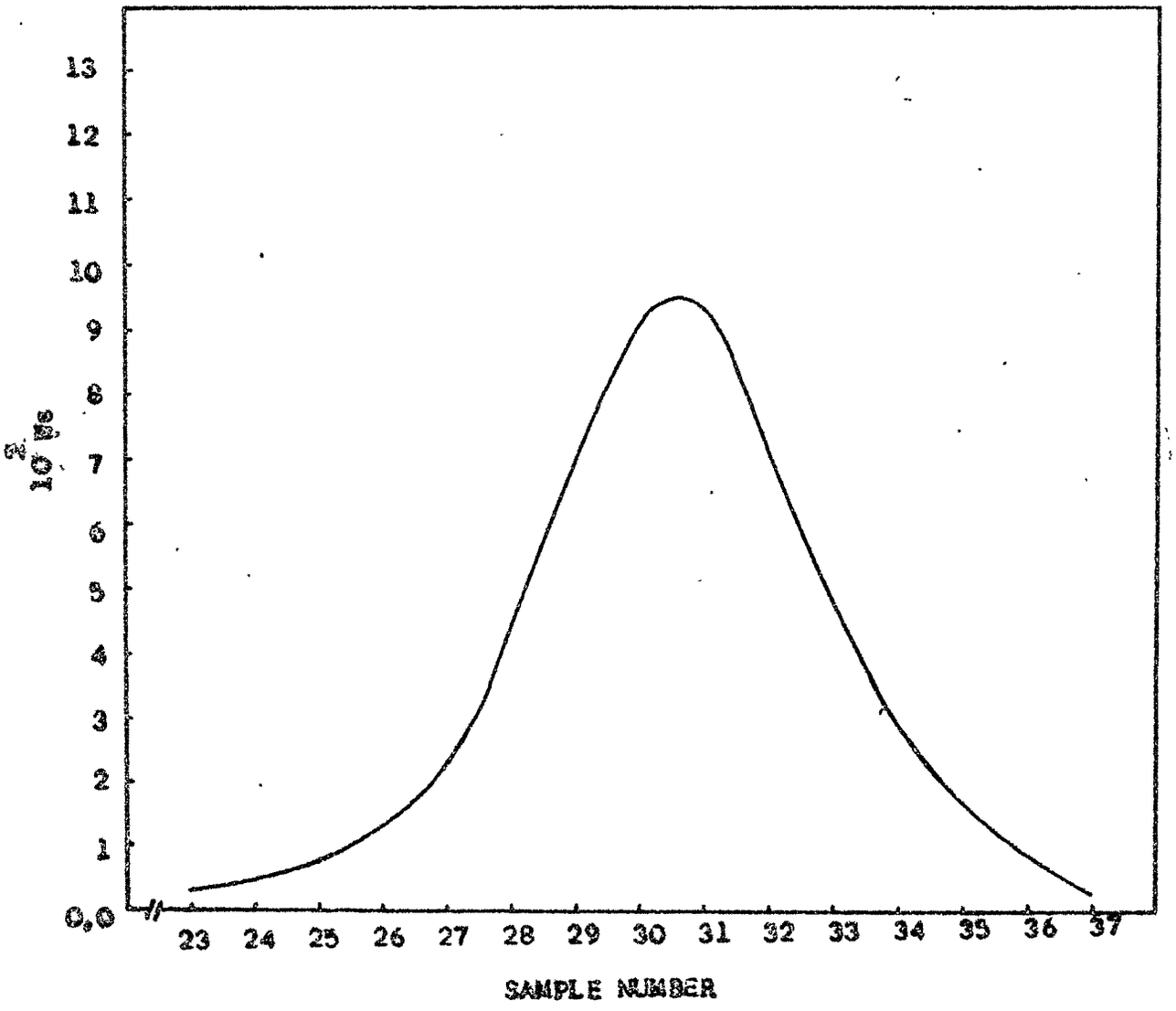

Fig. 3.3-2 : Plot of Ws versus sample number for the column elution of glutaric acid on the column of resin Dowex 50W-X2 (100-200) using distilled water as solvent and eluent.

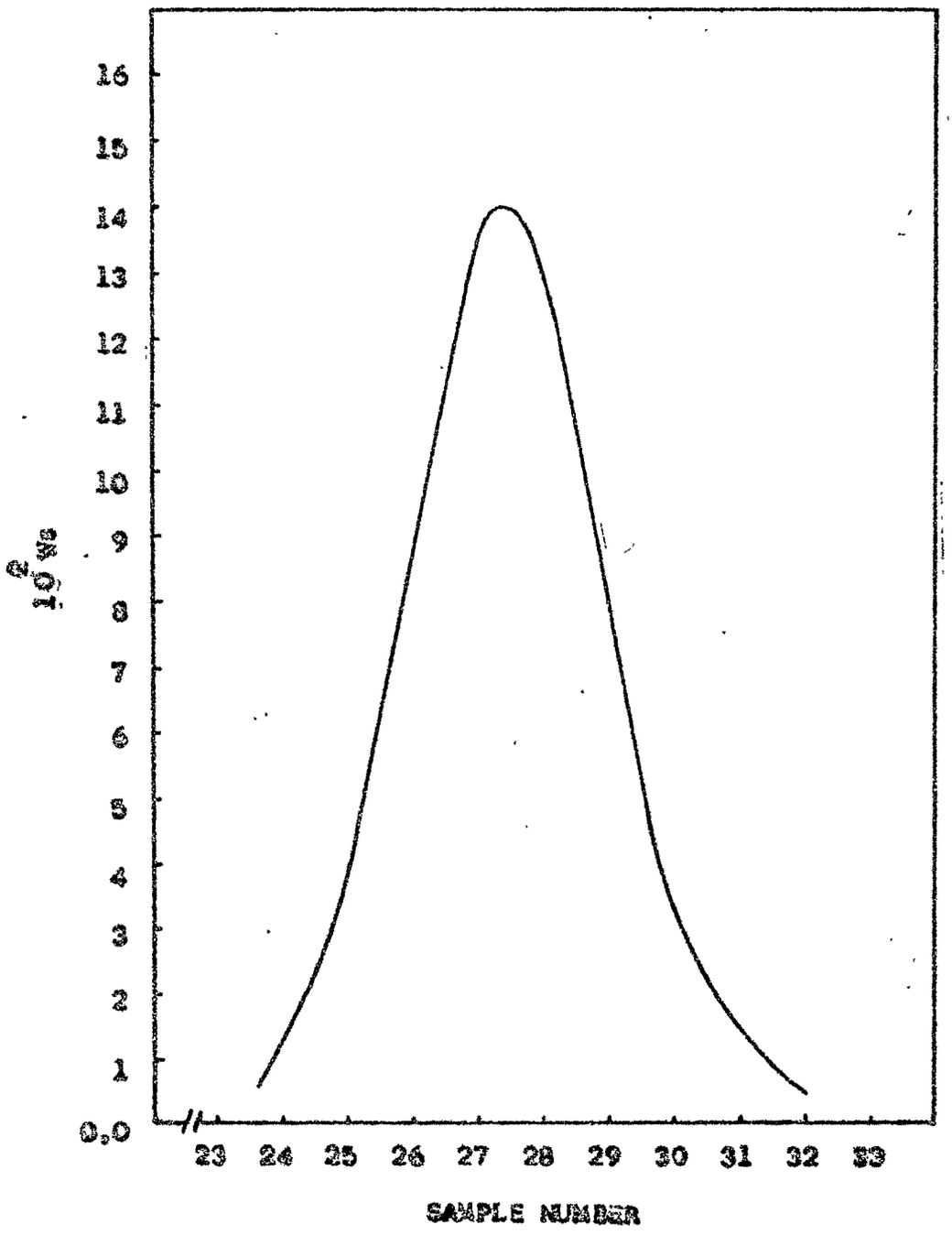

Fig. 3.3-3 : Plot of Ws versus sample number for the column elution of gluteric acid on column of resin Dowex 50W-X4 (100-200)using distilled water as solvent & eluent.

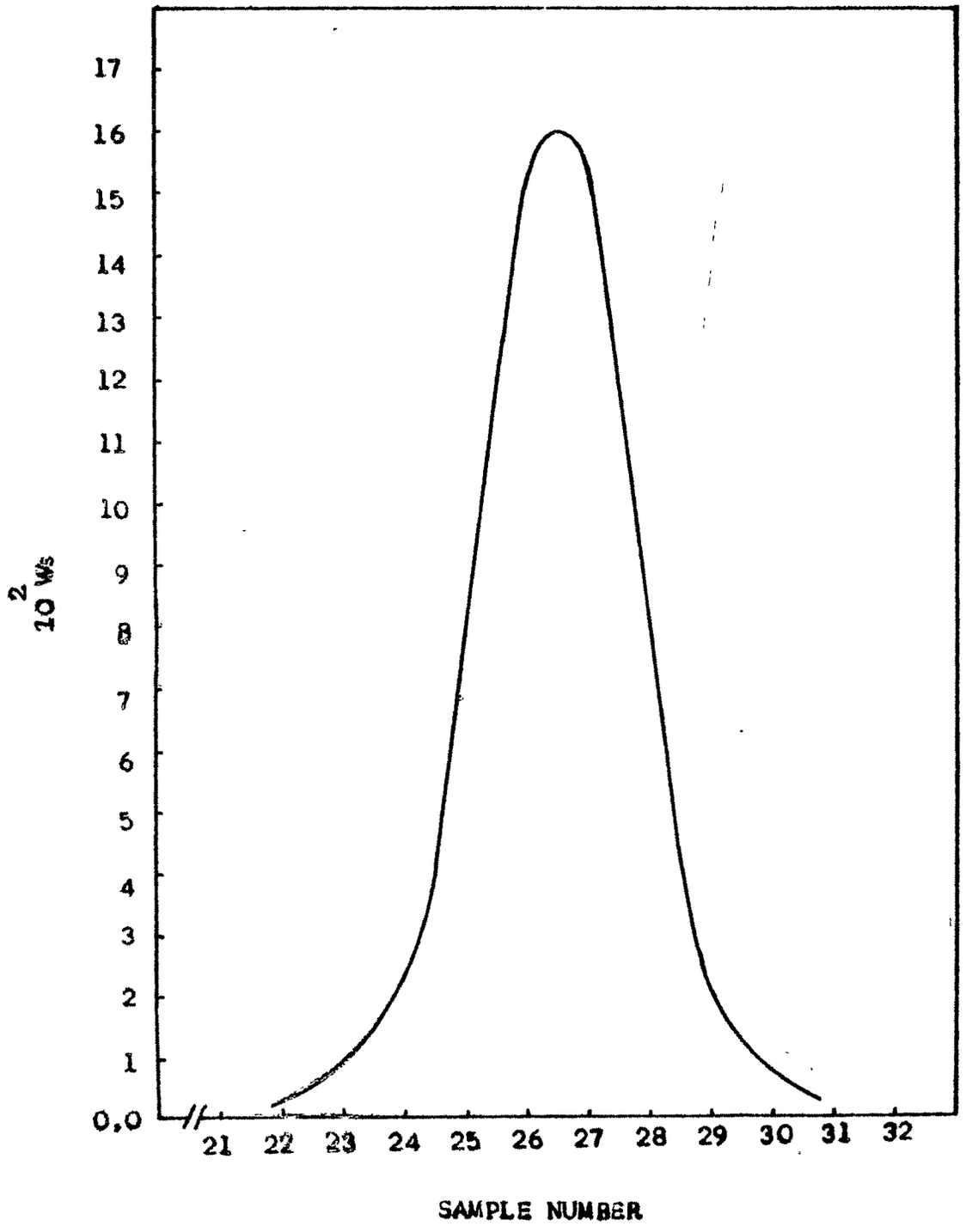

Table 3.3-3 : Elution runs of Glutaric acid on the column of resins X8, X12, X16 and Amberlite-200 in aqueous medium.

Sample No.		X8	X12	X16	Amb-200
	10^2W =	100	50	50	100
	Vf =	10	5	5	10
	Vs =	5	5	5	5
			10^2Ws		
1-12		-	-	-	-
13		-	1.5	0.5	-
14		-	6.0	2.2	-
15		-	8.6	5.0	0.5
16		0.6	9.1	6.8	2.5
17		4.2	8.0	7.2	6.5
18		11.0	6.4	6.8	10.7
19		18.8	4.5	5.6	13.8
20		21.8	2.5	4.3	14.4
21		18.4	1.5	3.4	13.5
22		12.6	0.9	2.5	11.1
23		6.8	0.5	1.9	8.7
24		3.2	0.3	1.4	6.0
25		1.6	0.3	0.9	4.0
26		0.8	-	0.7	2.6
27		0.6	-	0.5	1.6
28		-	-	0.3	0.9
29		-	-	-	0.5
30		-	-	-	0.3
31		-	-	-	-

Fig. 3.3-4 : Plot of Ws versus sample number for the column elution of gluteric acid on the column of resin Dowex 50W-X8 (100-200) using distilled water as solvent and eluent.

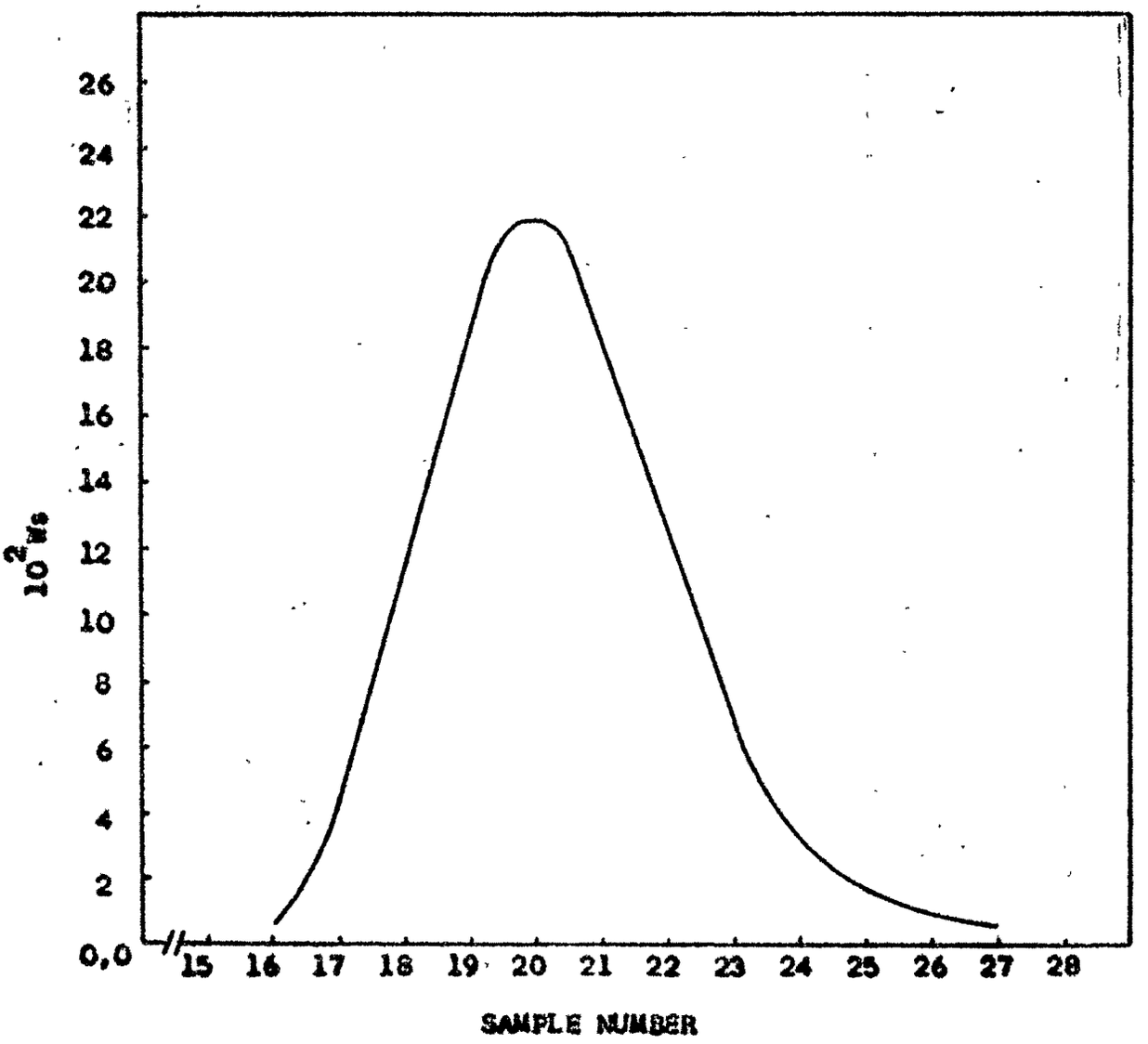

Fig. 3.3-5 : Plot of Ws versus sample number for the column elution of glutaric acid on the column of resin Dowex 50W-X12 (100-200) using distilled water as solvent and eluent.

