4. SORPTION OF WEAK AND NONELECTROLYTES

4.1. Introduction :

4.1 a Sorption of nonelectrolytes :

A quantitative theory for nonelectrolyte sorption on ion exchangers has not yet been developed. However, general rules have emerged, which may explain qualitatively in terms of physical forces and interactions and, with due caution, qualitative prediction of sorption equilibria can be made.

In the absence of interactions of any kind, the molal distribution coefficient should be unity ; actually, it is rarely so and the various interactions which cause deviations from ideality are discussed in the following. Ionic solvation and salting out : The fixed ionic groups and the counter ions in the ion exchanger form solvation shells and hence, only a fraction of the total internal solvent is free, in which the nonelectrolyte is dissolved. Hence, in the absence of any other interactions, the nonelectrolyte concentration in the free water in the ion exchanger should be same as the nonelectrolyte concentration in the external solution. Thus the molality of the nonelectrolyte in the ion exchanger, which refers to the total solvent in the ion exchanger is less than that in the external solution. The nonelectrolyte is then " salted out ".

" Salting out " effects should be more pronounced when the fraction of solvent in the ion exchanger, which is free, is smaller. This is the case when the resin is highly

crosslinked and the counter ions are strongly solvated. Hence, with salting out as predominant effect, the molal distribution coefficient decreases with increasing degree of crosslinking and increasing solvation number of the counter ion.

If salting out effect is the predominent effect sorption of the nonelectrolyte solute can be increased by adding a electrolyte to the external solution. Addition of electrolyte results is salting out in the solution also and thus counteracts salting out in the ion exchanger.

Interactions with counter ions, salting in and complex formation : In certain systems, exactly the opposite of salting out is observed. The mechanism, which is responsible for such " salting in " effects is not yet quite clear. Analogous effects are observed with ion exchange resins.

Interactions between nonelectrolyte and the counter ions become more pronounced when inorganic counter ions are replaced by organic ions. The most striking effects are noted when the solute forms complexes with counter ions.

London and dipole interactions : Sorption of organic non-electrolytes with hydrocarbon groups by ion exchange resins with hydrocarbon matrices is likely to be affected by two kinds of interactions. First, sorption is favoured by London interactions between the solute and the matrix. These forces are rather weak. A second and stronger contribution may come from dipole-dipole interactions

of the polar solvent molecules with one another and with polar groups of the solute. The result of such interactions is that the hydrocarbon groups tend to coagulate or to be squeezed out of the polar solvent into a phase boundry. Both the London and the dipole interactions favour local adsorption of the hydrocarbon groups of the solute on the matrix and thus enhance the sorption of the nonelectrolyte. Both interactions are more pronounced when the hydrocarbon group of the solute is larger (provided that the polar group remains the same). Hence, in a homologous series, the distribution coefficient usually increases with increasing molecular weight of the solute, at least as long as sorption is not limited by molecular size effects.

London forces are specific interactions and depend on the molecular structure of the solute and the matrix. Different types of resins may widely differ in their sorption behaviour. Strong sorption may be expected when the chemical cofigurations of the solute and the matrix are similar. Large molecules with very strong affinity may even be sorbed irreversibly.

Molecular size, swelling pressure and sieve action : The molecular size of the solute, in combination with the crosslinking of the resin, may considerably influence the sorption of the nonelectrolyte. The interior of the swollen resin is under rather high swelling pressure, which tends to squeeze the solvent and solute molecules out of the resin. Larger molecules are more strongly affected. This may be

expressed by the equation,

$$\Pi v_N = - RT \ln \frac{\bar{a}_N}{a_N} \qquad (4.01)$$

A given swelling pressure Π reduced the internal activity $\bar{a}_N$ of a species N more strongly, if the partial molar volume v_N of the species is large. The equilibrium swelling pressure, in turn, is high if the resin is highly crosslinked. With resins of moderate crosslinking and smaller nonelectrolyte molecules, this swelling pressure effect is rather small and is often overshadowed by other interactions which favour sorption of larger molecules. However, with increasing size of the solute molecule or increasing degree of crosslinking, the effect becomes more important. The distribution coefficient in a homologous series may then have maximum value at medium molecular size.

Sorption of larger molecule is further restricted by the purely mechanical sieve action of the matirx. Molecules, which are too large for passing through the meshes of the matrix are excluded by the resin.

Of course, sieve action does not impose a sharp limit on the molecular size of the solute, since the mesh width of the matrix is not uniform. Swelling pressure and sieve effects are, hence, difficult to distinguish. Also, the sorption rate becomes very low, when the molecular size of the solute approaches the critical range. Hence, uptake of large molecules under ordinary experimental conditions may be low, because sorption equilibrium, no matter how favourable, is not attained.

Dependence on solution concentration : The uptake of the solute by the resin increases with increase in the concentration of the solution. The sorption isotherm usually has a negative curvature. This is particularly true for solutes which are strongly sorbed even from dilute solutions. Here, the saturation of the resin is fairly complete at relatively low solution concentrations, so that the isotherm flattens out after an initial steep rise. However, in a number of cases,isotherms with positive curvature are observed. Usually, a Langmuir or Freundlich isotherm can be fitted reasonably to the experimental results.

Dependence on temperatures and pressure : The effect of temperature on sorption equilibria is complex and has not yet been studied systematically. Not only the heat of the actual sorption process is involved, but also the temperature dependence of swelling, solvation and in some cases, of the dissociation of ion pairs or complexes in the resin. Usually the temperature dependence of sorption is small. In cases of strong specific sorption, the temperature coefficient is likely to be negative.

The effect of pressure on sorption of solutes has so far received little attention. However, one may expect that the pressure dependance is insignificant, since sorption usually occurs without much change in the volume of the total system.

4.1b Sorption of weak electrolytes :

Weak electrolytes are little affected by Donnan exclusion and thus are sorbed in essentially the same way as nonelectrolytes. The dissociation of weak electrolytes and hence, their uptake by ion exchangers depends on the pH of the solution. The pH dependence can be used for elution. Weak electrolytes can also be sorbed, without simultaneous ion exchange, by resins containing multivalent counter ions.

4.2 The ultraviolet absorption spectrum of phenylacetic acid in aqueous solution.

4.2.a Introduction :

From the survey of the available literature it appears that there is no detailed study reported on the ultraviolet absorption spectrum of phenylacetic acid and the effect of monocarboxylic aliphatic acids on it. Hence it was,considered to be of interest to study the ultraviolet absorption spectrum of phenylacetic acid in aqueous solution, with a view to assess the applicability of this method in the estimation of phenylacetic acid in binary mixtures of phenylacetic acid and other simple aliphatic monocarboxylic acids.

4.2.b Experimental :

Chemicals : The chemicals used were of A.R. or C.P.quality.

Procedure : The stock solution of phenylacetic acid was first prepared in distilled water and the concentration in gram equivalents per liter was evaluated by titration with standard sodium hydroxide solution. The stock solution was then suitably diluted with distilled water for ultraviolet absorption spectrum. The ultraviolet absorption spectrum was studied with Beckman Model DU Spectrophotometer using 10 mm. quartz cells in the range 240-290 mμ. The values of extinction coefficient, ϵ were calculated by dividing the observed optical density, D, by the concentration of phenylacetic acid in gram equivalents per liter.

4.2.c Results :

Table (4.2.1) and figure (4.2.1) give the ultraviolet absorption spectrum of phenylacetic acid in aqueous solution.

Table (4.2.2) gives the data for ultraviolet absorption spectrum of benzene (in ethyl alcohol) from (1) and phenylacetic acid in aqueous solution from the present work.

Fig. 4.2.1 Ultraviolet absorption spectrum of phenylacetic acid in water.