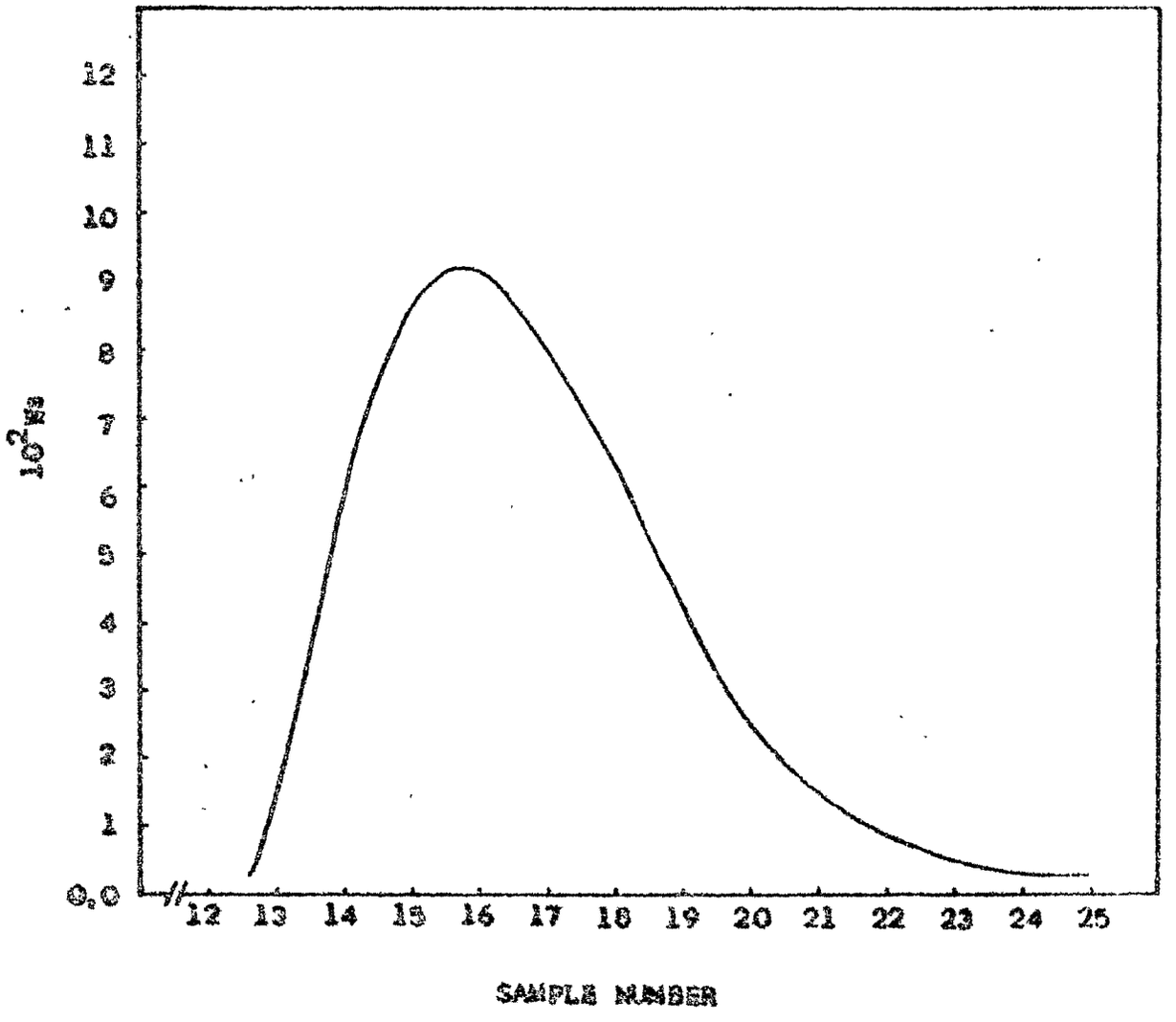

Fig. 3.3-6 : Plot of Ws versus number for the column elution of glutaric acid on the column of resin Dowex 50W-X16 (20-50) using distilled water as solvent and eluent.

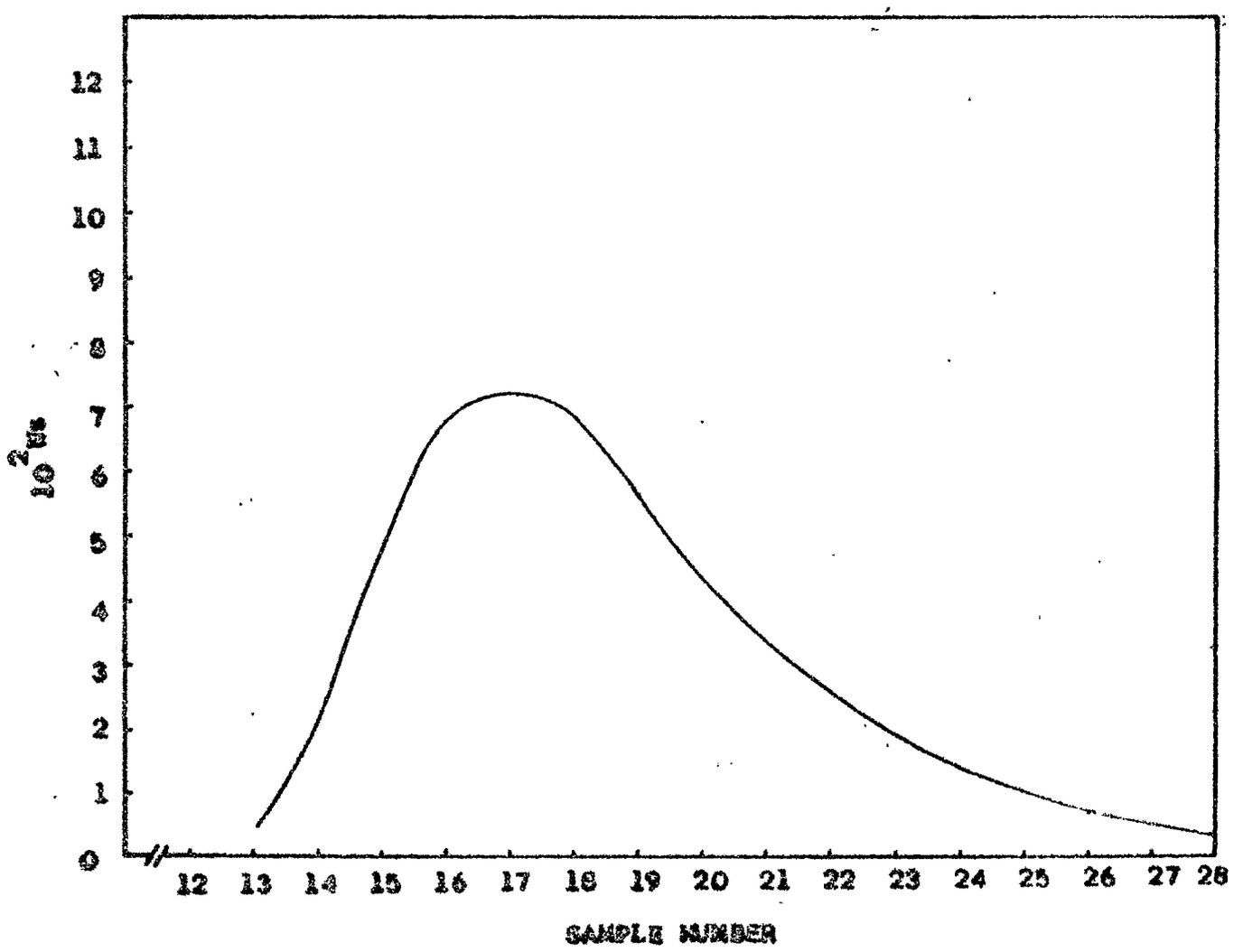

Fig. 3.3-7 : Plot of Ws versus sample number for the column elution of glutaric acid on the column of resin Amberlite-200 (20-50) using distilled water as solvent and eluent.

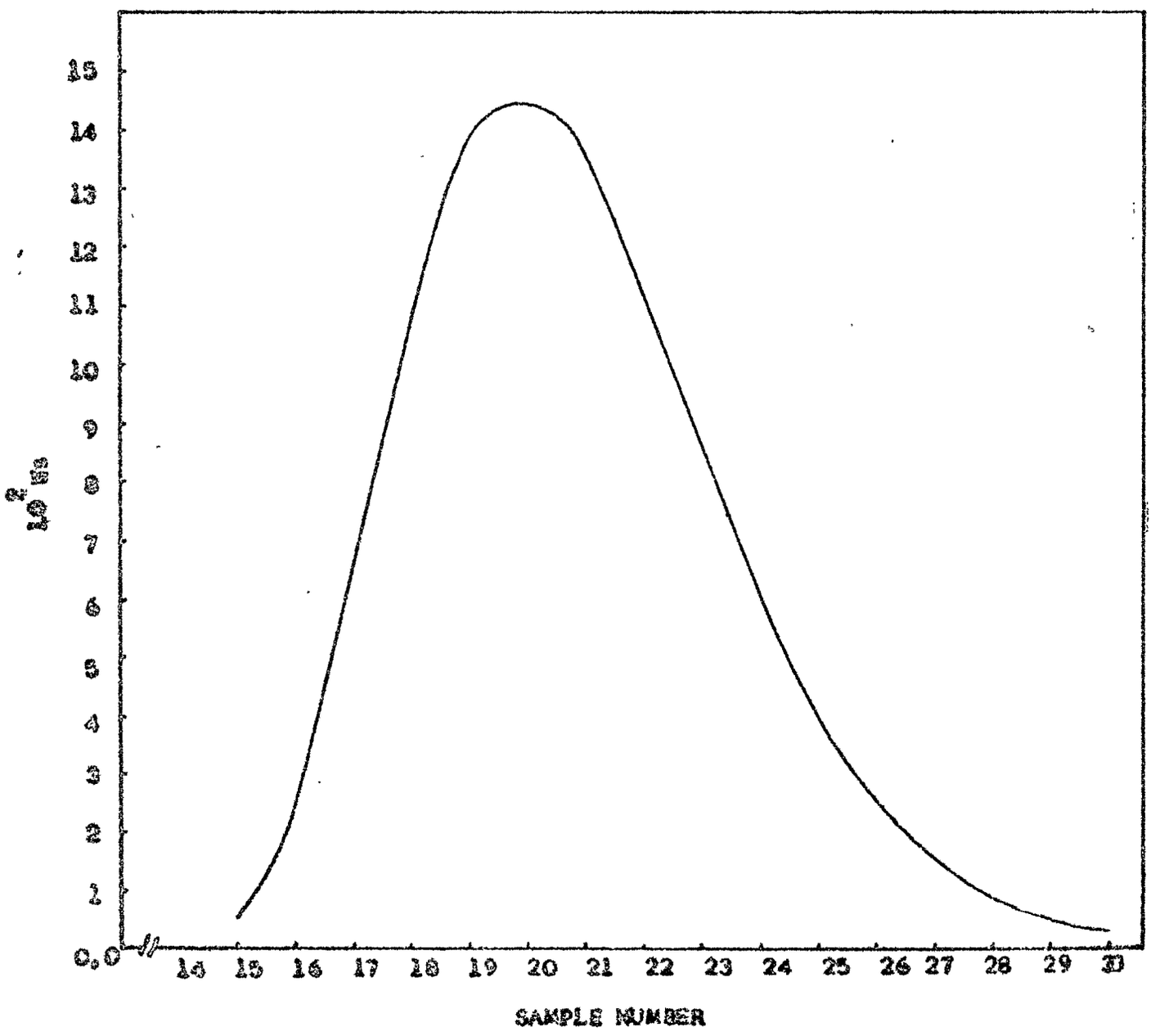

Table 3.3-4 : Elution runs of Oxalic, Malonic, Succinic and Glutaric acids on the column of resin Amberlite-200 in aqueous medium.

Sample No.	Acid	Oxalic	Malonic	Succinic	Glutaric
	10^2W =	100	100	100	100
	Vf =	10	10	10	10
	Vs =	5	5	5	5
			10^2Ws		
1-12		-	-	-	-
13		2.4	0.5	-	-
14		4.9	1.3	-	-
15		11.4	3.6	1.0	0.5
16		16.2	8.4	3.8	2.5
17		19.5	13.1	9.6	6.5
18		18.7	16.2	13.9	10.7
19		14.6	17.5	14.8	13.8
20		10.6	15.4	15.3	14.4
21		2.4	13.1	13.9	13.5
22		-	7.9	12.0	11.1
23		-	2.6	8.6	8.7
24		-	1.0	4.8	6.0
25		-	0.5	2.4	4.0
26		-	-	1.0	2.6
27		-	-	-	1.6
28		-	-	-	0.9
29		-	-	-	0.5
30		-	-	-	0.3
31		-	-	-	-

Table 3.3-5 : Elution runs of Adipic, Pimelic and Suberic acids on the column of resin Amberlite-200 in aqueous medium.

Sample No.	Acid	Adipic	Pimelic	Suberic
	10^2W =	100	100	35
	Vf =	10	10	10
	Vs =	5	5	5
			10^2Ws	
1-15		-	-	-
16		2.1	0.9	0.1
17		4.7	2.4	0.2
18		9.3	4.8	0.5
19		12.5	8.1	1.1
20		13.5	10.9	1.9
21		14.5	12.0	2.7
22		12.5	12.4	3.4
23		10.4	11.5	3.8
24		8.8	10.0	3.9
25		5.7	8.5	3.8
26		3.9	6.7	3.3
27		2.1	4.1	2.9
28		1.0	3.5	2.5
29		-	2.0	2.1
30		-	1.1	1.5
31		-	0.9	1.2
32		-	0.5	0.7
33		-	0.4	0.6
34		-	0.2	0.3
35		-	-	0.2
36		-	-	0.1
37		-	-	0.1
38		-	-	-

Table 3.3-6 : Elution runs of Azelaic and Sebacic acids on the column of resin Amberlite-200 in aqueous medium

Sample No.	Acid	Azelaic	Sebacic
	10^2W =	35	6.4
	Vf =	10	10
	Vs =	10	10
		10^2Ws	
1- 7		-	-
8		0.05	-
9		0.11	-
10		0.51	0.05
11		1.68	0.13
12		3.71	0.21
13		5.40	0.32
14		5.29	0.43
15		4.88	0.54
16		3.97	0.62
17		3.16	0.64
18		2.24	0.62
19		1.53	0.55
20		1.02	0.51
21		0.56	0.45
22		0.25	0.39
23		0.20	0.34
24		0.20	0.29
25		0.15	0.24
26		0.11	0.20
27		-	0.14
28		-	0.09
29		-	0.07
30		-	-

Table 3.3-7 : Chromatographic parameters of column elution runs for aliphatic dicarboxylic acids with resin Dowex 50W-X1 in aqueous medium.

C = 80 meq ; Vb = 146 ml ; Vd = 6.5 ml.

Parameters		Oxalic	Malonic	Succinic	Glutaric	Adipic	Pimelic	Suberic	Azelaic	Sebacic
Vf		5	5	5	5	5	5	10	10	25
10^2W		50	50	50	50	50	50	35	35	16
Vm	Exp.	83.00	133.50	143.00	153.00	168.50	200.00	260.00	355.00	525.00
	Cal.	132.04	135.48	141.40	151.80	169.80	201.08	257.90	352.28	523.96
$\bar{V}m$	Exp.	18.10	68.60	78.10	88.10	103.60	135.10	195.10	290.10	460.10
	Cal.	67.14	70.58	76.50	86.90	104.90	136.18	193.00	287.48	459.06
V_θ	Exp.	0.195	0.826	0.945	1.070	1.2640	1.6580	2.3760	3.5640	5.5950
	Cal.	0.808	0.851	0.925	1.055	1.2800	1.6710	2.3500	3.5310	5.5820
σ	Exp.	-	8.250	9.150	10.30	12.250	15.500	23.200	33.800	55.100
	Cal.	8.061	8.445	9.107	10.27	12.283	15.780	22.691	33.255	54.101

Cont.....

σ_θ	Exp.	-	0.857	0.930	1.058	1.276	1.640	2.407	3.592	5.694
	Cal.	0.808	0.851	0.925	1.055	1.280	1.671	2.350	3.531	5.582
β	Exp.	-	23.50	26.00	29.15	34.50	44.25	65.10	95.20	155.6
	Cal.	22.80	23.89	25.76	29.05	34.74	44.64	64.18	94.07	153.0
$10^2 C_m$	Exp.	2.400	2.400	2.150	1.900	1.650	1.300	0.600	0.400	0.115
	Cal.	2.475	2.362	2.190	1.942	1.624	1.264	0.615	0.420	0.118
N	Exp.	-	69.14	72.86	73.16	71.52	75.97	70.72	73.67	69.73
	Cal.	69.37	69.85	70.56	71.60	72.94	74.48	72.34	74.73	72.00
N_θ	Exp.	-	0.929	1.033	1.023	0.981	1.022	0.974	0.984	0.966
	Cal.	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

Table 3.3-6 : Chromatographic parameters of column elution runs for aliphatic dicarboxylic acids with resin Dowex 50W-X2 in aqueous medium.

C = 120 meq ; Vd = 6.5 ml ; Vb = 142.5 ml.

Parameters		Oxalic	Malonic	Succinic	Glutaric	Adipic	Pimelic	Suberic	Azelaic	Sebacic
Vf		5	5	5	5	5	5	10	10	25
$10^2 W$		50	50	50	50	50	50	35	35	16
Vm	Exp.	77.50	115.00	124.00	137.00	168.00	212.00	296.00	441.00	697.80
	Cal.	109.08	114.12	123.00	136.32	165.60	212.52	296.86	439.66	696.52
$\bar{V}m$	Exp.	14.000	51.500	60.500	73.500	104.50	148.50	232.50	377.50	634.30
	Cal.	45.580	50.620	59.500	72.820	102.10	149.02	233.36	376.16	633.02
V_θ	Exp.	00.096	00.408	00.483	00.592	00.850	1.2170	1.8960	3.1040	5.1820
	Cal.	00.359	00.401	00.475	00.586	00.830	1.2210	1.9030	3.0930	5.1710
σ	Exp.	-	5.1000	6.1000	7.2000	10.100	14.100	22.600	35.700	61.000
	Cal.	4.7530	5.2240	6.0340	7.2390	9.9110	14.192	22.453	35.374	60.300

Cont.....

σ_θ	Exp.	-	0.408	0.467	0.586	0.837	1.212	1.929	3.108	5.190
	Cal.	0.358	0.401	0.475	0.585	0.829	1.220	1.898	3.078	5.126
β	Exp.	-	14.90	16.80	21.00	28.20	40.00	64.10	100.7	172.3
	Cal.	13.44	14.78	17.07	20.48	28.03	40.14	63.51	100.1	170.6
$10^2 Cm$	Exp.	4.000	3.900	3.250	2.800	2.000	1.400	0.600	0.400	0.110
	Cal.	4.197	3.818	3.306	2.756	2.013	1.406	0.622	0.395	0.106
N	Exp.	-	94.42	98.37	104.2	107.1	110.9	105.8	111.8	108.1
	Cal.	91.96	93.89	97.24	101.2	106.1	110.3	108.0	113.1	110.2
N_θ	Exp.	-	1.000	1.070	1.021	1.031	1.008	0.966	0.997	0.997
	Cal.	1.006	1.000	1.000	1.003	1.002	1.002	1.005	1.010	1.018

Table 3.3-9 : Chromatographic parameters of column elution runs for aliphatic dicarboxylic acids with resin Dowex 50W-X4 in aqueous medium.