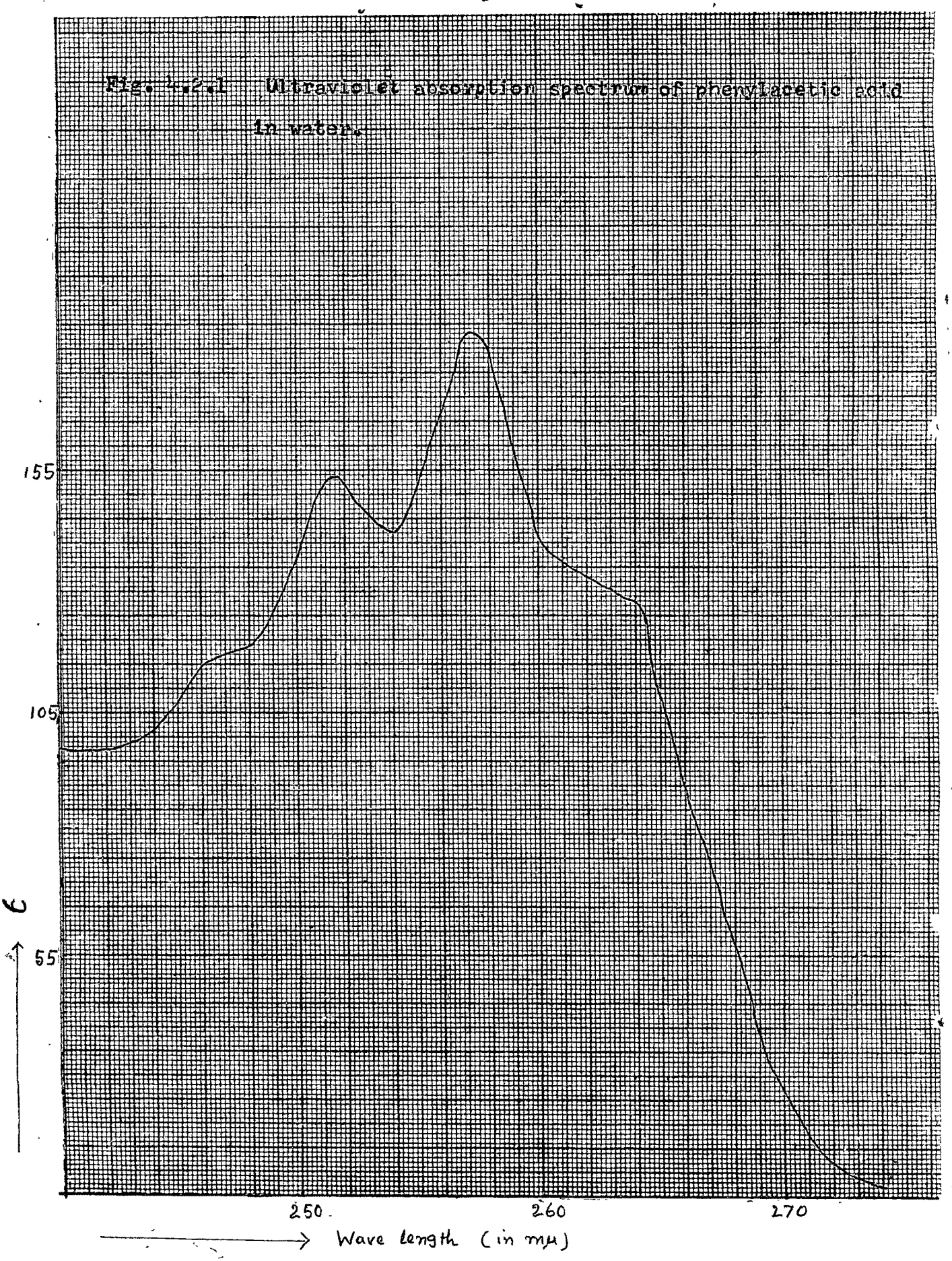


Table 4.2.1

Ultraviolet absorption spectrum of phenylacetic acid in aqueous solution

Wave length (mμ)	ϵ	Wave length (mμ)	ϵ
240	99.7	264	128.1
242	97.43	265	107.6
244	101.6	266	88.98
246	115.3	267	76.47
248	118.6	268	59.05
250	138.4	269	42.04
251	151.1	270	27.63
251.5	153.9	271	20.02
252	152.5	272	12.41
253	146.3	273	9.208
254	142.7	274	7.006
255	153.9	275	5.564
256	169.4	276	4.704
257	183.5	277	4.243
257.5	183.0	278	4.004
258	177.4	280	3.703
259	158.1	285	2.763
260	139.8	290	1.901

4.2.d Discussion :

The ultraviolet absorption spectrum of phenylacetic acid has four maxima at λ = 246-48, 251.5, 257 and 260-64 mμ. The first and last maxima (246-48 mμ and 260-64 mμ) are relatively less well defined than other maxima at 251.5 and 257 mμ. The data for phenylacetic acid in aqueous solution and the data from (1) for benzene in ethyl alcohol are given in table (4.2.2). The maxima marked, ± are less well defined for benzene in ethyl alcohol but are better resolved at low temperature. For all the maxima for phenylacetic acid in aqueous solution the wave length seems to be essentially same as for benzene (in ethyl alcohol). The resolution of first maxima at 246-48 mμ and last maxima at 260-64 mμ is better for benzene and the resolution at the maxima 251.5 mμ and 257, for phenylacetic acid. This may be due to the substitution in benzene ring and / or the solvent effect and presumably the absorption is due to the benzene nucleus.

Effect of simple aliphatic monocarboxylic acids :

In this study, it was observed that the presence of simple aliphatic monocarboxylic acids (acetic acid, isobutyric acid, propionic acid, n-butyric acid, n-valeric acid, n-caproic acid, and isovaleric acid) have practically no effect on ultraviolet absorption of phenylacetic acid at λ max. = 257 mμ. Hence, in latter study, in binary mixtures of phenylacetic acid with the above acids,

Table 4.2.2

Values of λmax. and ϵ obtained from figure 4.2.1

Benzene (in ethyl alcohol) from (1)	Phenylacetic acid (in water) from the present work	
λmax.	λmax.	ϵ
238.7	-	-
242.8	-	-
248.4	246-48	115-118.6
÷ 251.4	251.5	153.9
254.1	-	-
÷ 257.6	257	183.5
260.4	260-64	140-128
÷ 263.9	-	-
÷ 267.9	-	-

phenylacetic acid was estimated by ultraviolet absorption at 257 mμ and the total acids were estimated by titration with standard sodium hydroxide solution. Thus the composition of binary mixtures could be estimated.

4.3 Sorption of monocarboxylic acids of $R\text{-}CH_2COOH$ type in aqueous medium

4.3.1 Sorption equilibrium studies :

4.3.1.a Introduction :

The sorption of weak organic acids and phenols on hydroxylic, carboxylic and sulfonic acid cation exchange resins in the hydrogen form had been studied earlier (2). The sorption isotherms were studied for each class of substances with the different resins. The results indicated the similarities and differences when the ionogenic groups vary. Since no sorption was observed on polystyrene, styrene-divinylbenzene copolymer and polyethylene, the molecular sorption could not be a property of the hydrocarbon matrix alone and should be related to the ionogenic groups present. Next (3), the column study of phenyl sorption-desorption on these resins had been summarised. Meanwhile several (4-21) significant investigations in this field have been published.

In this section, the study of the effect of the relative degree of crosslinking of the resin on the sorption of monocarboxylic acids of the $R-CH_2COOH$ type on sulfonic acid cation exchange resins is described.

4.3.1.b Experimental :

Resins : Resins used were sulfonated styrene-divinylbenzene copolymer type sulfonic acid Dowex 50 W cation exchange resins (Dow Chemical Co) of -100, + 200 mesh, with X suffixes of 4,8 and 12 respectively (X denotes the per cent of combined divinylbenzene in the styrene copolymer used as the resin matrix for preparing the sulfonate).

These are further referred to as resins X4, X8 and X12.

Moisture and capacity of the resins :

The resins were washed, cycled between sodium chloride and hydrochloric acid, regenerated with a large excess of hydrochloric acid, washed free of acid, filtered air dried and stored in well stoppered containers.

Moisture contentwas determined by heating weighed samples (ᔕ 0.5 gms.) of air dry resin in clean, dry weighing bottles, in an oven (ᔕ 100-103 ^{o}C) to a constant weight and % moisture content was then calculated.

For the estimation of capacity of the resins, weighed samples (ᔕ 0.5 gms.) of air dry resins were contacted with 50 cc. of 1 N barium chloride solution in well stoppered flasks with frequent shaking. Next day, the liberated acid was estimated by titration with standard sodium hydroxide solution, and the capacity was then calculated. Preliminary work had indicated that increase in contact time did not increase the amount of acid liberated. Table (4.3.1.1) gives the obtained values of % moisture content and the capacity of the different resins.

Chemicals : All chemicals used were of A.R. or C.P.grade and the solutions were prepared in distilled water.

Procedure : Acid solutions of known volumes and concentration were placed in contact with weighed amounts of air dry resins in well stoppered flasks, with frequent shaking, at room temperature (ᔕ 30 ^{o}C) for 24 hours. Then the equilibrium concentration was estimated by titrating aliquots

with standard sodium hydroxide solution. Preliminary work had indicated that this contact time was considerably more than that required for the establishment of sorption equilibrium. From the initial and equilibrium concentration, the acid sorbed on the resins was calculated.

4.3.1.c Nomenclature :

Co, Ce	= initial and equilibrium concentration of acid in gm. equivalents per liter.
Ca	= Co - Ce / Ce
Cr	= capacity of air dry resin added per liter of acid solution ; in this study, 70.8 meq./ liter or 70.8×10^{-3} eq. / liter
B	= Co-Ce / Ce. Cr
X	= relative degree of crosslinking of the resin (% nominal divinylbenzene content.)
n_c ,n_b ,n_r	= number of straight chain and branchedchain carbon atoms and benzene rings in R of acid molecule $R-CH_2COOH$
Av.*	= The average value

4.3.1.d Results :

Table (4.3.1.1) gives the moisture and capacity of the sulfonic acid cation exchange resins.

Table (4.3.1.2) gives the sorption of monocarboxylic acids on the resin X4.

Table (4.3.1.3) gives the sorption of monocarboxylic acids on the resin X8.

Table (4.3.1.4) gives the sorption of monocarboxylic acids on the resin X12.

Table (4.3.1.5) gives the average values of BX obtained from tables (4.3.1.2 to 4.3.1.4).

Table (4.3.1.6) gives the values of log BX from table (4.3.1.5) and those obtained according to equation (4.02).

Table 4.3.1.1

The moisture and capacity of the sulfonic acid cation exchange resins.

Resin	Moisture %	Capacity, Meq./gm. Air-dry resin	Capacity, Meq./gm. Oven-dry resin
X4	29.9	3.55	5.06
X8	27.6	3.54	4.89
X12	27.1	3.54	4.85

Table 4.3.1.2

Sorption of monocarboxylic acids on the resin X4

Acid	10^3Ce	10^3Ca	10^3B	10^3 BX
Acetic	495.3	8.870	-	-
	298.5	9.046	-	-
	99.0	8.890	-	-
		Av.,8.936	126.3	505.2
Propionic	480.5	15.82	-	-
	290.2	15.51	-	-
	96.2	15.75	-	-
		Av.,15.69	221.6	886.4
n-Butyric	191.2	27.20	-	-
	95.9	27.10	-	-
	48.0	27.08	-	-
		Av., 27.12	383.1	1532
n-Valeric	180.2	47.72	-	-
	108.3	48.02	-	-
	36.1	47.08	-	-
		Av., 47.60	672.3	2689
n-Caproic	73.10	80.70	-	-
	43.53	82.70	-	-
		Av.,81.70	1154	4616

Table 4.3.1.2 (Continued)

Acid	10^3Ce	10^3Ca	10^3B	10^3BX
n-Caprylic	2.500	246.4	-	-
	1.520	250.0	-	-
		Av., 248.2	3506	14024
Isobutyric	394.0	17.00	-	-
	295.7	16.91	-	-
	197.4	16.72	-	-
		Av.,16.87	238.3	953.2
Isovaleric	193.9	28.88	-	-
	116.5	29.18	-	-
	38.7	28.42	-	-
		Av.,28.82	407.0	1628
Phenylacetic	54.00	74.08	-	-
	40.00	75.00	-	-
	20.00	75.00	-	-
		Av., 74.70	1055	4220

Table 4.3.1.3

Sorption of monocarboxylic acids on the resin X8

Acid	10^3Ce	10^3Ca	10^3B	10^3BX
Acetic	297.5	4.422	-	-
	299.9	4.334	-	-
		Av., 4.378	61.84	494.7
Propionic	484.3	7.688	-	-
	292.4	7.864	-	-
		Av., 7.776	109.8	878.4
n-Butyric	193.8	13.42	-	-
	97.2	13.37	-	-
		Av.,13.39	189.2	1514
n-Valeric	184.5	23.30	-	-
	110.9	23.84	-	-
	36.96	22.70	-	-
		Av.,22.28	328.9	2631
n-Caproic	75.90	40.84	-	-
	45.33	39.68	-	-
		Av., 40.26	568.5	4548

Table 4.3.1.3 (Continued)

Acid	10^3Ce		10^3Ca	10^3B	10^3BX
n-Caprylic	2.776		122.5	-	-
	1.700		117.6	-	-
		Av.,	120.0	1695	13560
Isobutyric	397.3		8.558	-	-
	298.2		8.384	-	-
	199.0		8.542	-	-
		Av.,	8.494	119.9	959.2
Isovaleric	196.6		14.75	-	-
	118.2		14.38	-	-
		Av.,	14.56	205.6	1645
Phenylacetic	55.90		37.58	-	-
	41.50		36.14	-	-
		Av.,	36.86	520.6	4165

Table 4.3.1.4

Sorption of monocarboxylic acids on the resin X12

Acid	10^3Ce	10^3Ca	10^3B	10^3BX
Acetic	498.3	2.810	-	-
	300.3	2.996	-	-
		Av., 2.903	41.01	492.1
Propionic	485.5	5.356	-	-
	293.2	5.118	-	-
		Av., 5.237	73.98	887.8
n-Butyric	194.6	9.250	-	-
	97.6	9.224	-	-
		Av., 9.237	130.5	1566
n-Valeric	185.9	15.60	-	-
	111.7	16.11	-	-
		Av., 15.85	224.0	2688
n-Caproic	76.90	27.32	-	-
	45.90	26.80	-	-
		Av., 27.06	382.2	4586

Table 4.3.1.4 (Continued)

Acid	10^3Ce	10^3Ca	10^3B	10^3BX
n-Caprylic	2.880	81.96	-	-
	1.756	82.02	-	-
		Av.,81.99	1158	13896
Isobutyric	398.4	5.774	-	-
	299.0	5.686	-	-
	199.6	5.510	-	-
		Av., 5.656	79.89	958.7
Isovaleric	197.6	9.614	-	-
	118.7	10.11	-	-
		Av., 9.862	139.3	1672
Phenylacetic	56.60	25.18	-	-
	42.00	23.80	-	-
		Av., 24.49	345.9	4151

4.3.1.e Discussion :

The sulfonic acid cation exchange resins in the hydrogen form may be regarded as macromolecular insoluble acids, with sulfonic acid groups as ionogenic groups, attached to the hydrocarbon matrix. When the resin particle is placed in a polar solvent, the polar groups interact with the polar solvent molecules and the solvent is sorbed. As a result, the resin particle swells. But the crosslinks oppose this. The result is a limited swelling. The amount of solvent sorbed and the extent of swelling are dependent on X and decrease with increase in X. The swollen resin is permeable to the solute molecules in the external solution, provided these are not so large that the steric effects become effective.

The sorption of carboxylic acids studied is essentially nonionic because of the high concentration of H^+ ions in the resin phase, and may be influenced by two types of interactions : the London interactions between the carboxylic acid molecules and the resin matrix and the dipole-dipole interactions of the polar solvent molecules between one another and with the polar groups of the carboxylic acid molecules. In a homologous series, these interactions should tend to increase the sorption of solute molecules with increasing chain length.