C = 160 meq ; Vb = 139.4 ml ; Vd = 6.5 ml.

Parameters		Oxalic	Malonic	Succinic	Glutaric	Adipic	Pimelic	Suberic	Azelaic	Sebacic
Vf		5	5	5	5	5	5	10	25	25
$10^2 W$		50	50	50	50	50	50	35	87.5	16
V_m	Exp.	73.000	106.50	118.00	132.50	158.50	208.00	296.00	455.50	737.50
	Cal.	102.20	107.32	116.44	132.12	159.64	207.96	295.90	456.36	737.00
$\bar{V}_m$	Exp.	10.700	44.200	55.700	70.200	96.200	145.70	233.70	393.20	675.20
	Cal.	39.940	45.060	54.180	69.860	97.380	145.70	233.64	394.10	674.74
V_θ	Exp.	00.051	00.260	00.333	00.423	00.586	00.895	1.4290	2.3790	4.1420
	Cal.	00.234	00.266	00.323	00.421	00.593	00.895	1.4290	2.3850	4.1390
σ	Exp.	-	4.1000	5.0000	6.2000	8.1000	12.000	19.450	33.200	52.750
	Cal.	3.7930	4.1980	4.9060	6.1460	8.2840	12.003	19.317	33.050	52.594

Cont.....

σ_θ	Exp.	-	0.258	0.329	0.424	0.574	0.883	1.406	2.295	3.828
	Cal.	0.234	0.266	0.322	0.420	0.589	0.883	1.395	2.283	3.828
β	Exp.	-	11.70	14.00	17.50	23.10	33.90	55.45	93.60	149.1
	Cal.	10.73	11.87	13.88	17.38	23.43	33.95	54.64	93.49	148.8
$10^2 C_m$	Exp.	5.000	4.850	3.950	3.200	2.450	1.650	0.700	1.051	0.120
	Cal.	5.295	4.752	4.066	3.246	2.408	1.662	0.723	1.056	0.121
N°	Exp.	-	116.2	124.1	128.2	141.1	147.4	144.4	140.3	163.8
	Cal.	110.9	115.2	121.9	129.2	138.2	147.4	146.3	142.2	164.6
N_θ	Exp.	-	1.016	1.024	0.995	1.042	1.027	1.033	1.075	1.171
	Cal.	1.000	1.000	1.006	1.005	1.013	1.027	1.049	1.091	1.169

Table 3.3-10 : Chromatographic parameters of column elution runs for aliphatic dicarboxylic acids with resin Dowex 50W-X8 in aqueous medium

C = 279 meq ; Vb = 146 ml ; Vd = 6.5 ml.

Acid	Vf (ml)	10^2 W (mmol)	Vm (ml)		$\bar{V}m$ (ml)		Ve (ml/meq)	
			Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
Oxalic	10	100	69.0	79.94	4.1	15.04	0.006	0.036
Malonic	10	100	82.0	83.01	17.1	18.11	0.052	0.047
Succinic	10	100	89.0	88.59	24.1	23.69	0.068	0.067
Glutaric	10	100	99.5	98.64	34.6	33.74	0.106	0.103
Adipic	10	100	115.0	115.94	50.1	51.04	0.162	0.165
Pimelic	10	100	147.5	147.46	82.6	82.56	0.278	0.278
Suberic	10	35	205.0	205.22	140.1	140.32	0.484	0.485
Azelaic	10	35	315.0	314.58	250.1	249.68	0.878	0.877
Sebacic	10	6.4	535.0	533.60	470.1	468.70	1.667	1.662

Table 3.3-11 : Chromatographic parameters of column elution runs for aliphatic dicarboxylic acids with resin Dowex 50W-X12 in aqueous medium.

C = 307 meq ; Vb = 140 ml ; Vd = 6.5 ml.

Acid	Vf (ml)	10^2W (mmol)	Vm (ml)		$\bar{V}m$ (ml)		V_θ (ml/meq)	
			Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
Oxalic	5	50.0	66.0	67.46	3.5	4.96	0.003	0.008
Malonic	5	50.0	70.0	69.61	7.5	7.11	0.016	0.015
Succinic	5	50.0	73.5	72.68	11.0	10.18	0.028	0.025
Glutaric	5	50.0	79.0	78.51	16.5	16.01	0.046	0.044
Adipic	5	50.0	86.5	88.64	24.0	26.14	0.070	0.077
Pimelic	5	50.0	101.0	105.83	38.5	43.33	0.117	0.133
Suberic	25	87.5	140.5	146.22	78.0	83.72	0.213	0.232
Azelaic	25	87.5	176.0	198.72	113.5	136.22	0.329	0.403
Sebacic	25	16.0	239.5	289.90	177.0	227.40	0.536	0.700

Table 3.3-12 : Chromatographic parameters of column elution runs for aliphatic dicarboxylic acids with resin Dowex 50W-X16 in aqueous medium.

C = 289 meq ; Vb = 140 ml ; Vd = 6.5 ml.

Acid	Vf (ml)	10^2W (mmol)	Vm (ml)		$\bar{V}$m (ml)		Vθ (ml/meq)	
			Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
Oxalic	5	50.0	66.0	69.05	3.5	6.55	0.003	0.014
Malonic	5	50.0	72.0	71.94	9.5	9.44	0.024	0.024
Succinic	5	50.0	76.5	76.85	14.0	14.35	0.040	0.041
Glutaric	5	50.0	85.0	85.81	22.5	23.31	0.069	0.072
Adipic	5	50.0	95.0	101.13	32.5	38.63	0.104	0.125
Pimelic	5	50.0	111.5	127.71	49.0	65.21	0.161	0.217
Suberic	25	87.5	160.0	183.95	97.5	121.45	0.294	0.377
Azelaic	25	87.5	205.5	264.01	143.0	201.51	0.452	0.654
Sebacic	25	16.0	289.5	403.59	227.0	341.09	0.742	1.137

Table 3.3-13 : Chromatographic parameters of column elution runs for aliphatic dicarboxylic acids with resin Amberlite-200 in aqueous medium.

C = 234 meq ; Vd = 139.0 ml ; Vd = 6.5 ml.

Acid	Vf (ml)	10^2W (mmol)	Vm (ml)		$\bar{V}m$ (ml)		V_θ (ml/meq)	
			Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
Oxalic	10	100.0	87.0	96.12	24.9	34.02	0.085	0.124
Malonic	10	100.0	95.5	96.82	33.4	34.72	0.121	0.127
Succinic	10	100.0	98.0	97.99	35.9	35.89	0.132	0.132
Glutaric	10	100.0	100.0	100.09	37.9	37.99	0.141	0.141
Adipic	10	100.0	103.0	103.60	40.9	41.50	0.153	0.156
Pimelic	10	100.0	109.0	109.69	46.9	47.59	0.179	0.182
Suberic	10	35.0	120.0	120.45	57.9	58.35	0.226	0.228
Azelaic	10	35.0	138.0	138.94	75.9	76.84	0.303	0.307
Sebacic	10	6.4	170.0	171.23	107.9	109.13	0.440	0.445

Table 3.3-14

Illustration of effects due to variation of feed volume, load, feed concentration and bed length.

Acid : Adipic ; Resin : Dowex 50W-X4 ; Vd = 6.5 ml.

Vf ml	10^2W mmol	fc	Vb ml	L cm	C meq	Vm ml Exp	Vm ml Cal	**
1	10	0.100	139.40	57.80	160	157.4	157.61	
2	20	0.100	139.40	57.80	160	157.8	158.11	
4	40	0.100	139.40	57.80	160	159.4	159.11	
6	60	0.100	139.40	57.80	160	160.7	160.11	
8	80	0.100	139.40	57.80	160	161.2	161.11	
10	100	0.100	139.40	57.80	160	161.9	162.11	
12	120	0.100	139.40	57.80	160	163.0	163.11	
15	150	0.100	139.40	57.80	160	165.0	164.61	
5	10	0.020	139.40	57.80	160	159.5	159.61	
5	20	0.040	139.40	57.80	160	160.0	159.61	
5	30	0.060	139.40	57.80	160	158.7	159.61	
5	40	0.080	139.40	57.80	160	159.1	159.61	
5	50	0.100	139.40	57.80	160	158.5	159.61	
5	60	0.120	139.40	57.80	160	158.9	159.61	
5	75	0.150	139.40	57.80	160	159.0	159.61	
5	100	0.200	139.40	57.80	160	159.8	159.61	
8	100	0.125	139.40	57.80	160	160.7	161.11	
12	100	0.083	139.40	57.80	160	162.8	163.11	
15	100	0.067	139.40	57.80	160	164.9	164.61	
17	100	0.059	139.40	57.80	160	165.9	165.61	
20	100	0.050	139.40	57.80	160	166.0	167.11	
22	100	0.045	139.40	57.80	160	168.1	168.11	
25	100	0.040	139.40	57.80	160	170.0	169.61	
10	100	0.100	34.85	14.45	40	49.0	49.15	
10	100	0.100	69.70	28.90	80	87.0	86.80	
10	100	0.100	104.55	43.35	120	125.1	124.46	
10	100	0.100	174.25	72.25	200	200.2	199.76	
10	100	0.100	209.10	86.70	240	237.0	237.41	
10	100	0.100	243.95	101.15	280	277.4	275.06	
10	100	0.100	278.80	115.60	320	308.8	312.72	

** horizontally cont....

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$\bar{V}m$ ml		V_θ ml/meq		σ ml		σ_θ ml/meq		**
Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal	
95.14	95.35	0.5915	0.5928	7.45	7.62	0.576	0.589	
95.54	95.85	0.5909	0.5928	7.80	7.78	0.590	0.589	
97.14	96.85	0.5946	0.5928	8.00	8.12	0.580	0.589	
98.44	97.85	0.5965	0.5928	8.60	8.45	0.600	0.589	
98.60	98.85	0.5913	0.5928	8.84	8.78	0.593	0.589	
99.64	99.85	0.5915	0.5928	8.90	9.12	0.572	0.589	
100.74	100.85	0.5921	0.5928	9.50	9.45	0.593	0.589	
102.74	102.35	0.5953	0.5928	10.00	9.95	0.593	0.589	
97.24	97.35	0.5921	0.5928	8.20	8.28	0.582	0.589	
97.74	97.35	0.5953	0.5928	8.20	8.28	0.582	0.589	
96.44	97.35	0.5871	0.5928	8.25	8.28	0.586	0.589	
96.84	97.35	0.5896	0.5928	8.30	8.28	0.590	0.589	
96.20	97.35	0.5859	0.5928	8.10	8.28	0.574	0.589	
96.64	97.35	0.5884	0.5928	8.35	8.28	0.456	0.589	
96.74	97.35	0.5890	0.5928	8.40	8.28	0.598	0.589	
97.54	97.35	0.5940	0.5928	8.50	8.28	0.560	0.589	
98.44	98.85	0.5903	0.5928	8.85	8.78	0.594	0.589	
100.54	100.85	0.5901	0.5928	9.50	9.45	0.593	0.589	
102.64	102.35	0.5946	0.5928	9.85	9.95	0.581	0.589	
103.64	103.35	0.5946	0.5928	10.10	10.28	0.574	0.589	
103.74	104.85	0.5859	0.5928	11.00	10.78	0.582	0.589	
105.84	105.85	0.5928	0.5928	11.00	11.12	0.580	0.589	
107.74	107.35	0.5953	0.5928	11.70	11.62	0.596	0.589	
28.56	28.71	0.5890	0.5928	5.10	5.39	0.543	0.589	
52.62	52.42	0.5953	0.5928	6.35	6.39	0.524	0.589	
76.78	76.14	0.5982	0.5928	8.00	8.12	0.578	0.589	
124.00	123.56	0.5950	0.5928	9.90	10.00	0.582	0.589	
146.86	147.27	0.5911	0.5928	10.90	10.79	0.596	0.589	
173.32	170.98	0.6011	0.5928	11.40	11.52	0.582	0.589	
190.78	194.70	0.5806	0.5928	12.20	12.20	0.589	0.589	

** horizontally cont...

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β ml		10^2Cm mmol/ml		N		N_θ	
Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal
21.10	21.55	0.50	0.52	163.08	156.58	1.054	1.013
22.10	22.00	1.05	1.03	150.03	151.78	1.003	1.013
22.30	22.97	2.00	1.97	147.44	142.26	1.051	1.013
24.00	23.90	2.90	2.83	131.02	134.09	0.988	1.013
25.00	24.83	3.45	3.64	124.41	126.75	0.994	1.013
25.20	25.80	4.45	4.38	125.34	119.87	1.068	1.013
27.05	26.73	5.10	5.07	112.45	113.89	0.997	1.013
28.90	28.14	6.00	6.02	105.56	105.81	1.008	1.013
23.80	23.42	0.40	0.48	140.62	138.23	1.035	1.013
23.70	23.42	1.00	0.96	142.07	138.23	1.046	1.013
23.75	23.42	1.50	1.45	136.45	138.23	1.004	1.013
23.55	23.42	2.00	1.93	136.13	138.23	0.999	1.013
23.10	23.42	2.45	2.41	141.05	138.23	1.042	1.013
23.85	23.42	2.65	2.89	133.95	138.23	1.665	1.013
23.95	23.42	3.20	3.61	132.63	138.23	0.970	1.013
24.20	23.42	4.20	4.82	131.68	138.23	1.125	1.013
24.70	24.83	4.50	4.54	123.72	126.75	0.988	1.013
26.80	26.73	4.00	4.22	112.00	113.89	0.990	1.013
28.35	28.14	4.00	4.01	108.58	105.81	1.047	1.013
29.20	29.08	3.90	3.88	105.30	101.07	1.073	1.013
30.85	30.49	3.60	3.70	94.00	94.60	1.013	1.013
31.75	31.45	3.55	3.59	92.58	90.61	1.045	1.013
33.45	32.87	3.25	3.43	84.80	85.35	0.998	1.013
15.20	15.25	7.40	7.40	31.36	28.37	1.177	1.013
18.00	18.07	6.40	6.24	68.67	67.30	1.291	1.013
23.00	22.97	5.00	4.91	92.11	87.93	1.071	1.013
28.70	28.28	3.85	3.99	156.88	152.67	1.045	1.013
30.15	30.52	3.70	3.70	181.53	186.29	0.984	1.013
33.00	32.58	3.50	3.46	231.15	220.29	1.067	1.013
34.20	34.51	3.10	3.27	244.54	254.69	0.972	1.013

Table 3.3-15 : Column elution of mixture of (1) Succinic and (2) Adipic acids on the column of resin Dowex 50W-X4 in aqueous medium.

C = 160 meq ; Vf = 5 ml ; Vs = 5 ml.

Sample No.	Acids 10^2W	Succinic + Adipic 10^2Ws	
		25	25
1-19		-	-
20		0.10	-
21		0.80	-
22		2.82	-
23		8.30	-
24		9.30	-
25		3.82	-
26		0.80	-
27		0.10	-
28		-	0.10
29		-	1.50
30		-	3.50
31		-	5.63
32		-	6.10
33		-	4.36
34		-	2.25
35		-	0.80
36		-	0.15
37		-	-

Table 3.3-16 : Column elution of Malonic acid and a mixture of Glutaric and Pimelic acids on the column of resin Dowex 50W-X4 in aqueous medium

Vf = 5 ml ; Vs = 5 ml ; C = 160 meq

Sample NO.	Acid 10^2W	Malonic 25	Glutaric + Pimelic 25 10^2Ws
1 -15		-	-
16		0.12	-
17		0.26	-
18		0.60	-
19		1.22	-
20		3.23	-
21		11.60	-
22		7.70	0.25
23		1.38	0.37
24		0.12	1.37
25		-	3.82
26		-	7.22
27		-	7.42
28		-	3.40
29		-	1.10
30		-	0.25
31-34		-	-
35		-	-
36		-	0.37
37		-	0.75
38		-	1.36
39		-	2.25
40		-	3.17
41		-	4.00
42		-	4.10
43		-	3.38
44		-	2.44
45		-	1.50
46		-	0.85
47		-	0.35
48		-	0.12
49		-	-

Table 3.3-17 : Column elution of dihydroxybenzoic acids on the column of resin Dowex 50W-X4 using 0.01N aqueous hydrochloric acid as solvent and eluent.

Vf = 25 ml ; Vs = 25 ml ; C = 160 meq.

Sample No.	Acid 10^2W	2,6-diOHI 2.35	3,5-diOHI 2.56	2,4-diOHI 6.21
			10^2Ws	
1- 4		-	-	-
5		0.01	-	-
6		0.27	-	-
7		1.20	-	-
8		0.80	-	-
9		0.08	-	-
10		0.02	-	-
11		0.01	-	-
12		-	0.01	-
13		-	0.06	-
14		-	0.51	-
15		-	1.14	-
16		-	0.61	-
17		-	0.21	-
18		-	0.04	-
19-24		-	-	-
25		-	-	0.05
26		-	-	0.28
27		-	-	0.83
28		-	-	1.34
29		-	-	1.34
30		-	-	1.02
31		-	-	0.66
32		-	-	0.39
33		-	-	0.21
34		-	-	0.10
35		-	-	0.05
36		-	-	-

Table 3.3-18 : Column elution of dihydroxybenzoic acids on the column of resin Dowex 50W-X4 using 10 % dioxan in 0.01 N aqueous hydrochloric acid as solvent and eluent.

Vf = 25 ml ; Vs = 25 ml ; C = 160 meq.

Sample No.	Acid 10^2W	2,6-diOHI 3.04	3,5-diOHI 1.43	2,4-diOHI 3.51
			10^2Ws	
1- 2		-	-	-
3		0.14	-	-
4		1.72	-	-
5		0.95	-	-
6		0.08	-	-
7		0.05	-	-
8		0.03	0.12	-
9		0.02	0.79	--
10		-	0.49	-
11		-	0.04	-
12		-	-	0.01
13		-	-	0.04
14		-	-	0.48
15		-	-	1.44
16		-	-	1.16
17		-	-	0.36
18		-	-	0.04
19		-	-	-

Table 3.3-19 : Column elution of Benzoic acid(I) and dihydroxybenzoic acids on the column of resin Dowex 50W-X4 using 0.01 N aqueous hydrochloric acid as solvent and eluent

Vf = 25 ml ; Vs = 25 ml ; C = 80 meq.

Sample No.	Acid	I	2,6-diOHI	3,5-diOHI + 2,4-diOHI	
	10^2W	0.39	1.06	2.50	4.00
				10^2Ws	
1		-	-	-	-
2		-	0.16	-	-
3		-	0.78	-	-
4		-	0.16	-	-
5		-	0.02	-	-
6		-	-	0.02	-
7		-	-	0.32	-
8		-	-	1.44	-
9		-	-	0.75	-
10		-	-	0.03	-
11		0.01	-	-	-
12		0.13	-	-	0.08
13		0.18	-	-	0.62
14		0.08	-	-	1.27
15		0.01	-	-	1.25
16		-	-	-	0.60
17		-	-	-	0.20
18		-	-	-	0.02
19		-	-	-	-

Table 3.3-20 : Column elution of mixture of dimethoxyl benzoic acids on the column of resin Dowex 50W-X4 using 10% dioxan in 0.01 N aqueous hydrochloric acid as solvent and eluent. 119

Vf = 25 ml ; Vs = 25 ml ; C = 160 meq.

Sample No.	Acids 10^2W	2,6-diOMeI + 1.77	2,4-diOMeI + 1.48	3,5-diOMeI 0.65
			10^2Ws	
1 -10		-	-	-
11		0.15	-	-
12		0.80	-	-
13		0.69	-	-
14		0.15	-	-
15		0.02	-	-
16-22		-	-	-
23		-	0.02	-
24		-	0.07	-
25		-	0.18	-
26		-	0.29	-
27		-	0.33	-
28		-	0.27	-
29		-	0.17	-
30		-	0.08	-
31		-	0.03	-
32		-	0.01	-
33		-	-	0.002
34		-	-	0.020
35		-	-	0.043
36		-	-	0.066
37		-	-	0.088
38		-	-	0.107
39		-	-	0.109
40		-	-	0.094
41		-	-	0.071
42		-	-	0.043
43		-	-	0.025
44		-	-	0.010
45		-	-	0.002
46		-	-	-

3.4 DISCUSSION

For the treatment of the resin-solvent-solute system, one may consider a column of the resin as made up of three parts, viz. (a) the liquid between the resin beads, (b) the liquid within the resin beads and (c) the resin net work. The nonionic solute will not be restricted by electrostatic forces in the external solvent, but distributes on and through the resin and the external solvent. The uptake of the solute by the resin is characterized by the distribution coefficient which can be expressed in various ways such as volume distribution coefficient, Kv, weight distribution coefficient, Kw. In chromatography, distribution coefficient is the important factor as it determines the rate of movement of the solute down the column. It is related to the peak elution volume, the width of the elution curve and the resolution.

In the present study the distribution coefficient is expressed in terms of the sorption coefficient, B (defined in Chapter 2). This is related to the volume distribution coefficient Kv (per ml of the resin) and weight distribution coefficient Kw (per gram of the resin) as,

$$B = Kv/c' = Kw/c$$

where c' denotes capacity of the resin in equivalents per ml of the resin and c, the capacity in equivalents per gm of the resin. Therefore, it follows that it would be possible to correlate the sorption coefficient, B, with the following :

(1) the peak elution volume,

(2) the width and peak height of the elution curve,

(3) the number of theoretical plates and

(4) the resolution

by simple equations and these equations may be compared with the equations given in the literature (313-339), where the above equations are related to either volume distribution coefficient or weight distribution coefficient.

Generally the equations are based on the assumption that the elution curves are symmetric and could be described mathematically by a Gaussian curve. However, when certain components are eluted from the chromatographic column, they are seen as asymmetric peaks - customarily called bands with a diffuse or sharp trailing or leading front. Trailing is associated with lowered binding at higher concentration, so that the center of the peak moves rapidly than the wings, and the sorption coefficient decreases with increase in concentration. Conversely, fronting involves increased binding and sorption coefficient at higher concentration, i.e. binding of some sample on to the stationary phase increases the affinity for binding more sample. Fronting is thereforea co-operativity phenomenon and may bear some resemblance to the binding of hydrophobic molecule together in bio-membranes (237). In such cases calculations based on Gaussian distribution may lead to considerable errors.

3.4.1 Aliphatic Dicarboxylic Acids

Several series of runs were carried out with aliphatic dicarboxylic acids (from oxalic to sebacic) on the column of resins X1, X2, X4, X8, X12, X16 and Amberlite-200 (group I, VI Table 2.3-1) to study the effect of load, feed volume, concentration, bed volume or column length and degree of crosslinking of the resin using water as solvent and eluent.

Since the elution study involves a large number of runs, all the runs and graphs of all the elution curves are not given, instead the results are summarized in Section 3.3. Interpretation of the results were made for different column parameters in the following ways :

3.4.1.1 Peak Elution Volume

The peak elution volume, Vm, denotes the volume of the eluent from the start of the elution run to the mid-point of the peak. Taking interstitial volume of the column as 0.4 Vb, it may be expressed as :

$$Vm = Vd + 0.4\ Vb + \bar{\bar{V}}m \qquad \text{-----(17)}$$

where Vd is disc volume, Vb is bed volume and $\bar{\bar{V}}m$ may be expressed as following :

$$\bar{\bar{V}}m = 0.5\ Vf + C \cdot V_\theta \qquad \text{-----(18)}$$

where Vf is feed volume, C is the total exchange capacity of resin in the column and

$$V_\theta = \alpha_1 + \alpha_2 B + \alpha_3 B^2 \qquad \text{-----(19)}$$

Here α_1, α_2 and α_3 are constants (Table 3.3-1) determined by the resin-solute-solvent system. For each homologous series, the values of α_1, α_2 and α_3 were calculated from the experimental values of Vm for the members of corresponding series. α_1 can be thought of as dependent on the shape and size of the substituents in the homologous series and degree of crosslinking of the resin but independent of the chain length of solute molecule. α_2 depends on the molecular destortion due to the polar functional group present in the solute molecule and independent of the crosslinkage of the resin containing ionogenic groups of the same type. Generally in straight chain compounds, the value of α_2 increases with the increase of such polar groups. However, the total increase may be less than the simple addition of values of individual groups. α_3 can be considered as a measure of the phase separation in the resin medium. Alternatively, it may be considered as a measure of gel-permiation of the homologous series in the swollen resin. It is realized that these ideas are in the nature of suggestion and modification in the nature of thinking when more detailed data become available need not be ruled out.

Above equations give the variation of Vm with feed volume, column capacity or column length and sorption coefficient B. Further it is indicated that Vm is independent of load. If we assume an ideal column in which interstitial and disc volumes are negligible and feed

volume is sufficiently small then from the above equations it follows that :

(1) Vm is directly proportional to B

(2) Vm is directly proportional to C and for the given column C is directly proportional to length of the resin bed L. Hence Vm is also directly proportional to L. Then the above equations resume the form

$$Vm = B \cdot C \qquad \text{------(20)}$$

The column runs with resins X1, X2 and X4 were quite symmetrical (Figs. 3.3-1 to 3.3-3) and could be described by Gaussian curves. However, somewhat band spreading was observed with the resin of lower degree of crosslinking such as X1. Table 3.3-2 gives illustrative elution runs for glutaric acid with these resins. Further, with the resins of higher degree of crosslinking such X8, X12 and X16, the elution curves were rather asymmetric and there was trailing at the end of the run (Figs. 3.3-4 to 3.3-6). Table 3.3-3 gives illustrative runs for glutaric acid with these resins alongwith the resin Amberlite-200, whose behaviour was also similar (Fig. 3.3-7), although it has an open high-internal-surface structure. The trailing also increases with increase in the chain length of the solute molecule among the homologous series (Tables 3.3-4 to 3.3-6).

The values of V_θ are calculated according to equation (19) using the values of B from Table 2.3-9 for dicarboxylic acids studied with various resins. These are

compared (Tables 3.3-7 to 3.3-13) with the experimental values of V_e obtained by carrying out actual column elution runs of these acids on column of different resins. Not all but some elucidative runs and elution curves are given where necessary. Data indicate that the experimental values of V_e are significantly lower than the calculated values as the crosslinking of the resin and the chain length of the solute molecule become high. For solutes of relatively smaller chain length, this difference is negligible. The difference is particularly significant for resins of crosslinking 12 and 16 and for solutes of larger chain length. This may be explained as follows :

The resins of lower degree of crosslinking swell considerably in aqueous medium and hence almost all sites are available for sorption even for larger molecules. However as the crosslinking of the resin increases, the swelling in aqueous medium decreases. Hence in such resins, all the sorption sites may be available for solutes of relatively smaller chain length but some of the sorption sites may not be available for sorption of solutes of relatively larger chain length because of the sieve action. It is realized that there could be no clearcut boundary line for this sieve action and the operation of this effect would depend both on the crosslinking of the resin and chain length of the solute molecules. Table 3.3-14 illustrates the applicability of above equations for different values of feed volume, feed concentration,

bed volume or bed length and load. Tables 3.3-7 to 3.3-13 give some illustrative values of Vm for different acids for the resins used from several runs carried out. The comparision between the experimental values of Vm and those calculated from equations (17), (18) and (19) is again satisfactory, except for oxalic acid indicating that the equation is applicable for the rest of the acids. For oxalic acid, the calculated values of Vm and V_θ are higher than the experimental values. This may be attributed to the fact that the oxalic acid is relatively stronger acid (pK_1 = 1.27) and hence, the lower experimental values of Vm and V_θ should be due to the operation of ion exclusion. This view is also supported by the observation that, the value of V_θ with water as solvent and eluent is equal to about 0.05, while, using 0.2 N aqueous hydrochloric acid solution as solvent and eluent, the value of V_θ increased to 0.18. Which may be due to the partial suppression of the ionization of oxalic acid. This conclusion gets further support from the observations of Tanaka, N and Thornton, E.R. that, the effects of head groups (here - COOH groups) include possible effects extending to the first methylene group or so, whose environment might be altered by chain-end effects including specific solvation of polar head groups (237). This in turn would affect ionization and hence sorption.

From all above observations it may be concluded that, in this homologous series, homology may not be operative until the first $-CH_2$ unit (n_c = 1) is introduced into an

unique molecular environment of ground molecule i.e. the second member (malonic acid) of the series.

3.4.1.2 Band Width

As indicated in Section 3.1, the width of an elution curve is a measure of column performance or column efficiency. Narrower is the width, better will be the column performance. Two parameters may be used to describe peak width ; (i) σ, the half of the width measured at the ordinate $Cm/\sqrt{e}$, also referred to as 'standard deviation' and (ii) β, the width measured at the ordinate Cm/e. Where Cm is the peak height (Section 3.4.1.3) of the elution curve and e is the base of natural logarithm. For a Gaussian curve, these two parameters are related as :

$$\beta = 2\sqrt{2} \cdot \sigma \qquad \text{------(21)}$$

In the literature equations are given correlating σ^2 (variance) with the distribution coefficient and the column parameters. This means that width of an elution curve depends on the sorption coefficient of the solute and the column parameters such as, resin particle size, area of cross-section, bed length, flow rate, feed volume and temperature. By considering one variable at a time holding other parameters constant, its effect on the width of an elution curve can be studied.

In this work the effect of sorption coefficient, column length, feed volume, feed concentration, column capacity and load on σ and β has been studied keeping other parameters

constant. Under these conditions it would be possible to give an equation correlating σ with σ_θ (or B) and C as :

$$\sigma = \frac{Vf}{6} + \sqrt{C} \cdot \sigma_\theta \qquad \text{-----(22)}$$

and σ_θ may be expressed as :

$$\sigma_\theta = f_1\alpha_1 + f_2\alpha_2 B \qquad \text{-----(23)}$$

where f_1 and f_2 are constants (Table 3.3-1) determined by the particle size of the resin bead. Since σ and β are related (equation : 21), we can also express β in terms of B and C as :

$$\beta = 2\sqrt{2}\left[\frac{Vf}{6} + \sqrt{C}(f_1\alpha_1 + f_2\alpha_2 B)\right] \qquad \text{-----(24)}$$

Above equations give the variation of σ or β with sorption coefficient B and column parameters. It further follows that σ and β should be independent of load. Table 3.3-14 illustrates the effect of feed volume, feed concentration, column length or column capacity and load on the values of σ and σ_θ. Tables 3.3-17 to 3.3-19 give experimental and calculated values of σ, σ_θ and β for aliphatic straight chain dicarboxylic acids studied from the several runs carried out. The experimental determination of Vm, σ and β are shown in Section 3.4.1.6. Experimental values of σ_θ can be obtained by substituting the values of Vf, C and experimental σ in equation (22). Above tables demonstrate fair applicability of the equations suggested. However, when trailing or fronting is involved, e.g. with resins

of higher degree of crosslinking such as X8, X12, X16 and Amberlite-200, there is remarkable departure from Gaussian distribution. In such cases equations reported can not be effectively applied. Hence resin X4 onwards, values of σ and other dependent quantities have not been mentioned in the rest of the tables.

3.4.1.3 Peak Height

The peak height, Cm, is the concentration at the peak elution volume. This depends upon (i) the amount of the solute loaded, W, which refers to the area under the elution curve and (ii) the width of the elution curve. For a Gaussian curve these two are related as :

$$Cm = \frac{W}{\sqrt{2\pi}.\ \sigma} \qquad \text{-----(25)}$$

From equations (22), (23) and (25) it follows that

$$Cm = \frac{W}{\sqrt{2\pi}\left[\frac{Vf}{6}+\sqrt{C}\ (f_1\alpha_1 + f_2\alpha_2 B)\right]} \qquad \text{-----(26)}$$

The above equation indicates the dependence of Cm on load and band width (i.e. B and C). The values of Cm calculated according to above equation for various dicarboxylic acids with different resins are compared (Tables 3.3-7 to 3.3-9) with the experimental values of Cm obtained by carrying out actual column elution runs of these acids on different resin columns. Experimental determination of Cm is demonstrated in Section 3.4.1.6. Table 3.3-14 shows

the variation of Cm with different column parameters which include feed volume, feed concentration, load and column length or column capacity. Data indicate that the equations (25) and (26) are fairly applicable for the runs described by Gaussian curve.

3.4.1.4 Number of Theoretical Plates

The number of theoretical plates, N, or the plate height, H, is an indirect measure of the width of an elution curve and hence the column performance or column efficiency. For the particular solute, larger the number of theoretical plates in the given column, smaller will be the width of the elution curve or greater will be the column efficiency and Vice versa. Hence for the particular compound, the experimental determination of the number of theoretical plates in the given column involves the experimental determination of peak elution volume and either the width (σ or β) or peak height of the elution curve. These are related to the number of theoretical plates by the following equations :

$$N = \left[\frac{\bar{V}m}{\sigma}\right]^2 \qquad \text{------(27)}$$

$$\text{or} \quad N = 8\left[\frac{\bar{V}m}{\beta}\right]^2$$

$$N = 2\Pi\left[\frac{\bar{V}m \cdot Cm}{W}\right]^2 \qquad \text{------(28)}$$

Further from equations (18), (22) and (27) it follows that

$$N = \frac{0.5\ Vf + C\ (\alpha_1 + \alpha_2 B + \alpha_3 B^2)}{\frac{Vf}{6} + \sqrt{C}\ (f_1\alpha_1 + f_2\alpha_2 B)} \qquad \text{----(29)}$$

The equation (29) expresses N in terms of B and C.

Defining N_θ as N/C when Vf = 0, we have,

$$N_\theta = \left[\frac{V_\theta}{\sigma_\theta}\right]^2 \qquad \text{------(30)}$$

The experimental and calculated values of the number of theoretical plates were computed according to the equation (28) and (29) respectively. Both these values of the number of theoretical plates for the column elution runs of various dicarboxylic acids on different resin columns are recorded in Tables 3.3-7 to 3.3-9 together with the experimental and calculated values of N_θ. Requisite quantities for the evaluation of N_θ are V_θ and σ_θ, whose experimental and calculational determinations are given at relevant places in Section 3.4.1. The calculated values were found to be in agreement with the experimental values obtained from several series of runs which were carried out.

3.4.1.5 Resolution (separation study)

The extent of separation of the two components is conveniently expressed in terms of resolution, R_n, as :

$$R_n = \frac{\Delta Vm}{n(\sigma_1 + \sigma_2)} = \frac{Vm_2 - Vm_1}{n(\sigma_1 + \sigma_2)} \qquad \text{----(31)}$$

where ΔVm is the gap between the centers of the peaks of neighbouring elution curves and n is an integer greater than zero. The subscripts 1 and 2 denote solute 1 and solute 2. The magnitude of n indicates the degree of

separation and it depends on the type of problem and chromatography. The generally accepted criterion of minimum resolution in liquid-solid chromatography is to select the value of n as 3. This means that after having divided the effluent, Ve, into fraction at a point $Ve = Vm_1 + 3\sigma_1$, at least 99.86 % of each of the components is in its appropriate fraction and the impurity amounts to at most 0.14 % of the peaks of the contagious components. Combining equations (17), (22) and (31), we get

$$R_n = \frac{C\,(V_{\theta_2} - V_{\theta_1})}{3\sqrt{C}\,(\sigma_{\theta_1} + \sigma_{\theta_2}) + Vf} \qquad \text{-----(32)}$$

From equation (32) it follows that for the given pair of components having the sorption coefficients B_1 and B_2, the resolution, R_n for the particular column i.e. particular value of C) can be calculated and thus the extent of separation could be predicted before carrying out the actual column runs.

An illustrative calculation of R_n for a mixture of succinic acid ($B_{cal} = 0.0826$) and adipic acid ($B_{cal} = 0.2494$) on the column of resin X4 is shown in Section 3.4.1.6 alongwith the summary of intermediate values involving in the procedure (Table 3.4.1-1). Experimental R_n is also calculated from equation (31) by substituting the experimentally determined values of Vm and σ for these two acids from their individual column elution runs on the same column. The two values of R_n thus obtained are in fair agreement. Then the actual separation was tried by taking the mixture

of these acids. The two components were separated in accordance with the resolution computed from their B values and from their individual runs.

For some other pairs of dicarboxylic acids of interest, the values of R_n (calculated from B values and also from the individual column elution runs) are quoted in Table 3.4.1-2 in Section 3.4.1.6. The column elution runs with number of mixtures were carried out and the elution of each component was practically unaffected by the presence of the other. The elution runs of mixtures of some illustrative pairs have been cited in Tables 3.3-15 and 3.3-16.