The data obtained indicate that the values of B obtained for resin X8 are in good agreement with those given in table (III, p.313 from earlier work by Bafna and

Table 4.3.1.5

Values of BX obtained from tables (4.3.1.2 to 4.3.1.4)

Acids	Resin X4 10^3 BX	Resin X8 10^3 Bx	Resin X12 10^3 BX	Av. 10^3 BX	log (Av.), BX
Acetic	505.2	494.7	492.1	497.3	- 0.3033
Propionic	886.4	878.4	887.8	884.2	- 0.0534
n-Butyric	1532	1514	1566	1537	+ 0.1867
n-Valeric	2689	2631	2688	2669	+ 0.4264
n-Caproic	4616	4548	4586	4583	+ 0.6612
n-Caprylic	14024	13560	13896	13827	+ 1.1409
Isobutyric	953.2	959.2	958.7	957.0	- 0.0191
Isovaleric	1628	1645	1672	1648	+ 0.2170
Phenylacetic	4220	4165	4151	4179	+ 0.6210

Table 4.3.1.6

Values of log BX obtained from table (4.3.1.5) and equation (4.02)

Acids	n_c	n_b	n_r	log BX	
				From Table	From Equation
Acetic	0	0	0	-0.3033	-0.30
Propionic	1	0	0	-0.0534	-0.06
n-Butyric	2	0	0	+0.1867	+0.18
n-Valeric	3	0	0	+0.4264	+0.42
n-Caproic	4	0	0	+0.6612	+0.66
n-Caprylic	6	0	0	+1.1409	+1.14
Isobutyric	1	1	0	-0.0191	-0.02
Isovaleric	2	1	0	+0.2170	+0.22
Phenylacetic	0	0	1	+0.6210	+0.62
1-Naphthalene acetic	0	0	2	+1.5439	+1.54

Govindan (2) for sulfonic acid resin of the same type, Nalcite HCR. Since the particle sizes of these two resins are different, the results support the conclusion that sorption may be considered to be independent of particle size for these resins, implying that sorption takes place through the whole of the resin particle. Further, the amount of acid sorbed per unit capacity of the resins studied is directly proportional to the equilibrium concentration of the acid and inversely proportional to X, the relative degree of crosslinking of the resin.

The values of log BX for $R\text{-}CH_2COOH$ type acids studied may be represented by

$$\log BX = 0.24\, n_c + 0.04\, n_b + 0.92\, n_r - 0.30 \qquad (4.02)$$

Table (4.3.1.6) gives the values of log BX from table (4.3.1.5) and those obtained according to equation (4.02). The value of log BX for 1-naphthalene acetic acid given in table (4.3.1.6) is obtained by multiplying the value of B for its sorption on sulfonic acid resin, Nalcite HCR (2) by 8, the value of X for that resin. Since log B is related to the free energy change, ΔF, because of the interactions in the process of sorption, the validity of equation (4.02) suggests that the contributions to the free energy change due to increase in n_c, n_b and n_r are essentially additive.

4.3.2 Separation studies :

4.3.2.a Introduction :

In previous section, the study of sorption equilibria of some monocarboxylic acids of $R-CH_2COOH$ type on sulfonated styrene-divinylbenzene copolymer type sulfonic acid resins of different relative degree of crosslinking was described.

In this section, the separation of some binary mixtures of such acids with a sulfonic acid resin of relative degree of crosslinking as four, is described.

4.3.2.b Experimental :

Materials : The chemicals and resin Dowex 50 W - X4 (-100, + 200 mesh), used were from the samples used in the previous section and the solutions were prepared in distilled water.

Procedure : A column containing 46 gms. of air dry resin, Dowex 50 W- X4, was set up. The column data were as follows : Moisture content of air dry resin, 29.9 % ; capacity of air dry resin, 3.55 meq./gm. ; bed volume, 131 cc. ; bed length, 53 cms. ; flow rate of effluent, 2 cc. / min.

The water level in the column was brought to the resin bed level and 25 cc. of acid solutions were added. When the liquid level was again at the bed level, 25 cc. of distilled water were added and the column was connected to an overhead resevoir of distilled water. The effluent was collected in measuring containers. The first sample was equal to void volume. Then 25 cc.

samples were collected and numbered 1,2,3 and so on. Acid content was estimated as milliequivalents of acid in 25 cc. by titration with standard sodium hydroxide solution. Phenylacetic acid in solution was also estimated by ultraviolet absorption at 257 mμ with a Beckman Model DU spectrophotometer, using 10 mm. quartz cells.

4.3.2.c Nomenclature :

v.v. = sample volume equal to void volume.

W = acid content, meq., in 25 cc. of acid solution and sorbed on the resin bed.

Ws = acid content, meq., in 25 cc. of effluent sample.

4.3.2.d Results :

Table (4.3.2.1a and 4.3.2.1b) give the column elution of monocarboxylic acids of $R-CH_2COOH$ type with the resin X4.

Table (4.3.2.2 and figure 4.3.2.2) give the separation of acetic acid from n-valeric acid, n-caproic acid and phenylacetic acid with the resin X4.

Table (4.3.2.3 and figure 4.3.2.3) give the separation of propionic acid from n-caproic acid and phenylacetic acid with the resin X4.

Table (4.3.2.4 and figure 4.3.2.4) give the separation of isobutyric acid from n-caproic acid and phenylacetic acid with the resin X4.

Table (4.3.2.5 and figure 4.3.2.5) give the separation of n-butyric acid and isovaleric acid from phenylacetic acid with the resin X4.

Table 4.3.2.1 a

Column elution of monocarboxylic acids with the resin X4

Acid	Acetic	Propionic	n-Butyric	Isobutyric
W =	1.250	1.263	1.230	1.253
Sample No.		Ws =		
v.v.	-	-	-	-
1	-	-	-	-
2	-	-	-	-
3	0.0533	-	-	-
4	0.9183	0.2854	-	0.0279
5	0.2689	0.7762	0.3882	0.7078
6	0.0102	0.1611	0.6939	0.4845
7	-	0.0279	0.1015	0.0254
8	-	0.0116	0.0190	0.0076
9	-	-	0.0152	-
10	-	-	0.0127	-
11	-	-	-	-
12	-	-	-	-
13	-	-	-	-
14	-	-	-	-
15	-	-	-	-
16	-	-	-	-
17	-	-	-	-

Table 4.3.2.1 b

Column elution of monocarboxylic acids with the resin X4

Acid	n-Valeric	Isovaleric	n-Caproic	Phenylacetic
W =	1.275	1.240	1.238	1.253
Sample No.		Ws =		
v.v.	-	-	-	-
1	-	-	-	-
2	-	-	-	-
3	-	-	-	-
4	-	-	-	-
5	-	0.0305	-	-
6	0.0507	0.5353	-	-
7	0.4098	0.5784	-	-
8	0.6368	0.0558	-	-
9	0.1433	0.0254	0.0216	-
10	0.0178	0.0152	0.1523	0.0102
11	0.0101	-	0.4566	0.0837
12	0.0069	-	0.4033	0.2689
13	-	-	0.1269	0.4338
14	-	-	0.0292	0.3197
15	-	-	0.0203	0.1217
16	-	-	0.0152	0.0153
17	-	-	0.0127	-
18	-	-	-	-

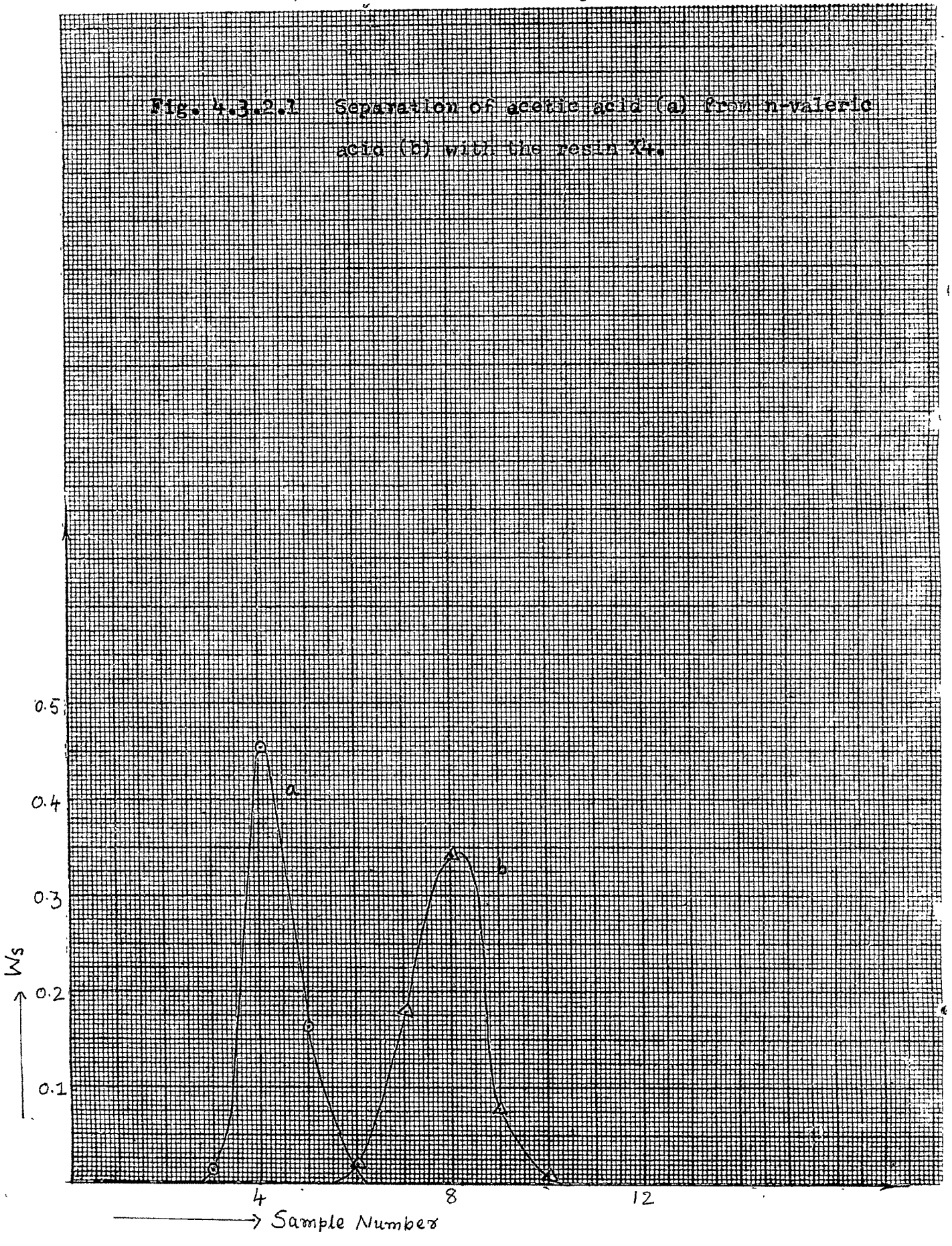


Fig. 4.3.2.1 Separation of acetic acid (a) from n-valeric acid (b) with the resin X4.

Fig. 4.3.2.2 Separation of acetic acid (a) from n-caproic acid (b) and phenylacetic acid (c) with the resin X4.

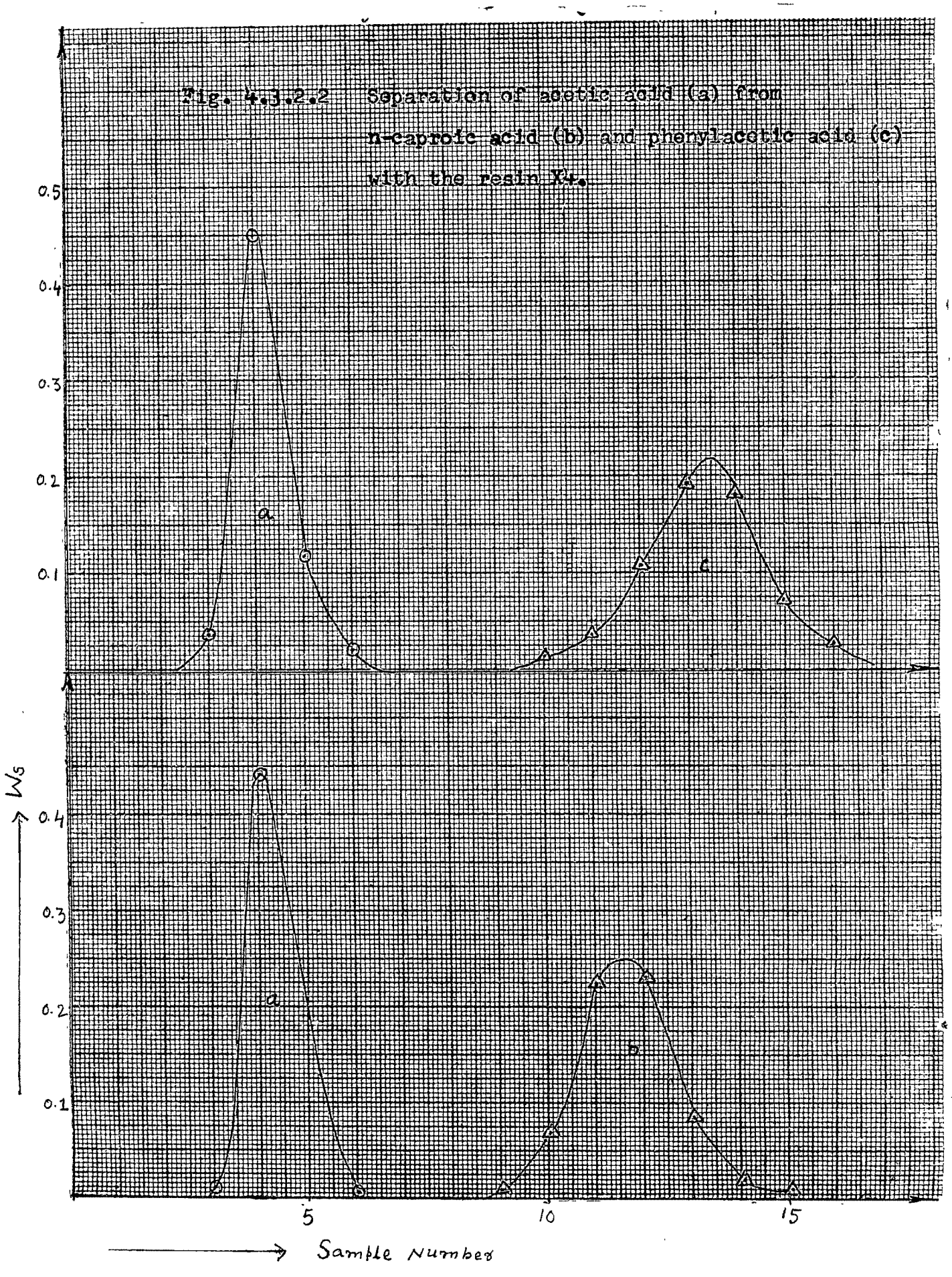


Table 4.3.2.2

Separation of acetic acid from n-valeric acid, n-caproic acid and phenylacetic acid with the resin X4

Acid	Acetic + n-Valeric		Acetic + n-Caproic		Acetic + Phenylacetic	
W =	0.6292 + 0.6292		0.6292 + 0.6290		0.6253 + 0.6240	
Sample No.	Ws =		Ws =		Ws =	
v.v.	-	-	-	-	-	-
1	-	-	-	-	-	-
2	-	-	-	-	-	-
3	0.0152	-	0.0102	-	0.0381	-
4	0.4515	-	0.4414	-	0.4515	-
5	0.1624	-	0.1725	-	0.1167	-
6	-	0.0203	0.0051	-	0.0190	-
7	-	0.1801	-	-	-	-
8	-	0.3449	-	-	-	-
9	-	0.0787	-	0.0076	-	-
10	-	0.0051	-	0.0672	-	0.0127
11	-	-	-	0.2220	-	0.0343
12	-	-	-	0.2283	-	0.1078
13	-	-	-	0.0837	-	0.1928
14	-	-	-	0.0152	-	0.1827
15	-	-	-	0.0050	-	0.0685
16	-	-	-	-	-	0.0254
17	-	-	-	-	-	-

Fig. 4.3.2.3 Separation of propionic acid (a) from n-caproic acid (b) and phenylacetic acid (c) with the resin X4.