As seen earlier, Vm is proportional to C and σ is proportional to $\sqrt{C}$. Therefore, R_n increases with $\sqrt{C}$ thus always reaching unity-indicating a satisfactory separation, if suitable column length is used. By setting $R_n = 1$ in equation (32), the minimum number of equivalents of the resin, C_{min} required for the separation of the desired pairs of dicarboxylic acids can be calculated. The equation of C_{min} can be written as :

$$1 = \frac{C_{min}\,(V_{\theta_2} - V_{\theta_1})}{3\sqrt{C_{min}}\,(\sigma_{\theta_1} + \sigma_{\theta_2}) + Vf} \qquad \text{-----(33)}$$

A number of mixtures were experimentally tried and the agreement between the experimental and calculated values of C_{min} was fair. In Table 3.4.1-2 are given values of C_{min} calculated according to equation (33) using calculated values of V_θ and σ_θ from Tables 3.3-7 to 3.3-9.

Depending on the value of R_n, separation may be classified as :

1. Quantitative and efficient separations : These have R_n value as unity or almost unity. This in fact, is the object of any chromatographic separation.

2. Quantitative but inefficient separations : These have R_n value considerably greater than unity, thus resulting in a waste of time and eluent.

3. Qualitative and incomplete separations : These have R_n value less than unity and peaks overlap considerably. However, the peaks can be easily identified. For identification purposes resolution need not always be unity.

The separation can be improved by increasing the column length if the cross-section of the column is kept constant, decreasing the feed volume and/or decreasing the particle size of exchangers depending on the practical limits of pressure drop, solubility of components in the solvent and their detectability in the effluent samples.

3.4.1.6 Model calculations and experimental determinations :

The method of calculation and experimental determination of various chromatographic quantities reported in Tables 3.3-7 to 3.3-13 for different elution runs are illustrated in this section by considering column elution of succinic acid (Fig. 3.4.1-1), adipic acid (Fig. 3.4.1-2) and a mixture of succinic and adipic acids (Fig. 3.4.1-3, Table 3.3-15).

Calculation I

Acid : Succinic

Resin : Dowex 50W-X4

Solvent & eluent : Distilled water

B_{exp} = 0.0830 B_{cal} = 0.0826

$10^2 W$ = 50 mmol Vf = 5 ml Vs = 5 ml

Vb = 139.4 ml Vd = 6.5 ml L = 57.8 cm C = 160 meq

The chromatogram of the elution run is obtained by plotting $10^2 Ws$ versus sample number, where Ws denotes the amount of the solute in millimoles present in the given volume of effluent sample (Vs ml). The points represent the analyzed fraction of the effluent. The smooth and continuous graph is drawn through these points and the resulting plot is the experimental elution curve (Fig. 3.4.1-1).

Now,

$$V_{\theta cal} = \alpha_1 + \alpha_2 B_{cal} + \alpha_3 B^2_{cal} \quad \text{(Table 3.3-1}$$

$$= 0.19 + (1.6 \times 0.0826) + 0.06\ (0.0826)^2$$

$$= 0.323 \text{ ml/meq}$$

Fig. 3.4.1-1 : Illustrative plot of W_e versus sample number for the column elution of succinic acid on the column of resin Dowex 50W-X4 (100-200) in aqueous medium.

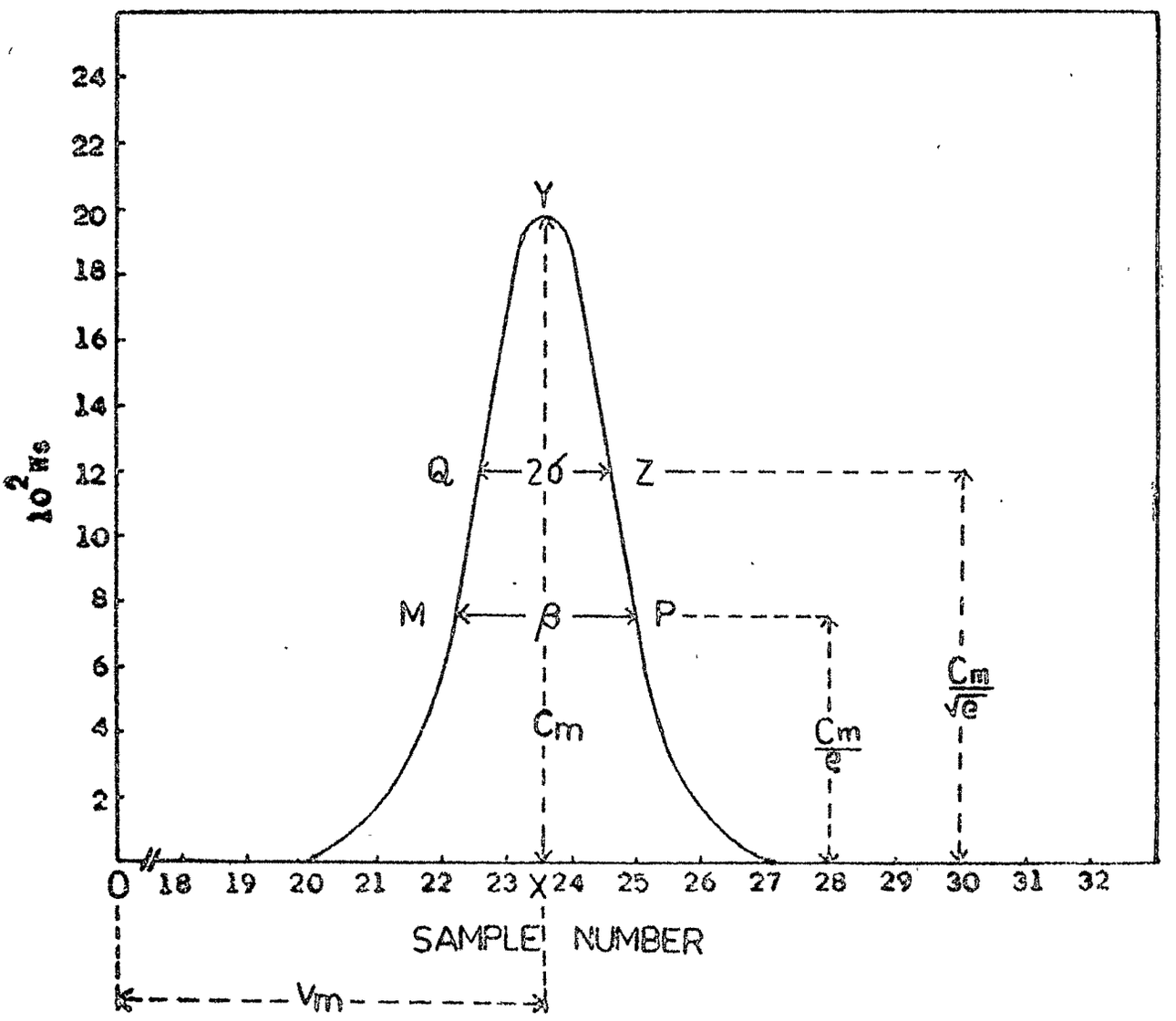


Fig. 3.4.1-2 : Plot of Ws versus sample number for the column elution of adipic acid on the column of resin Dowex 50W-X4 (100-200) in aqueous medium.

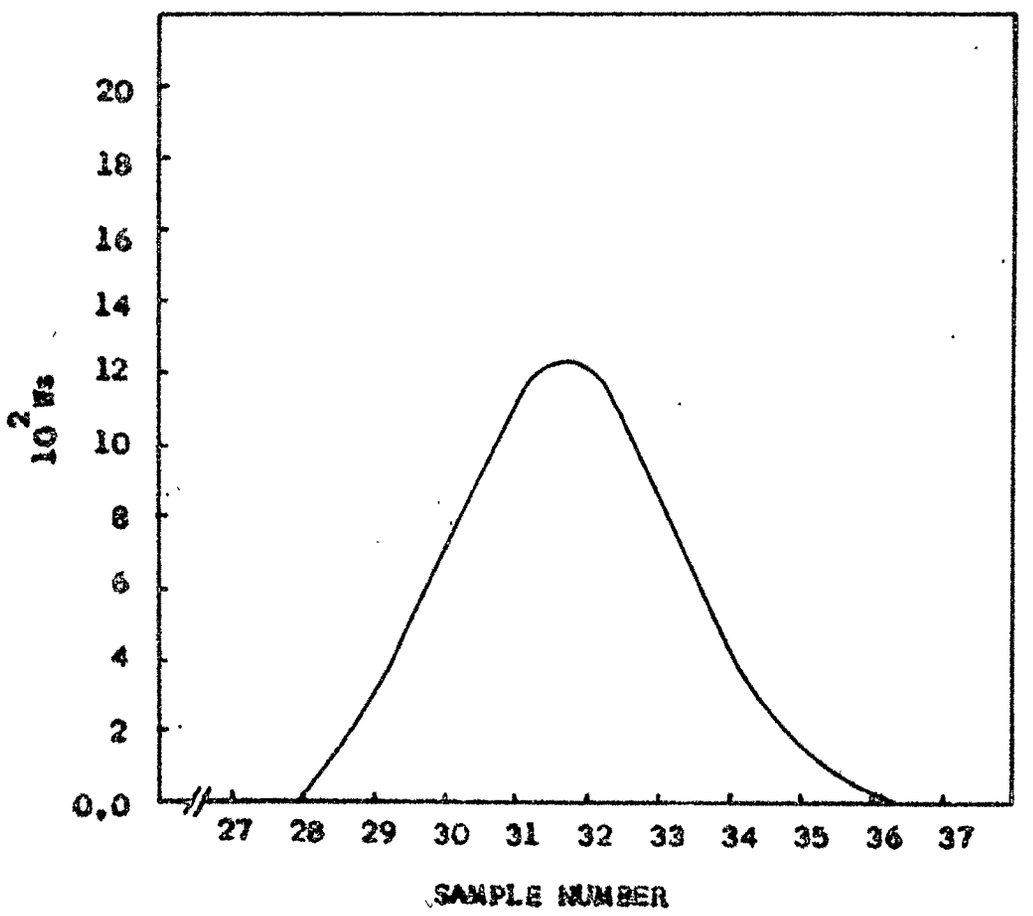
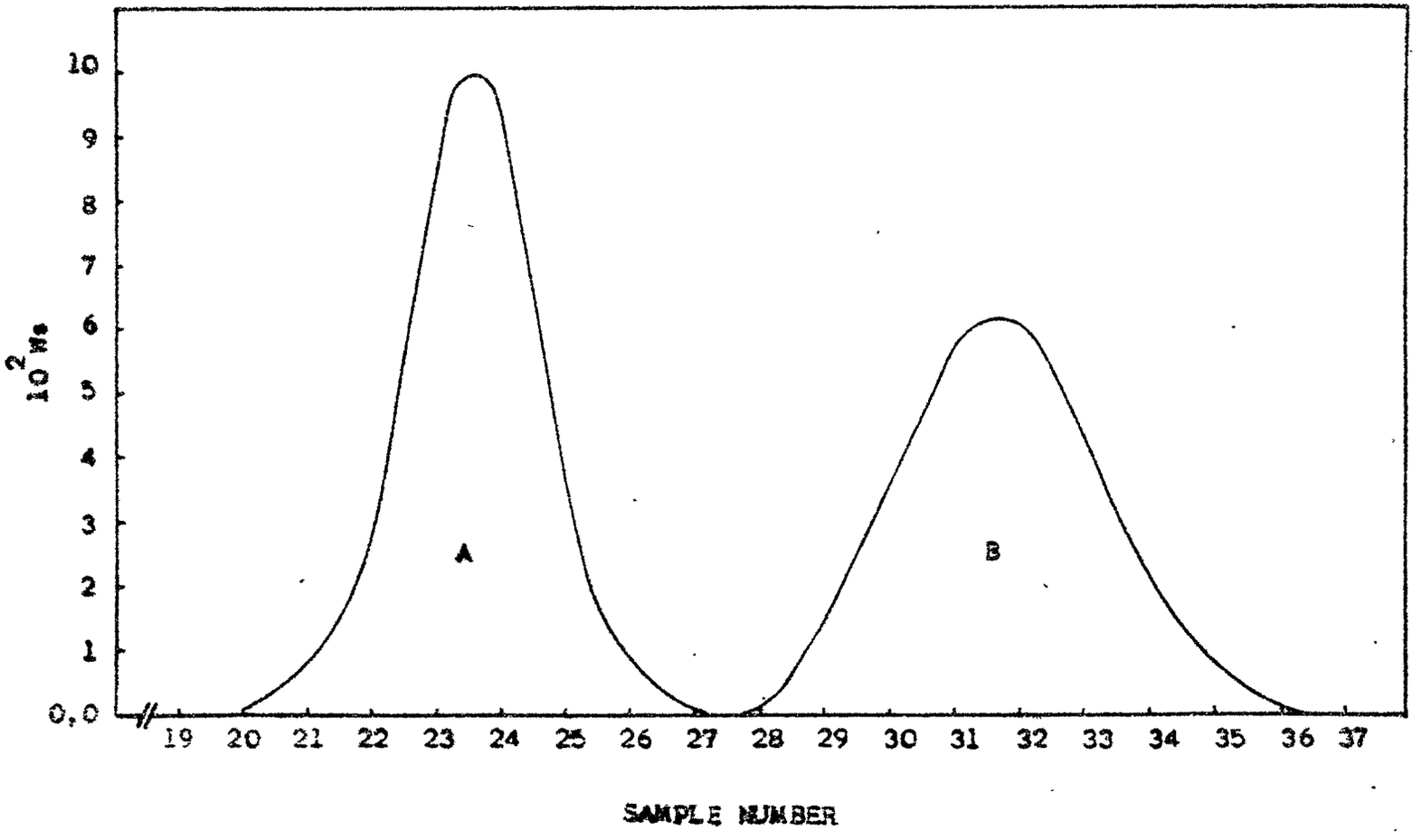


Fig. 3.4.1-3 : Plot of Ws versus sample number for the column elution of the mixture of (A) succinic acid and (B) adipic acid on the column of resin Dowex 50W-X4 (100-200) in aqueous medium.



$$\bar{V}m_{cal} = 0.5\ Vf + C \cdot V_{\theta\ cal}$$

$$= (0.5 \times 5) + (160 \times 0.323)$$

$$= 54.18\ ml$$

$$Vm_{cal} = Vd + 0.4\ Vb + \bar{V}m_{cal}$$

$$= 6.5 + (0.4 \times 139.4) + 54.18$$

$$= 116.44\ ml$$

$$Vm_{exp} = (OX)\ (Vs) \qquad \text{(Fig. 3.4.1-1)}$$

$$= 23.6 \times 5$$

$$= 118\ ml$$

$$\bar{V}m_{exp} = Vm_{exp} - Vd - 0.4\ Vb$$

$$= 118 - 6.5 - (0.4 \times 139.4)$$

$$= 55.74\ ml$$

$$V_{\theta\ exp} = \frac{\bar{V}m_{exp} - 0.5\ Vf}{C}$$

$$= \frac{55.74 - (0.5 \times 5)}{160}$$

$$= 0.333\ ml/meq$$

$$\sigma_{\theta\ cal} = f_1\alpha_1 + f_2\alpha_2 B_{cal} \qquad \text{(Table 3.3-1)}$$

$$= (1 \times 0.19) + (1 \times 1.6 \times 0.0826)$$

$$= 0.322\ \ ml/meq$$

$$\sigma_{cal} = Vf/6 + \sqrt{C} \cdot \sigma_{\theta\ cal}$$

$$= 5/6 + (\sqrt{160} \times 0.322)$$

$$= 4.906\ ml$$

σ_{exp} = 0.5 x QZ (Fig. 3.4.1-1)

= 0.5 x 10

= 5 ml

$\sigma_{\theta\ exp} = \dfrac{\sigma_{exp} - Vf/6}{\sqrt{C}}$

$= \dfrac{5 - 5/6}{\sqrt{160}}$

= 0.329 ml/meq

$\beta_{cal} = 2\sqrt{2} \cdot \sigma_{cal}$

$= 2\sqrt{2} \times 4.906$

= 13.88 ml

β_{exp} = MP (Fig. 3.4.1-1)

= 14 ml

$Cm_{cal} = \dfrac{W}{\sqrt{2\Pi} \cdot \sigma_{cal}}$

$= \dfrac{50 \times 10^{-2}}{2.5066 \times 4.906}$

$= 4.066 \times 10^{-2}$ mmol/ml

Cm_{exp} = XY/Vs (Fig. 3.4.1-1)

$= \dfrac{19.75 \times 10^{-2}}{5}$

$= 3.95 \times 10^{-2}$ mmol/ml

$N_{cal} = \left[\dfrac{\bar{V}m_{cal}}{\sigma_{cal}}\right]^2$

$= \left[\dfrac{54.18}{4.906}\right]^2$

= 121.96

$N_{exp} = \left[\dfrac{\bar{V}m_{exp}}{\sigma_{exp}}\right]^2$

$= \left[\dfrac{55.74}{5.00}\right]^2$

= 124.28

$N_{\theta\ cal} = \left[\dfrac{V_{\theta\ cal}}{\sigma_{\theta\ cal}}\right]^2$

$= \left[\dfrac{0.323}{0.322}\right]^2$

= 1.006

$N_{\theta\ exp} = \left[\dfrac{V_{\theta\ exp}}{\sigma_{\theta\ exp}}\right]^2$

$= \left[\dfrac{0.333}{0.329}\right]^2$

= 1.024

Calculation II

Acid : Adipic

Resin : Dowex 50W-X4

Solvent and eluent : Distilled water

B_{exp} = 0.2510 B_{cal} = 0.2494

10^2W = 50 mmol Vf = 5 ml Vs = 5 ml

Vb = 139.4 ml Vd = 6.5 ml L = 57.8 cm C = 160 meq

From Fig. 3.4.1-2, on calculation, the following results are obtained :

Vm_{cal}	= 159.64 ml	Vm_{exp}	= 158.5 ml
$\overline{Vm}_{cal}$	= 97.38 ml	$\overline{Vm}_{exp}$	= 96.24 ml
$V_{\theta cal}$	= 0.593 ml/meq	$V_{\theta\ exp}$	= 0.586 ml/meq
σ_{cal}	= 8.284 ml	σ_{exp}	= 8.1 ml
$\sigma_{\theta\ cal}$	= 0.589 ml/meq	$\sigma_{\theta\ exp}$	= 0.574 ml/meq
β_{cal}	= 23.43 ml/meq	β_{exp}	= 23.1 ml
$C_{m\ cal}$	= 2.408 mmol/ml	$C_{m\ exp}$	= 2.45 mmol/ml
N_{cal}	= 138.18	N_{exp}	= 141.17
$N_{\theta\ cal}$	= 1.013	$N_{\theta\ exp}$	= 1.042

Calculation III

Acids : Succinic (1) + Adipic (2)

Resin : Dowex 50W-X4

Solvent and eluent : Distilled water

$10^2W = (25 + 25) = 50$ mmol Vf = 5 ml Vs = 5 ml

Vb = 139.4 ml Vd = 6.5 ml L = 57.8 cm C = 160 meq

$$R_{n_{cal}} = \frac{C\,(V_{\theta_2 cal} - V_{\theta_1 cal})}{3\sqrt{C}\,(\sigma_{\theta_1 cal} + \sigma_{\theta_2 cal}) + Vf}$$

$$= \frac{160\,(0.593 - 0.323)}{3\sqrt{160}\,(0.322 + 0.589) + 5}$$

$$= 1.0917$$

$$R_{n_{exp}} = \frac{(Vm_2 exp - Vm_1 exp)}{3\,(\sigma_1 exp + \sigma_2 exp)}$$

$$= \frac{158.5 - 118.0}{3\,(5 + 8.1)}$$

$$= 1.0305$$

Calculated C_{min} is obtained by substituting the calculated quantities in the following equation

$$(V_{\theta_2} - V_{\theta_1})\,C_{min} - 3\,(\sigma_{\theta_1} + \sigma_{\theta_2})\,\sqrt{C_{min}} - Vf = 0$$

This is a quadratic equation of the form

$$aX^2 + bX + c = 0$$

roots of which can be given by

$$X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

where we have,

$$b = -3 (\sigma_{\theta_1} + \sigma_{\theta_2})$$
$$= -3 (0.322 + 0.589)$$
$$= -2.733$$

$$a = V_{\theta_2} - V_{\theta_1}$$
$$= 0.593 - 0.323$$
$$= 0.270$$

and $c = -5$

Therefore

$$\sqrt{C_{min}} = \frac{2.733 \pm \sqrt{7.469 + 5.4}}{0.54}$$

$$= \frac{2.733 + 3.587}{0.54}$$

$$= 11.705$$

and calculated $C_{min} = 137$ meq.

Similarly Exp. $C_{min} = 151.6$ meq.

Fig. 3.4.1-3 shows that the resolution is achieved as per the prediction. All results obtained in this way for separation of mixture of succinic and adipic acids are summarized in Table 3.4.1-1. In Table 3.4.1-2 are given the values of C_{min} computed alongiwth the corresponding column length L_{min} and Rn predicted for couple of mixtures of aliphatic dicarboxylic acids of interest.

Table 3.4.1-1 : Experimental and calculated values of column parameters for the resolution of mixture of succinic and adipic acids on the column of resin Dowex 50W-X4 in aqueous medium

Vd = 6.5 ml ; Vf = 5 ml ; Vs = 5 ml ; Vb = 139.4 ml ; C = 160 meq ; L = 57.8 cm

Parameter		Succinic		Adipic		Succinic + Adipic	
		Exp	Cal	Exp	Cal	Exp	
β	ml/meq	0.0830	0.0826	0.2510	0.2494	0.0830	0.2510
$10^2 W$	mmol	50	-	50	-	25	25
Vm	ml	118.00	116.44	158.50	159.64	118.00	159.00
$\bar{V}m$	ml	55.74	54.18	96.24	97.38	55.74	96.74
V_θ	ml/meq	0.3330	0.3230	0.5860	0.5930	0.3330	0.5890
σ	ml	5.00	4.906	8.1	8.284	5.000	8.1
σ_θ	ml/meq	00.329	00.322	00.574	00.589	00.329	00.574
β	ml	14.0	13.88	23.1	23.43	14.0	23.1
$10^2 Cm$	mmol/ml	3.95	4.066	2.45	2.408	1.98	1.23
N		124.28	121.96	141.17	138.18	124.28	142.64
N_θ		1.024	1.006	1.042	1.013	1.024	1.053
C_{min}	Exp	-	-	-	-	151.6	
	Cal	-	-	-	-	137.0	
R_n	Exp	-	-	-	-	1.0305	
	Cal	-	-	-	-	1.0917	

Table 3.4.1-2 : Some illustrative examples of separation of mixture of aliphatic dicarboxylic acids on the column of resin Dowex 50W-X4 in aqueous medium.

Mixture	Vf ml	C meq	L cms	Rn_1 Exp	Rn_1 Cal	Rn_2 Exp	Rn_2 Cal	C_{min} meq	L_{min} cms
Malonic + Glutaric	10	160	57.8	0.73	0.69			293.2	105.9
Malonic + Adipic	10	160	57.8	1.25	1.23			115.0	41.5
Succinic + Adipic	5	160	57.8	1.03	1.09			137.0	49.5
Succinic + Pimelic	10	160	57.8	1.61	1.64			70.6	25.5
Glutaric + Pimelic	10	160	57.8	1.27	1.28			106.0	38.3
Glutaric + Adipic	10	160	57.8	0.54	0.57			416.7	150.6
Adipic + Pimelic	10	160	57.8	0.76	0.73			276.7	100.0
Adipic + Suberic	10	160	57.8	1.58	1.57			72.7	26.3
Pimelic + Suberic	10	160	57.8	0.88	0.89			199.5	72.1
Pimelic + Azelaic	25	160	57.8	1.63	1.64			70.2	25.4
Pimelic + Sebacic	25	160	57.8	2.55	2.55			32.6	11.8
Suberic + Sebacic	25	160	57.8	1.94	1.94			50.2	18.1
Azelaic + Sebacic	25	160	57.8	1.10	1.09			136.3	49.2
Malonic + Glutaric + Pimelic	5	160	57.8	0.84	0.80	1.38	1.39	236.4	85.4
Succinic + Adipic + Suberic	10	160	57.8	0.91	0.97	1.58	1.57	168.0	60.7
Glutaric + Pimelic + Azelaic	25	160	57.8	1.01	1.02	1.63	1.64	155.6	56.2
Adipic + Pimelic + Suberic	10	160	57.8	0.76	0.73	0.88	0.89	276.7	100.0

3.4.2 Strong Mineral Acids

Series of elution runs were carried out with strong mineral acids such as HCl, H_2SO_4, $HClO_4$ and H_3PO_4 on the column of resins X1, X2, X4, X8, X12, X16 and Amberlite-200. Table 3.4.2-1 gives the values of V_θ for acids studied with given resins.

Since these acids are completely ionized in solution, they should be excluded from the resin phase. Hence, the values of sorption coefficient B should be practically zero and V_θ in such cases should be equal to α_1. For the resins of crosslinking 4, 8, 12 and 16, the value of V_θ is practically zero indicating that α_1 is zero for strong electrolytes. However, with resins of crosslinking 1 and 2, α_1 is not zero but has a value of 0.10 for X1 and 0.05 for X2. This should imply that when a strong electrolyte solution is passed through a column of resins having low degree of crosslinking such as X1 and X2, the electrolyte is not completely excluded from the resin phase and hence the downward motion of the electrolyte is somewhat retarded relative to the downward motion of the solvent. This should be due to the relatively higher degree of swelling and hence more open structure of these resins. This is further supported by the runs of the strong electrolytes with a resin Amberlite-200. This is a macroreticular resin with considerably open structure and hence in this respect its behaviour should be similar to that of resins of low degree of crosslinking. It is observed that for this resin V_θ = 0.09 indicating that for

Table 3.4.2-1 : Experimental values of V_θ for strong mineral acids

Resin	Acid	Vf (ml)	Vd (ml)	Vb (ml)	L (cm)	W (meq)	C (meq)	Vm (ml)	$\bar{V}m$ (ml)	V_θ (ml/meq)
Dowex 50W-X1	HCl	5	6.5	146.0	60.5	0.50	80	76	11.10	0.107
Dowex 50W-X2	HCl	5	6.5	142.5	59.0	0.50	120	72	8.50	0.050
Dowex 50W-X4	HCl	5	6.5	139.4	57.8	0.50	160	65	2.75	0.017
	H_2SO_4	5	6.5	139.4	57.8	0.50	160	65	2.75	0.017
	$HClO_4$	5	6.5	139.4	57.8	0.50	160	65	2.75	0.017
	H_3PO_4	5	6.5	139.4	57.8	0.50	160	65	2.75	0.017
Dowex 50W-X8	HCl	5	6.5	140.0	58.0	0.53	279	65	2.50	0.000
Dowex 50W-X12	HCl	5	6.5	140.0	58.0	0.50	306	65	2.50	0.000
Dowex 50W-X16	HCl	5	6.5	140.0	58.0	0.51	289	65	2.50	0.000
Amberlite-200	HCl	10	6.5	137.5	57.0	1.25	234	87	25.50	0.088

this resin also α_1 is different from zero. From this study, one may conclude that separation of strong electrolytes on the basis of sorption-elution is very very difficult due to their poor and similar sorption.

3.4.3 Disubstituted Benzoic Acids

Preliminary studies of the column behaviour of some of these benzoic acids using water as solvent and eluent have shown that these acids emerge out of the column as asymmetric bands with a smeared leading front and a sharp trailing front indicating that some parts of the zone move faster than the other. This is due to the partial exclusion of these acids from the resin phase. Hence for the acids with lower pK values, the departure from the Gaussian distribution will be more. In separation studies this is not desirable as it leads to the overlapping and therefore to a smeared separation of adjacent bands. Further, the chromatographic equations become less valid and may give erroneous results if applied.

However, this problem has been overcome by using 0.01N aqueous hydrochloric acid (WH) as solvent and eluent. In this solvent the ion exclusion mechanism become less or inoperative and the elution curves become fairly symmetric. In consistence with this observation, the column elution runs of all the benzoic acids were carried out in 0.01N aqueous hydrochloric acid (WH) and/or 10% dioxan in 0.01N aqueous hydrochloric acid (DWH).

Series of elution runs were carried out with six disubstituted benzoic acids viz. 2,4-, 2,6- and 3,5-dihydroxy benzoic acids and corresponding three dimethoxybenzoic acids on the column of resin Dowex 50W-X4 (100-200) in hydrogen form to study the effect of load, feed volume

and column length using WH and DWH as solvent and eluent. The elution curves were fairly symmetrical under suitable conditions and could be described as Gaussian curves. However, even in acidic solvents, solutes with low sorption coefficient e.g. 2,6-dihydroxybenzoic acid, showed some trailing i.e. the bands with a diffuse trailing front. This may be due to the overloading of the column. Trailing becomes more apparent with longer columns.

Equations worked out for various parameters in the study of dicarboxylic acids are equally valid for these benzoic acids but for the parameter V_θ, where the third term being negligible, may be neglected giving the equation of V_θ as :

$$V_\theta = \alpha_1 + \alpha_2 B$$

Constants involved in the chromatographic equations for this study are summarized in Table 1 as follows :

Table : 1 Value of constants

Solvent	α_1	α_2	f_1	f_2
WH	0.250	1.0	1.0	0.71
DWH	0.115	1.0	1.48	1.03*
				0.84@

* for dihydroxybenzoic acids and benzoic acid

@ for dimethoxybenzoic acids

Below is given a set of revised equations worked out for various chromatographic quantities for elution study of disubstituted benzoic acids.

Peak Elution Volume

The peak elution volume, Vm , may be given by

$$Vm = Vd + 0.4\ Vb + 0.5\ Vf + C\ (\alpha_1 + \alpha_2 B)$$

where α_1 and α_2 are constants (Table 1) determined by the resin-solute-solvent system. The values of Vm are calculated according to above equation for disubstituted benzoic acids studied and these are compared with the experimental values of Vm obtained by carrying out the actual column elution runs of these acids. Some of them are given in Tables 3.3-17 to 3.3-19. The calculated and the experimental values of Vm are reported in Table 3.4.3-1.

Peak Width

The peak width, σ or β, can be expressed as :

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

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

where fs and αs are constants (Table 1) of which fs are determined by the particle size of the resin. Table 3.4.3-1 gives the calculated and the experimental values of σ, σ_θ and β for disubstituted benzoic acids from the several runs carried out. The experimental values of these quantities are obtained as shown in Section 3.4.1.6.

Peak Height

The peak height, Cm, can be expressed as :

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

Experimental Cm has been determined as shown earlier and the values thus obtained are compared (Table 3.4.3-1) with the values calculated according to above equation.

Number of Theoretical Plates

The number of theoretical plates, N, can be given by the following equations :

$$N_{cal} = \frac{0.5\ Vf + C\,(\alpha_1 + \alpha_2 B)}{\sqrt{C}\,(f_1\alpha_1 + f_2\alpha_2 B) + \frac{Vf}{6}}$$

$$N_{exp} = \left[\frac{\bar{V}_m}{\sigma}\right]^2$$

Both the calculated and experimental values of N are given in Table 3.4.3-1. Table 3.4.3-2 illustrates the applicability of above equations for different values of feed volume, feed concentration, bed volume or bed length and load.

Resolution

The extent of separation of the mixture of components is expressed in terms of resolution, Rn, as :

$$Rn_{cal} = \frac{C\,(V_{\theta_2} - V_{\theta_1})}{3\sqrt{C}\,(\sigma_{\theta_1} + \sigma_{\theta_2}) + Vf}$$

$$Rn_{exp} = \frac{Vm_2 - Vm_1}{3\,(\sigma_1 + \sigma_2)}$$

The resolution of some mixtures is not actually achieved as predicted by the Rn value calculated according to above equation. This is more frequent for the acids with lower pK values, e.g. 2,6-dihydroxybenzoic acid, where there is a departure from Gaussin distribution due to partial exclusion. Such acids exhibit trailing which leads to the overlapping of bands and hence deviation from expected Rn value is observed.

The minimum number of equivalents of the resin, C_{min}, required for the complete separation of acids under investigation can be expressed as following

$$1 = \frac{C_{min}\,(V_{\theta_2} - V_{\theta_1})}{3\sqrt{C_{min}}\,(\sigma_{\theta_1} + \sigma_{\theta_2}) + Vf}$$

The illustrative elution runs for the separation of some mixtures are summarized in Tables 3.3-19 and 3.3-20. In Table 3.4.3-3 are given some illustrative examples of such mixtures alongwith the predicted values of Rn, C_{min} and corresponding column length.

Table 3.4.3-4 gives requisite step-values of calculation for the column elution of 3,5-dihydroxybenzoic acid (Fig. 3.4.3-1), 2,4-dihydroxybenzoic acid (Fig. 3.4.3-2) and a mixture of 3,5- and 2,4-dihydroxybenzoic acids (Fig. 3.4.3-3).

Table 3.4.3-1 : Chromatographic parameters of elution runs for disubstituted benzoic acids on the column of resin Dowex 50W-X4

Benzoic acid = I ; C = 160 meq ; Vb = 139.4 ml ; Vd = 6.5 ml ; Vf = 25 ml

Acid	Solvent	$10^2 W$ mmol	Vm ml		$\bar{V}m$ ml		V_θ ml/meq		σ ml	**
			Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal
I	WH	0.42	570.0	566.0	507.7	503.7	3.10	3.07	31.8	32.63
	DWH	0.95	320.0	318.0	257.7	255.7	1.53	1.52	26.1	24.66
3,5-diOHI	WH	2.56	385.0	383.6	322.7	321.3	1.94	1.93	23.0	22.38
	DWH	1.43	227.5	222.0	165.2	159.7	0.95	0.92	17.1	16.69
2,4-diOHI	WH	6.21	710.0	698.8	647.7	636.5	3.97	3.90	42.7	40.09
	DWH	3.51	383.0	372.4	320.7	310.1	1.93	1.86	26.0	28.96
2,6-diOHI	WH	2.35	185.0	178.8	122.7	116.5	0.69	0.65	19.0	10.87
	DWH	3.04	105.0	124.4	42.7	62.1	0.19	0.31	17.0	8.85
3,5-diOMeI	DWH	0.65	965.0	946.8	902.7	884.5	5.56	5.45	65.0	62.99
2,4-diOMeI	DWH	1.48	667.5	654.0	605.2	591.7	3.70	3.62	42.5	43.51
2,6-diOMeI	DWH	1.77	310.0	302.0	247.7	239.7	1.47	1.42	20.0	20.10

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σ_θ ml/meq		β ml		10^4Cm mmol/ml		N		N_θ	
Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal
2.18	2.25	90.3	92.29	1.89	2.000	254.9	238.3	2.008	1.862
1.73	1.62	68.2	69.75	7.15	7.000	97.50	107.5	0.782	0.880
1.49	1.44	64.8	63.30	4.60	4.563	196.9	206.1	1.695	1.796
1.02	0.99	47.5	47.21	3.36	3.418	93.3	91.6	0.867	0.864
3.05	2.84	118.5	113.39	5.60	6.180	230.1	252.1	1.694	1.886
1.73	1.96	74.5	81.91	5.00	4.835	152.1	114.7	1.245	0.901
1.17	0.53	53.0	30.75	5.00	8.625	41.7	114.9	0.348	1.504
1.01	0.37	48.5	25.03	7.00	13.703	6.3	49.2	0.035	0.702
4.81	4.65	185.0	178.16	0.44	0.412	192.9	197.2	1.336	1.374
3.03	3.11	125.0	123.07	1.44	1.357	202.8	184.9	1.491	1.355
1.25	1.26	57.5	56.85	3.52	3.513	153.4	142.2	1.383	1.270

Table 3.4.3-2

Illustration of effects due to variation of feed volume, load, feed concentration and bed length.