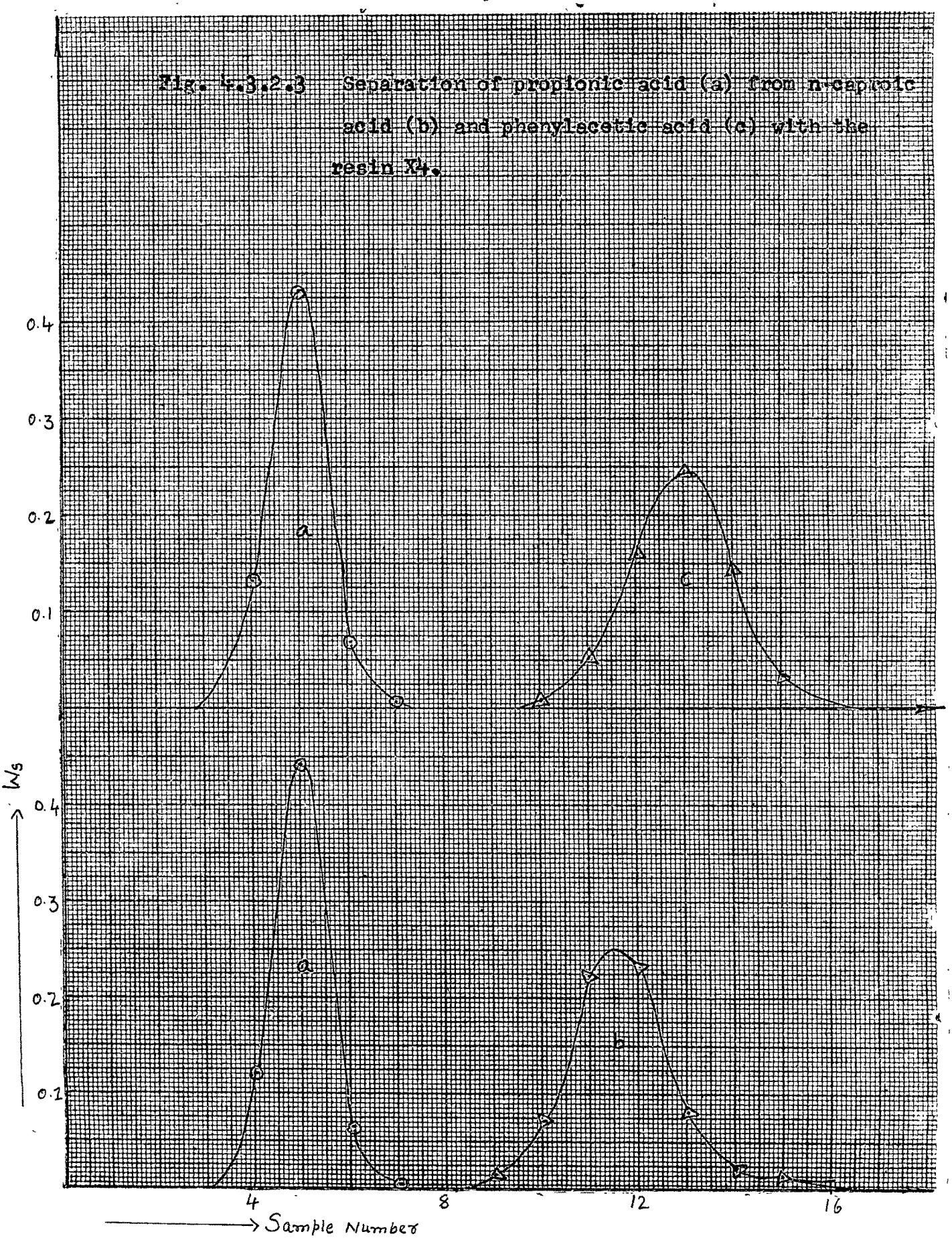


Table 4.3.2.3

Separation of propionic acid from n-caproic acid and phenylacetic acid with the resin X4

Acid	Propionic	+ n-Caproic	Propionic	+ Phenylacetic
W =	0.6317	+ 0.6266	0.6317	+ 0.6240
Sample No.	Ws =		Ws =	
v.v.	-	-	-	-
1	-	-	-	-
2	-	-	-	-
3	-	-	-	-
4	0.1217	-	0.1294	-
5	0.4388	-	0.4312	-
6	0.0660	-	0.0660	-
7	0.0051	-	0.0051	-
8	-	-	-	-
9	-	0.0127	-	-
10	-	0.0685	-	0.0051
11	-	0.2182	-	0.0507
12	-	0.2283	-	0.1573
13	-	0.0736	-	0.2435
14	-	0.0152	-	0.1395
15	-	0.0101	-	0.0279
16	-	-	-	-
17	-	-	-	-

Fig. 4.5.2.4. Separation of isobutyric acid (a) from n-caproic acid (b) and phenylacetic acid (c) with the resin X4.

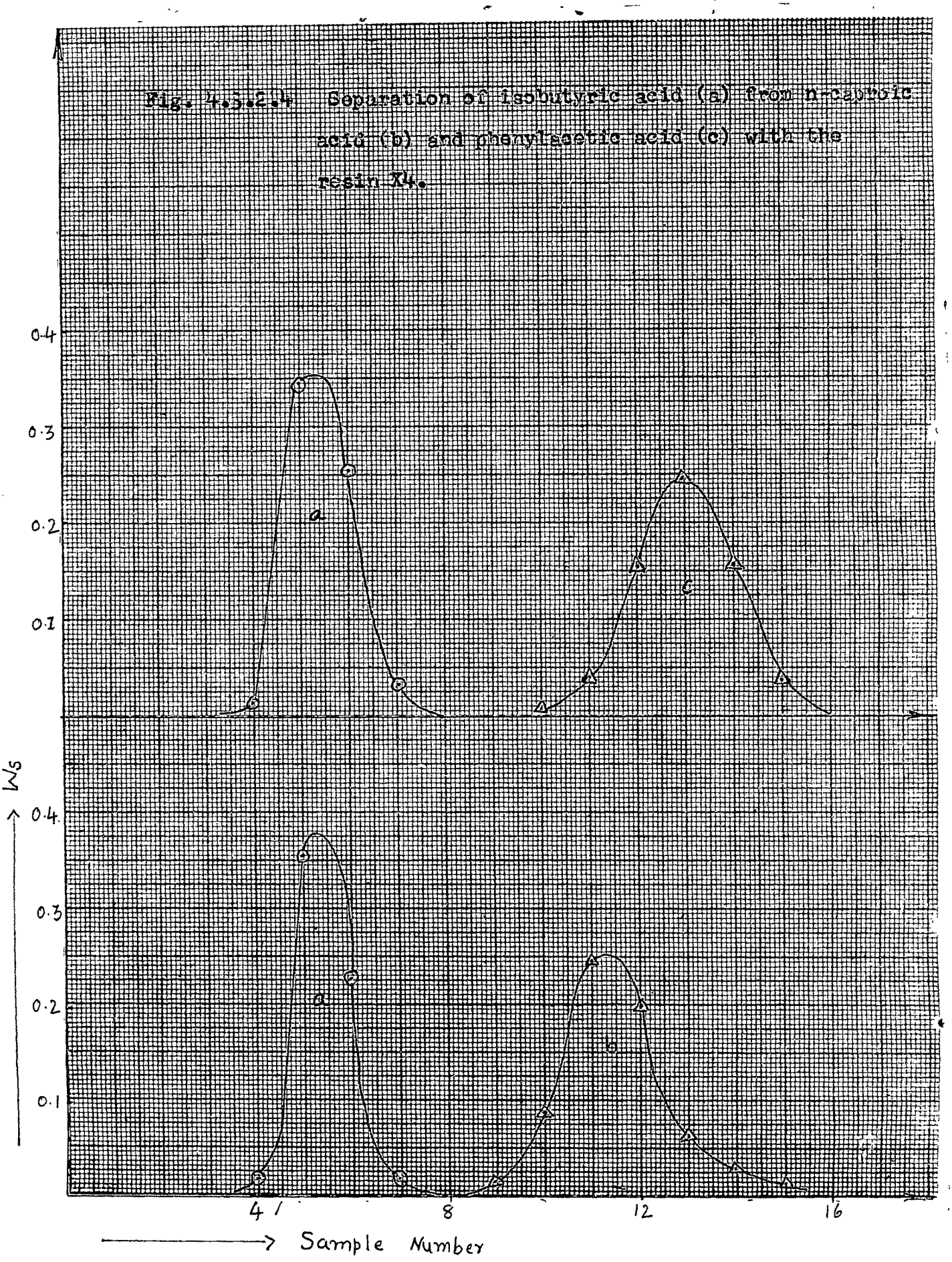


Table 4.3.2.4

Separation of isobutyric acid from n-caproic acid and phenylacetic acid with the resin X4