Acid : 3,5-diOHI Resin : Dowex 50W-X4

Solvent : WH Vd : 6.5 ml

Vf ml	10^3W mmol	10^3fc	Vb ml	L cm	C meq	Vm ml Exp	Vm ml Cal **
10.0	10.0	1.00	139.4	57.8	160	374.3	376.06
12.5	12.5	1.00	139.4	57.8	160	379.8	377.31
15.0	15.0	1.00	139.4	57.8	160	376.6	378.56
17.5	17.5	1.00	139.4	57.8	160	379.0	379.81
20.0	20.0	1.00	139.4	57.8	160	382.1	381.06
22.5	22.5	1.00	139.4	57.8	160	384.9	382.31
25.0	25.0	1.00	139.4	57.8	160	385.0	383.56
25.0	3.0	0.12	139.4	57.8	160	385.0	383.56
25.0	6.0	0.24	139.4	57.8	160	385.0	383.56
25.0	9.0	0.36	139.4	57.8	160	385.0	383.56
25.0	12.0	0.48	139.4	57.8	160	385.0	383.56
25.0	15.0	0.60	139.4	57.8	160	385.0	383.56
25.0	18.0	0.72	139.4	57.8	160	385.0	383.56
25.0	21.0	0.84	139.4	57.8	160	385.0	383.56
25.0	24.0	0.96	139.4	57.8	160	385.0	383.56
10.0	20.0	2.00	139.4	57.8	160	374.3	376.06
12.5	20.0	1.60	139.4	57.8	160	379.8	377.31
15.0	20.0	1.33	139.4	57.8	160	376.6	378.56
17.5	20.0	1.14	139.4	57.8	160	379.0	379.81
20.0	20.0	1.00	139.4	57.8	160	382.1	381.06
22.5	20.0	0.88	139.4	57.8	160	384.9	382.31
25.0	20.0	0.80	139.4	57.8	160	385.0	383.56
25.0	25.0	1.00	34.9	14.5	40	112.0	110.16
25.0	25.0	1.00	69.7	28.9	80	205.0	201.28
25.0	25.0	1.00	104.6	43.4	120	296.8	292.44
25.0	25.0	1.00	174.3	72.3	200	470.0	474.72
25.0	25.0	1.00	209.1	86.7	240	587.2	577.84
25.0	25.0	1.00	244.0	101.2	280	672.0	657.00
25.0	25.0	1.00	278.8	115.6	320	765.0	748.12

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$\bar{V}m$ ml		V_θ ml/meq		σ ml		σ_θ ml/meq **	
Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal
312.0	313.80	1.92	1.93	20.0	19.88	1.45	1.44
317.5	315.05	1.95	1.93	20.4	20.30	1.45	1.44
314.3	316.30	1.92	1.93	20.6	20.72	1.43	1.44
316.7	317.55	1.92	1.93	21.0	21.13	1.43	1.44
319.8	318.80	1.92	1.93	21.8	21.55	1.46	1.44
322.6	320.05	1.95	1.93	22.1	21.97	1.45	1.44
322.7	321.30	1.94	1.93	23.0	22.38	1.49	1.44
322.7	321.30	1.94	1.93	23.0	22.38	1.49	1.44
322.7	321.30	1.94	1.93	23.0	22.38	1.49	1.44
322.7	321.30	1.94	1.93	23.0	22.38	1.49	1.44
322.7	321.30	1.94	1.93	23.0	22.38	1.49	1.44
322.7	321.30	1.94	1.93	23.0	22.38	1.49	1.44
322.7	321.30	1.94	1.93	23.0	22.38	1.49	1.44
322.7	321.30	1.94	1.93	23.0	22.38	1.49	1.44
322.7	321.30	1.94	1.93	23.0	22.38	1.49	1.44
312.0	313.80	1.92	1.93	20.0	19.88	1.45	1.44
317.5	315.05	1.95	1.93	20.4	20.30	1.45	1.44
314.3	316.30	1.92	1.93	20.6	20.72	1.43	1.44
316.7	317.55	1.92	1.93	21.0	21.13	1.43	1.44
319.8	318.80	1.92	1.93	21.8	21.55	1.46	1.44
322.6	320.05	1.95	1.93	22.1	21.97	1.45	1.44
322.7	321.30	1.94	1.93	23.0	22.38	1.49	1.44
91.5	89.70	1.98	1.93	13.2	13.27	1.43	1.44
170.6	166.90	1.98	1.93	17.5	17.05	1.49	1.44
248.5	244.10	1.97	1.93	20.0	19.94	1.45	1.44
393.8	398.50	1.91	1.93	24.8	24.53	1.46	1.44
497.1	487.70	2.02	1.93	27.0	26.43	1.47	1.44
567.9	552.90	1.98	1.93	28.7	28.26	1.47	1.44
647.0	630.10	1.98	1.93	30.4	29.93	1.47	1.44

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β ml		10^4Cm mmol/ml		N		N_θ	
Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal
56.8	56.23	2.00	2.01	243.4	249.2	1.75	1.80
57.7	57.42	2.40	2.46	242.2	240.9	1.81	1.80
58.0	58.60	2.85	2.89	232.8	233.0	1.80	1.80
59.1	59.76	3.20	3.30	227.4	225.9	1.80	1.80
61.5	60.95	3.50	3.70	215.2	218.8	1.77	1.80
63.0	62.14	4.00	4.09	213.1	212.2	1.81	1.80
64.8	63.30	4.51	4.46	196.9	206.1	1.70	1.80
64.8	63.30	0.46	0.53	196.9	206.1	1.70	1.80
64.8	63.30	0.99	1.07	196.9	206.1	1.70	1.80
64.8	63.30	1.60	1.60	196.9	206.1	1.70	1.80
64.8	63.30	2.07	2.13	196.9	206.1	1.70	1.80
64.8	63.30	2.57	2.67	196.9	206.1	1.70	1.80
64.8	63.30	3.30	3.21	196.9	206.1	1.70	1.80
64.8	63.30	3.65	3.74	196.9	206.1	1.70	1.80
64.8	63.30	4.18	4.28	196.9	206.1	1.70	1.80
56.8	56.23	3.95	4.01	243.4	249.2	1.75	1.80
57.7	57.42	4.00	3.93	242.2	240.9	1.81	1.80
58.0	58.60	3.85	3.85	232.8	233.0	1.80	1.80
59.1	59.76	3.80	3.78	227.4	225.9	1.80	1.80
61.5	60.95	3.64	3.70	215.2	218.8	1.77	1.80
63.0	62.14	3.60	3.63	213.1	212.2	1.81	1.80
64.8	63.30	3.55	3.57	196.9	206.1	1.70	1.80
37.0	37.53	7.50	7.52	48.1	45.7	1.92	1.80
50.0	48.22	5.84	5.85	95.0	95.8	1.77	1.80
56.4	56.40	5.00	5.00	154.4	149.9	1.85	1.80
70.0	69.38	4.10	4.07	252.1	263.9	1.71	1.80
76.2	74.90	3.72	3.77	339.0	339.2	1.89	1.80
81.2	79.93	3.58	3.53	391.5	382.8	1.81	1.80
86.0	84.65	3.40	3.33	453.0	443.2	1.81	1.80

Table 3.4.3-3 : Some illustrative examples of separation of mixture of disubstituted benzoic acids on the column of resin Dowex 50W-X4.

Vf = 25 ml ; C = 160 meq ; L = 57.8 cm ; I = Benzoic acid

Mixture	Solvent	Rn_1		Rn_2		C_{min} meq	L_{min} cm
		Exp	Cal	Exp	Cal		
2,6-diOHI + 3,5-diOHI	WH	1.59	2.05			53.2	19.2
2,6-diOHI + 2,4-diOHI	WH	2.83	3.54			21.4	7.7
3,5-diOHI + 2,4-diOHI	WH	1.65	1.68			65.4	23.6
2,6-diOHI + 2,4-diOHI	DWH	2.16	2.19			47.1	17.0
3,5-diOHI + 2,4-diOHI	DWH	1.21	1.10			136.7	49.4
2,6-diOHI + 3,5-diOHI	DWH	1.19	1.27			111.7	40.4
2,6-diOMeI + 2,4-diOMeI	DWH	1.91	1.84			55.9	20.2
2,6-diOMeI + 3,5-diOMeI	DWH	2.57	2.59			30.5	11.0
2,4-diOMeI + 3,5-diOMeI	DWH	0.92	0.92			188.2	68.0
2,6-diOHI + 2,6-diOMeI	DWH	1.85	2.04			55.3	20.0
3,5-diOHI + 2,4-diOMeI	DWH	2.46	2.39			37.0	13.4
2,6-diOMeI + 2,4-diOHI	DWH	0.53	0.48			590.2	213.2
3,5-diOHI + 3,5-diOMeI	DWH	3.00	3.03			23.7	8.6
2,6-diOHI + 3,5-diOHI + 2,4-diOHI	WH	1.59	2.05	1.65	1.68	65.4	23.6
2,6-diOMeI + 2,4-diOMeI + 3,5-diOMeI	DWH	1.91	1.84	0.92	0.92	188.2	68.0
3,5-diOHI + 2,4-diOMeI + 3,5-diOmeI	DWH	2.46	2.39	0.92	0.92	188.2	68.0
2,6-diOHI + 3,5-diOHI + 2,4-diOMeI	DWH	1.19	1.27	2.46	2.39	111.7	40.4

Fig. 3.4.3-1 : Plot of W_s versus sample number for the column elution of 3,5-dihydroxybenzoic acid on the column of resin Dowex 50W-X4 (100-200) using 0.01N aqueous hydrochloric acid as solvent and eluent.

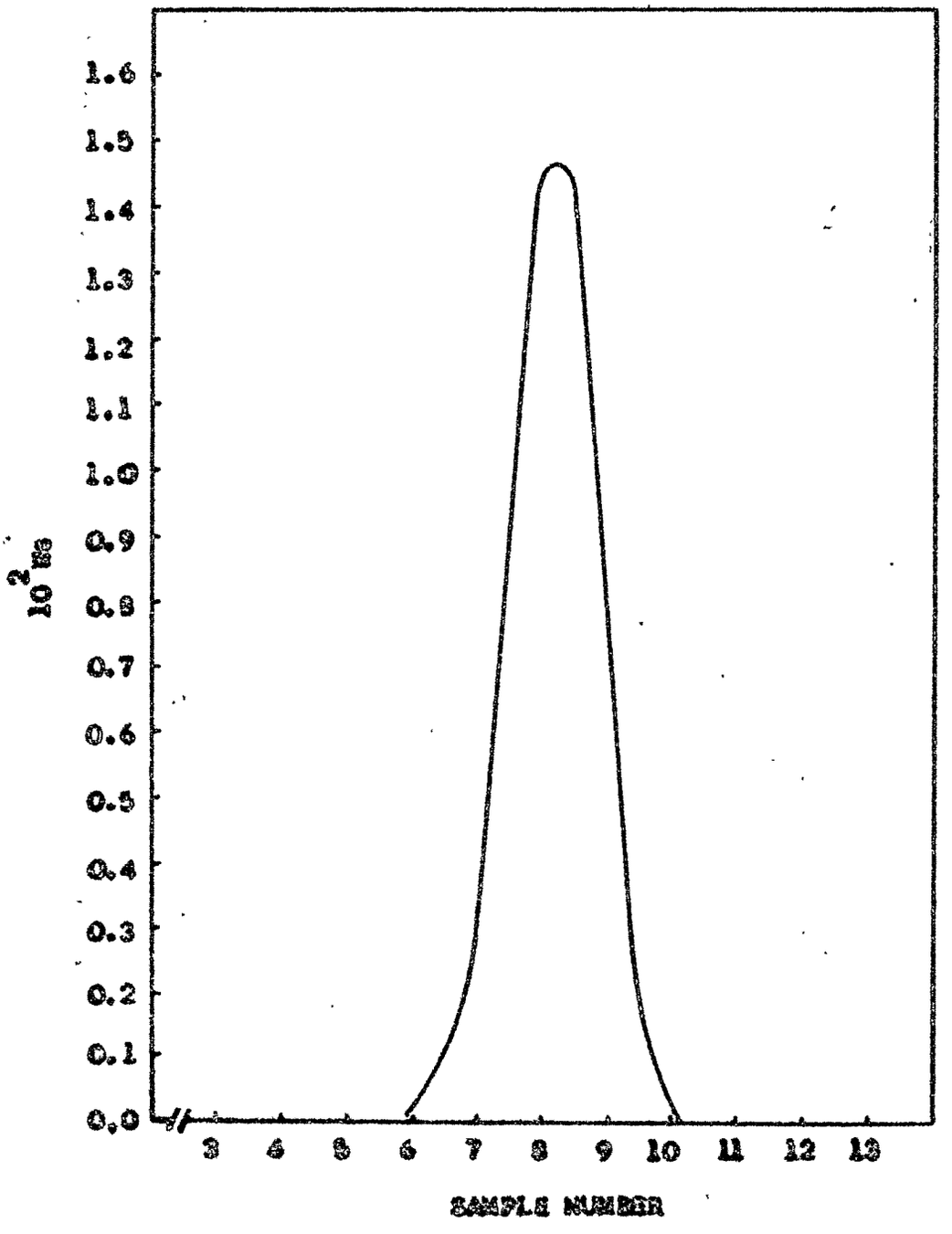


Fig. 3.4.3-2 : Plot of Ws versus sample number for the column elution of 2,4-dihydroxybenzoic acid on the column of resin Dowex 50W-X4 (100-200) using 0.01N aqueous hydrochloric acid as solvent and eluent.

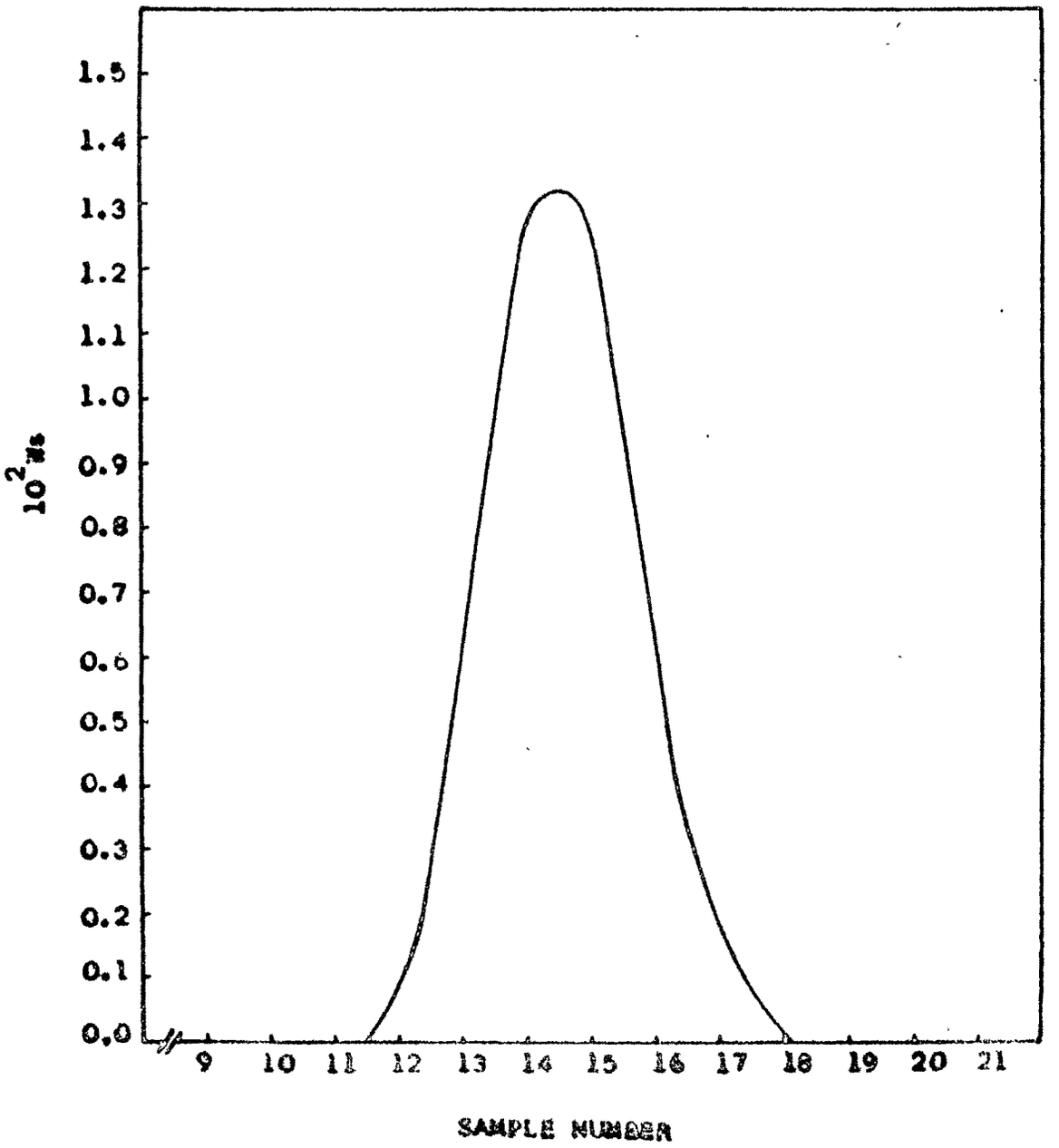


Fig. 3.4.3-3 : Plot of Ws versus sample number for the column elution run of the mixture of (A) 3,5-dihydroxybenzoic acid and (B) 2,4-dihydroxybenzoic acid on the column of resin Dowex 50W-X4 (100-200) using 0.01N aqueous hydrochloric acid as solvent and eluent.