Acid	Isobutyric	+ n-Caproic	Isobutyric	+ Phenylacetic
W =	0.6266	+ 0.6266	0.6266	+ 0.6240
Sample No.	Ws =		Ws =	
v.v.	-	-	-	-
1	-	-	-	-
2	-	-	-	-
3	-	-	-	-
4	0.0178	-	0.0101	-
5	0.3511	-	0.3375	-
6	0.2258	-	0.2511	-
7	0.0178	-	0.0279	-
8	0.0140	-	-	-
9	-	0.0152	-	-
10	-	0.0850	-	0.0050
11	-	0.2423	-	0.0380
12	-	0.1941	-	0.1523
13	-	0.0571	-	0.2435
14	-	0.0254	-	0.1523
15	-	0.0076	-	0.0330
16	-	-	-	-
17	-	-	-	-

Fig. 4.3.2.5 Separation of n-butyric acid (a) and isovaleric acid (b) from phenylacetic acid (c) with the resin X4.

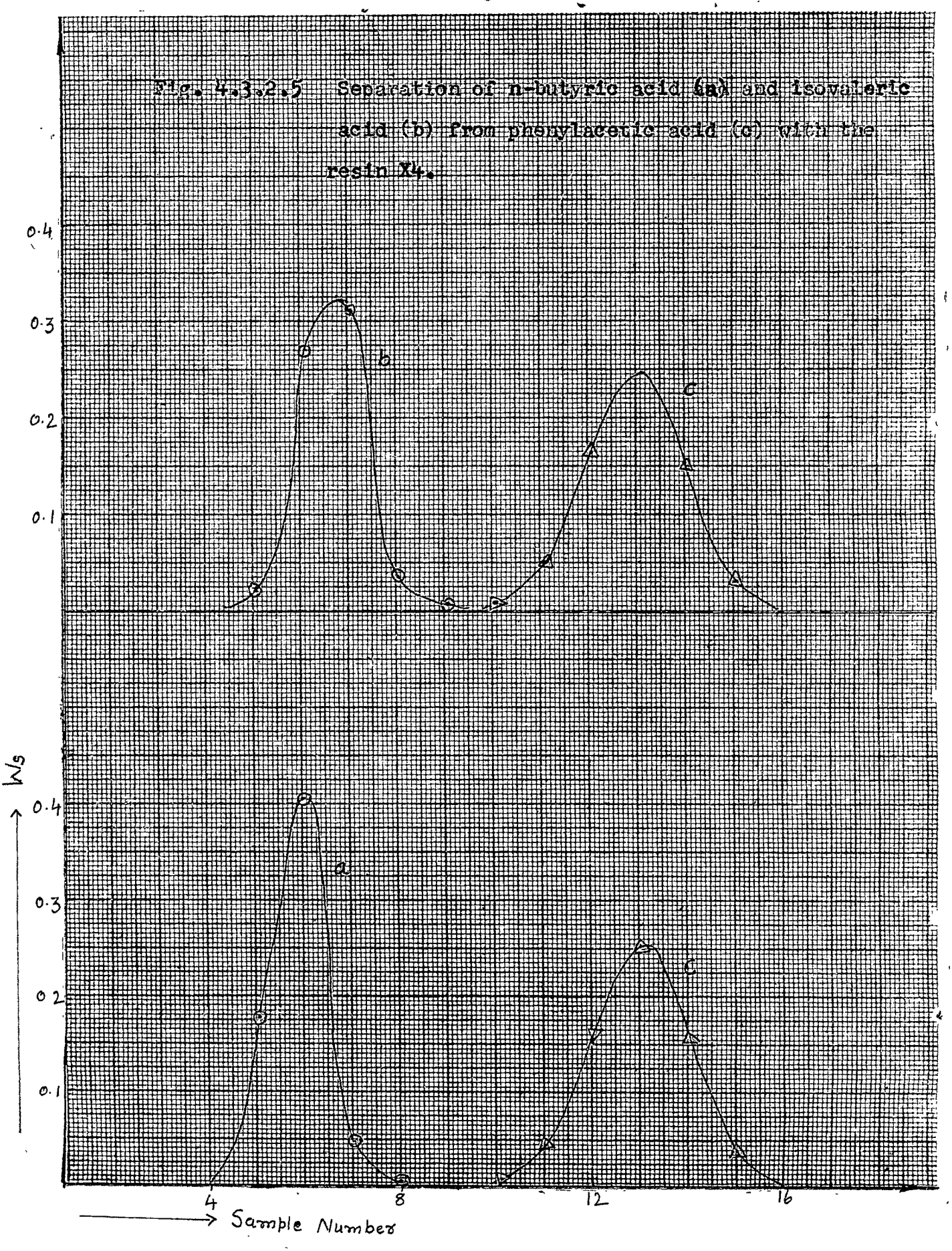


Table 4.3.2.5

Separation of n-butyric acid and isovaleric acid from phenylacetic acid with the resin X4

Acid	n-Butyric	+ Phenylacetic	Isovaleric	+ Phenylacetic
W =	0.6266	+ 0.6240	0.6240	+ 0.6240
Sample No.	Ws =		Ws =	
v.v.	-	-	-	-
1	-	-	-	-
2	-	-	-	-
3	-	-	-	-
4	-	-	-	-
5	0.1725	-	0.0152	-
6	0.4033	-	0.2664	-
7	0.0457	-	0.3095	-
8	0.0051	-	0.0304	-
9	-	-	0.0025	-
10	-	0.0050	-	0.0051
11	-	0.0406	-	0.0457
12	-	0.1547	-	0.1598
13	-	0.2461	-	0.2435
14	-	0.1497	-	0.1446
15	-	0.0279	-	0.0253
16	-	-	-	-
17	-	-	-	-

4.3.2.e Discussion :

Table (4.3.2.1) gives the elution data for each single acid studied. It is observed that the sorption is reversible and as the value of B for a acid (previous section 4.3.1) in a homologous series increases, the elution band becomes broader and reduced in height and the effluent volume before the breakthrough of the acid increases. Tables(4.3.2.2 to 4.3.2.5 and figures 4.3.2.1 to 4.3.2.5) give the elution data illustrating the separation of acetic acid from n-valeric acid, n-caproic acid and phenyl acetic acid, propionic acid from n-caproic acid and phenyl acetic acid, isobutyric acid from n-caproic acid and phenyl acetic acid and n-butyric acid and isovaleric acid from phenyl acetic acid.

4.4 Sorption equilibrium studies in organic solvents :

4.4 a Introduction :

In an earlier section (4.3.1), the study of sorption equilibria of some monocarboxylic acids of $R-CH_2COOH$ type on sulfonated styrene-divinylbenzene copolymer type sulfonic acid resins of different relative degree of crosslinking in aqueous medium was described.

In this section, the study of sorption equilibria of some of the acids of the same type in some organic solvents (n-hexane, cyclohexane, benzene, toluene, o-xylene, m-xylene and p-xylene) with the resin X4 is described.

4.4 b Experimental :

Resin : The resin, Dowex 50 W-X4 (-100, + 200 mesh), used was from the sample used in previous section.