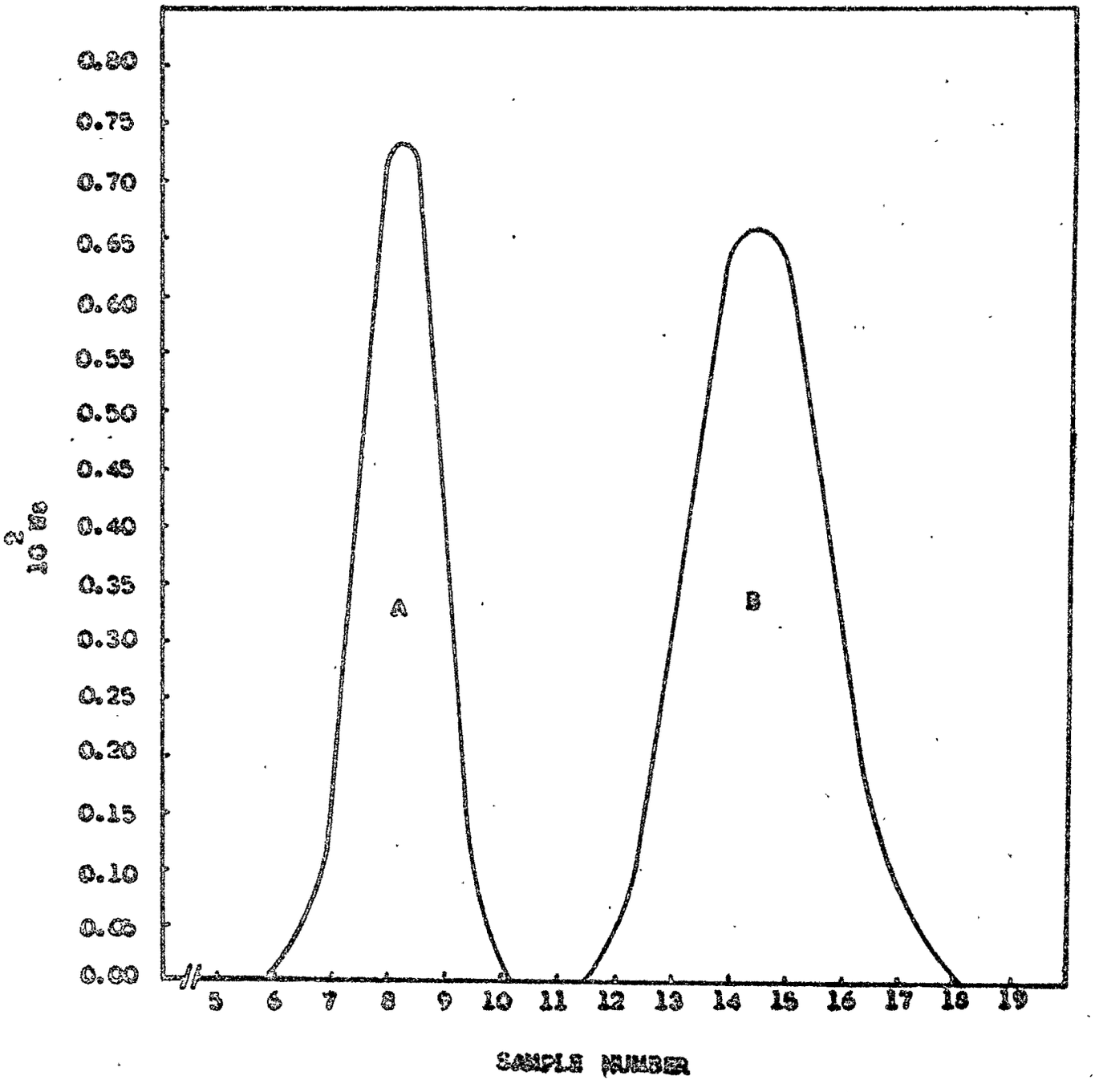


Table 3.4.3-4 : Step-values for the resolution of mixture of 3,5-dihydroxy and 2,4-dihydroxybenzoic acids on the column of resin Dowex 50W-X4 with 0.01N aqueous hydrochloric acid as solvent and eluent.

Vd = 6.5 ml ; Vf = 25 ml ; Vs = 25 ml ; Vb = 69.7 ml ; C = 80 meq ; L = 28.9 ml

Parameter		3,5-diOHI		2,4-diOHI		3,5-diOHI + 2,4-diOHI	
		Exp	Cal	Exp	Cal	Exp	
B	ml/meq	1.68	-	3.65	-	1.68	3.65
10^2W	mmol	2.50	-	4.00	-	1.25	2.00
Vm	ml	205.0	201.3	362.5	358.9	205.0	362.5
$\bar{V}m$	ml	170.6	166.9	328.1	324.5	170.6	328.1
V_θ	ml/meq	1.98	1.93	3.95	3.90	1.98	3.95
σ	ml	17.50	17.05	30.00	29.57	17.50	30.00
σ_θ	ml/meq	1.49	1.44	2.89	2.84	1.49	2.89
β	ml	50.00	48.22	85.00	83.64	50.00	85.00
10^4Cm	mmol/ml	5.84	5.85	5.28	5.40	2.92	2.64
N		95.00	95.80	119.6	120.4	95.00	119.6
N_θ		1.766	1.796	1.868	1.886	1.766	1.868
C_{min}	Exp	-	-	-	-	67.50	
	Cal	-	-	-	-	65.40	
R_n	Exp	-	-	-	-	1.106	
	Cal	-	-	-	-	1.127	

3.4.4 Geometrical Isomeric Acids

The elution runs were carried out with the column of resin Dowex 50W-X4 (100/200) for crotonic and maleic acids in aqueous medium. The value of V_θ obtained for crotonic acid is 0.47 which is the same as that of propionic acid (from colleague's work). Further, the values of V_θ for maleic and malonic acids are comparable. These observations support the earlier conclusion (Section 2.4.3) that the contribution of Vinyl (-CH=CH-) and methylene ($-CH_2-$) groups to the sorption are practically same, provided the rest of the molecular structure remains unchanged.

The separation of maleic and fumaric acids had been tried earlier (300), where a relatively longer column (210 cm) was used with a resin X4 of 50/100 mesh. The objective here was to improve upon the conditions of separation than those given earlier. In this study the same resin of 100/200 mesh is used with a more convenient column length (57.8 cm) to obtain the complete separation.

Number of runs were carried out for maleic and fumaric acids using water and aqueous hydrochloric acid of different concentrations as solvents and eluents. Tables 3.4.4-1 and 3.4.4-2 show such illustrative runs. Table 3.4.4-3 summarizes the values of V_θ for these runs. It is observed that fronting is more in the case of fumaric acid than maleic acid in aqueous medium, which is not

desirable for separation purpose. However, the fronting reduces to considerable extent in acidic medium. The another advantage of the acidic medium is that, with increase in pH of the solution, the V_θ values of fumaric acid decrease while those of maleic acid remain practically unchanged. This facilitates the process of separation. The different behaviour of these two acids in acidic medium may be attributed to the fact that the pK values of maleic and fumaric acids are comparable but a vast difference is there in their solubilities in water (Table 1.3-1). In acidic medium, the common ion effect causes the decrease in ionization as well as solubility of both the acids. The fumaric acid being very less soluble, suffers more due to this effect and favours resin phase. This increases the sorption and the resulting V_θ values decrease with increase in pH of the solution. On the other hand maleic acid being very highly soluble (about hundred times the solubility of fumaric acid), is affected to a much lesser extent or remains almost unchanged due to this effect, which causes no change in sorption and V_θ values.

It is observed that the quantitative separation of mixture of maleic and fumaric acids could be achieved using N/100 aqueous hydrochloric acid as solvent and eluent. The results are reported in Table 3.4.4-3 and shown in Fig. 3.4.4-1.

Table 3.4.4-1 : Elution runs of Maleic acid on the column of resin Dowex 50W-X4 in different solvents.

Sample No	Solvent	Water	N/1000 HCl	N/200 HCl	N/100 HCl	N/10 HCl	N/5 HCl
	10^2W	50	100	100	100	100	100
					10^2Ws		
1-15		-	-	-	-	-	-
16		0.33	-	-	-	-	-
17		0.71	0.85	-	1.47	-	-
18		2.86	5.22	1.96	2.45	2.77	1.47
19		8.57	16.39	10.29	12.25	15.34	8.33
20		17.86	29.26	25.48	29.40	27.91	24.00
21		16.67	29.50	29.89	33.81	28.97	31.36
22		4.29	14.33	21.07	21.07	18.54	23.52
23		0.48	2.06	5.39	4.90	4.90	6.86
24		-	0.61	0.98	1.96	1.07	1.47
25		-	0.24	0.45	1.47	0.45	-
26		-	-	-	-	-	-

Table 3.4.4-2 : Elution runs of Fumaric acid on the column of resin Dowex 50W-X4 in different solvents.

Sample No.	Solvent 10^2W	Water 55	N/1000 HCl 110	N/200 HCl 110	N/100 HCl 110	N/10 HCl 110	N/5 HCl 110
				10^2Ws			
1-17		-	-	-	-	-	-
18		0.33	-	-	-	-	-
19		0.47	-	-	-	-	-
20		0.71	-	-	-	-	-
21		0.81	-	-	-	-	-
22		1.19	-	-	-	-	-
23		1.67	1.43	-	-	-	-
24		2.62	3.10	0.98	-	-	-
25		3.05	6.67	2.50	-	-	-
26		7.14	13.10	6.67	4.45	1.65	1.44
27		11.19	23.10	16.93	13.36	6.55	4.30
28		15.48	29.52	24.40	25.05	16.67	14.41
29		11.43	25.48	24.89	29.51	24.50	25.22
30		1.90	11.67	19.40	23.39	23.85	25.94
31		0.48	1.67	9.47	11.14	17.31	19.82
32		-	0.24	3.00	3.90	10.13	12.61
33		-	-	0.50	0.57	4.90	5.76
34		-	-	-	-	1.65	1.08
35		-	-	-	-	-	-

Table 3.4.4-3 : Experimental values of V_θ for column elution of geometrical isomeric acids with the resin Dowex 50W-X4.

C = 160 meq ; Vd = 6.5 ml ; Vb = 139.4 ml ; Vs = 5 ml.

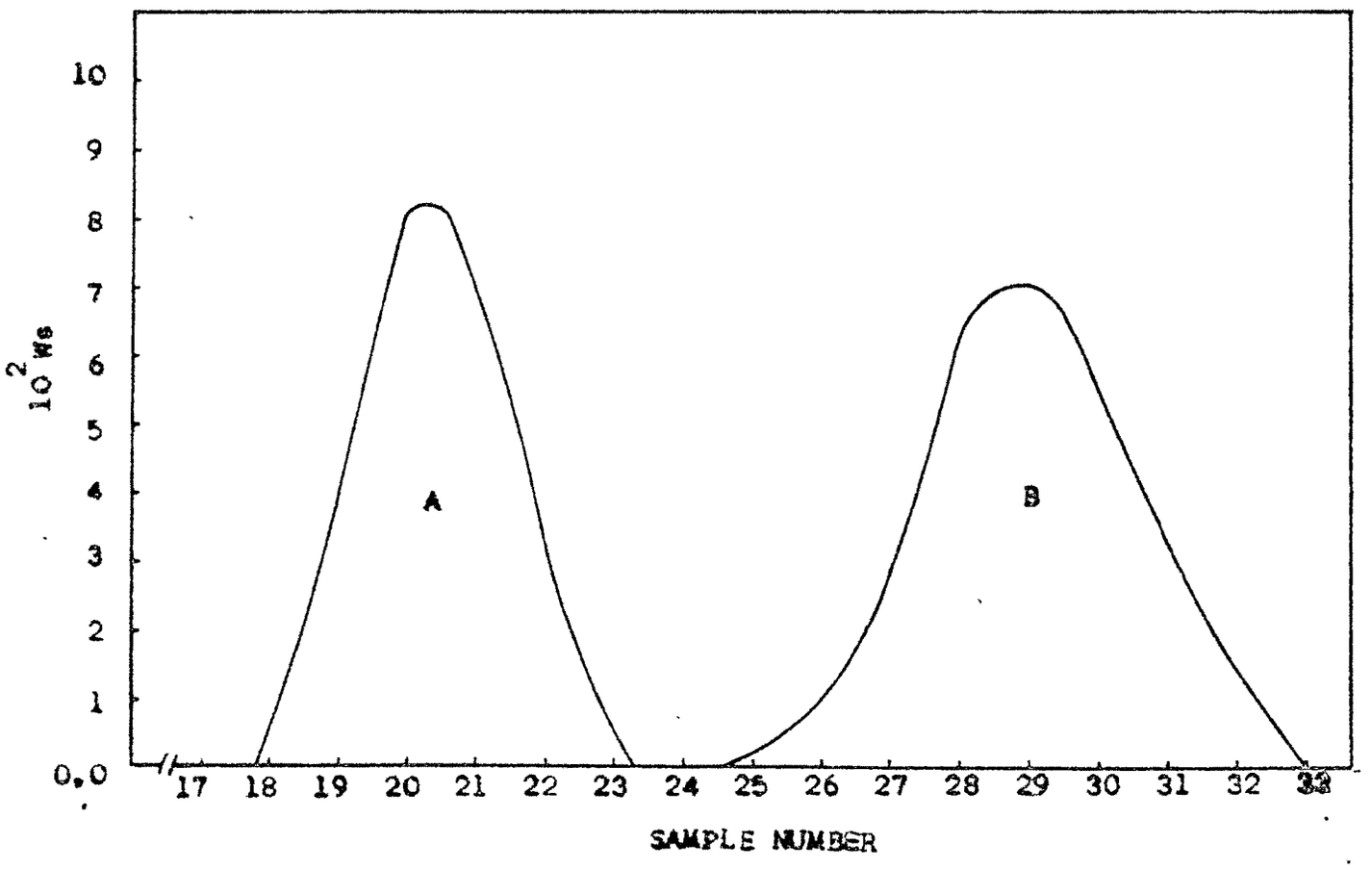
Solvent	Vf ml	Maleic				Fumaric				Crotonic			
		Vm ml	$\bar{V}m$ ml	V_θ ml/meq	σ ml	Vm ml	$\bar{V}m$ ml	V_θ ml/meq	σ ml	Vm ml	$\bar{V}m$ ml	V_θ ml/meq	σ ml
Water	5	104.5	42.2	0.233	6.50	143.0	80.7	0.473	beards	142.5	80.20	0.47	Trails
N/5 HCl	10	105.0	42.7	0.236	6.50	148.0	85.7	0.504	8.75	-	-	-	-
N/10 HCl	10	103.0	40.7	0.223	6.50	147.5	85.2	0.501	8.50	-	-	-	-
N/100 HCl	10	104.0	41.7	0.229	6.50	144.0	81.7	0.479	7.50	-	-	-	-
N/200 HCl	10	104.5	42.2	0.233	6.50	143.0	80.7	0.473	9.12	-	-	-	-
N/1000 HCl	10	103.0	40.7	0.223	6.25	141.0	78.7	0.461	7.50	-	-	-	-

Table 3.4.4-4 : Elution run of mixture of Maleic acid and Fumaric acid on the colum of resin Dowex 50W-X4 using N/100 HCl as solvent and eluent.

Vf = 10 ml ; Vs = 5 ml

Sample No.	Acids	Maleic	+	Fumaric
	10^2W	50		55
			10^2Ws	
1-17		-		-
18		0.94		-
19		7.52		-
20		16.00		-
21		14.10		-
22		6.60		-
23		0.94		-
24		-		-
25		-		1.00
26		-		1.90
27		-		5.64
28		-		12.22
29		-		14.10
30		-		11.28
31		-		6.60
32		-		2.82
33		-		-

Fig. 3.4.4-1 : Plot of Ws versus sample number for column elution of the mixture of (A) Maleic acid and (B) Fumaric acid on the column of resin Dowex 50W-X4 (100-200) using N/100 aqueous hydrochloric acid as solvent and eluent.



3.5 CONCLUSIONS

Some of the essential conclusions drawn from the study of sorption-elution behaviour of acids studied are as follows:

(1) Feed volume affects elution volume. The larger feed volume results in an increase in the peak elution volume and hence wastes time and eluent. The calculated value of Vm which includes feed volume supports this.

(2) Feed volume also affects the column efficiency. This is evident from the dependence of σ on the feed volume. If the feed volume is larger, there will be appreciable band spreading and the deviation of the peak shape from Gaussian increases. Thus, for acids having lower solubility (or higher B values) in given solvent, the elution curves get flattened and the observed σ values are higher than those calculated on the basis of Gaussian distribution. This effect is distinguished in the case of benzoic acids and the higher members of the homologous series of dicarboxylic acids where the feed volume and the volume of the fractions collected are both relatively higher, in consistence with the solubility of the acids and the detectability of the components in the effluent. However, it should be possible to decrease the value of σ or to increase the column efficiency by taking smaller feed volume.

(3) Increase in length (L) and hence C would seem to provide a solution to any separation problem. This is true

within some practical limits. If the column is too long, the flow rate will be very low and the process becomes time consuming. It may also happen that the zones, when separated, will be so dilute as to be undetectable.

(4) In liquid chromatogaaphy where the kinetics of sorption are controlled by particle diffusion, the 'theoretical plate height' is not a characteristic of the column alone, but depends also on the partition coefficients and on the diffusion coefficients of the substances to be separated. Therefore, we must expect different theoretical plate heights and numbers for almost every substance. Calculations have shown that the trend is as expected. The observed difference between N_{exp} and N_{cal} may be attributed to the fact that the square terms are involved and hence the experimental error gets magnified.

(5) The separation of the members of the homologous series can be achieved under suitable conditions. In the series of aliphatic dicarboxylic acids, the separation of alternate members is easier than the separation of adjacent members. In the later, elution curves overlap to some extent which can be overcome by decreasing the feed volume or by increasing the column length to improve the separation.

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

(7) The separation of molecules that differ in the nature of functional groups would be easier, e.g. separation of dihydroxybenzoic acid and dimethoxybenzoic acid.

(8) The separation of the position isomers of the disubstituted benzoic acids is possible. In general, sterically hindered isomers can be separated from other isomers in which the steric effect is lesser or negligible, e.g. separation of 2,6-dihydroxybenzoic (γ-resorcylic), 3,5-dihydroxybenzoic (α-resorcylic) and 2,4-dihydroxybenzoic (β-resorcylic) acids.

(9) A mixture of maleic and fumaric acid can not be completely separated in aqueous medium. However, a quantitative separation could be achieved using N/100 aqueous hydrochloric acid as solvent and eluent on a column of convenient length with resin Dowex 50W-X4 of 100/200 mesh.

(10) Quantitative separation could be easily achieved for any mixture whose difference of B values of components under isolation is substantial. However, by varying conditions, resolution for any mixture can be improved.

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

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

can be further improved by employing the smaller particle size of the same resin. However, with decreasing particle size, pressure drop increases and hence flow rate decreases. One may overcome this by using high pressure technique.

Thus the study provides a simple, convenient and useful technique for the separation of aliphatic as well as aromatic acids and in general, should be applicable to the separation of other similar families.