Chemicals : All chemicals used were of A.R. or C.P.grade.

Solvents : All solvents used were of C.P.grade and were distilled before use.

Procedure : Acid solutions in organic solvent of known volume and concentration were placed in contact with weighed amounts of air dry resin in well stoppered flasks, with frequent shaking, at room temperature ($\sim 30^{\circ}C$) for 24 hours. Then the equilibrium concentration was estimated by titrating aliquots with standard sodium hydroxide solution. Preliminary work had indicated that this contact time was more than that required for the establishment of sorption equilibrium. From the initial and equilibrium concentrations the acid sorbed on the resin was calculated.

3.4 c Nomenclature :

$S = Co - Ce / Cr$

n_{Me} = Number of methyl groups in benzene ring, other symbols used are same as given in the earlier section (4.3.1)

4.4 d Results :

Table (4.4.1) and figure (4.4.1) give the sorption of monocarboxylic acids on the resin X4 in n-hexane.

Table(4.4.2) and figure (4.4.2) give the sorption of monocarboxylic acids on the resin X4 in cyclohexane.

Table(4.4.3) and figure (4.4.3) give the sorption of monocarboxylic acids on the resin X4 in benzene.

Table (4.4.4) and figure (4.4.4) give the sorption of monocarboxylic acids on the resin X4 in toluene.

Table (4.4.5) and figures(4.4.5 and 4.4.6) give the sorption of monocarboxylic acids on the resin X4 in o-xylene.

Table (4.4.6) and figures (4.4.5 and 4.4.6) give the sorption of monocarboxylic acids on the resin X4 in m-xylene.

Table (4.4.7) and figures(4.4.5 and 4.4.6) give the sorption of monocarboxylic acids on the resin X4 in p-xylene.

Table (4.4.8) gives the values of log B and α obtained from figures (4.4.1 to 4.4.3) for monocarboxylic acids with the resin X4 in n-hexane,cyclohexane and benzene.

Table (4.4.9) gives the value of log B and α obtained from figures(4.4.3 to 4.4.6) for monocarboxylic acids with the resin X4 in benzene,toluene and xylene.

Table 4.4.1

Sorption of monocarboxylic acids with the resin X4 in n-hexane

Acid	10^2 Ce	10^2 S	Acid	10^2 Ce	10^2 S
Propionic	1.529	5.970	Phenylacetic	1.101	3.332
	3.339	8.620		2.387	5.591
	7.055	12.13		5.037	7.828
	10.73	14.21		7.676	9.518
	18.54	17.06		10.46	10.62
n-Butyric	3.927	3.981	Isobutyric	4.093	2.783
	8.015	4.898		8.213	3.975
	12.08	6.237		12.38	4.769
	16.17	7.000			
n-Valeric	3.713	1.950	Isovaleric	3.155	1.452
	5.394	2.291		9.772	2.073
	7.998	2.570		12.99	2.488
	19.15	3.578		17.65	2.696

Fig. 4.4.1 Variation of log S with log Ce for (1) propionic acid, (2) n-butyric acid, (3) n-valeric acid, (4) phenylacetic acid, (5) isobutyric acid and (6) isovaleric acid in n-hexane.

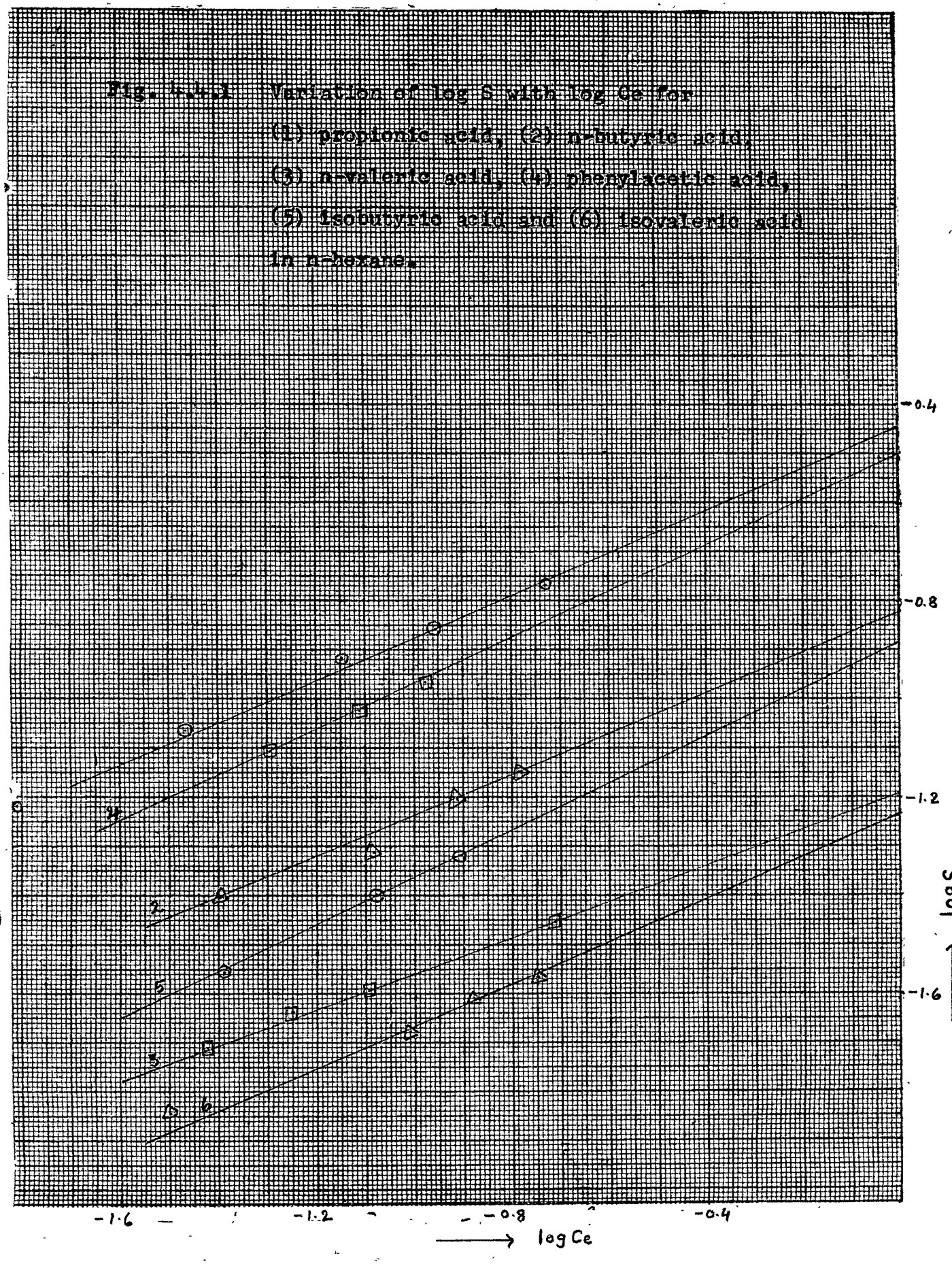


Table 4.4.2

Sorption of monocarboxylic acids with the resin X4 in cyclohexane

Acid	10^2 Ce	10^2 S	Acid	10^2 Ce	10^2 S
Propionic	4.146	9.120	Phenylacetic	1.611	3.997
	8.736	12.60		6.990	7.214
	18.23	17.00		10.59	9.114
	36.99	23.93			
	46.76	27.08			
n-Butyric	1.951	2.865	Isobutyric	3.376	3.446
	8.314	5.364		8.145	4.480
	12.54	6.290		12.14	5.169
	16.71	7.030		16.29	5.859
				20.78	6.548
n-Valeric	2.843	1.575	Isovaleric	3.749	1.288
	3.747	1.750		11.44	2.278
	4.794	1.908		15.40	2.640
	5.723	2.009			
	19.13	3.147			

Fig. 4.4.2 Variation of log S with log Ce for (1) propionic acid, (2) n-butyric acid, (3) n-valeric acid, (4) phenylacetic acid, (5) isobutyric acid and (6) isovaleric acid in cyclohexane.

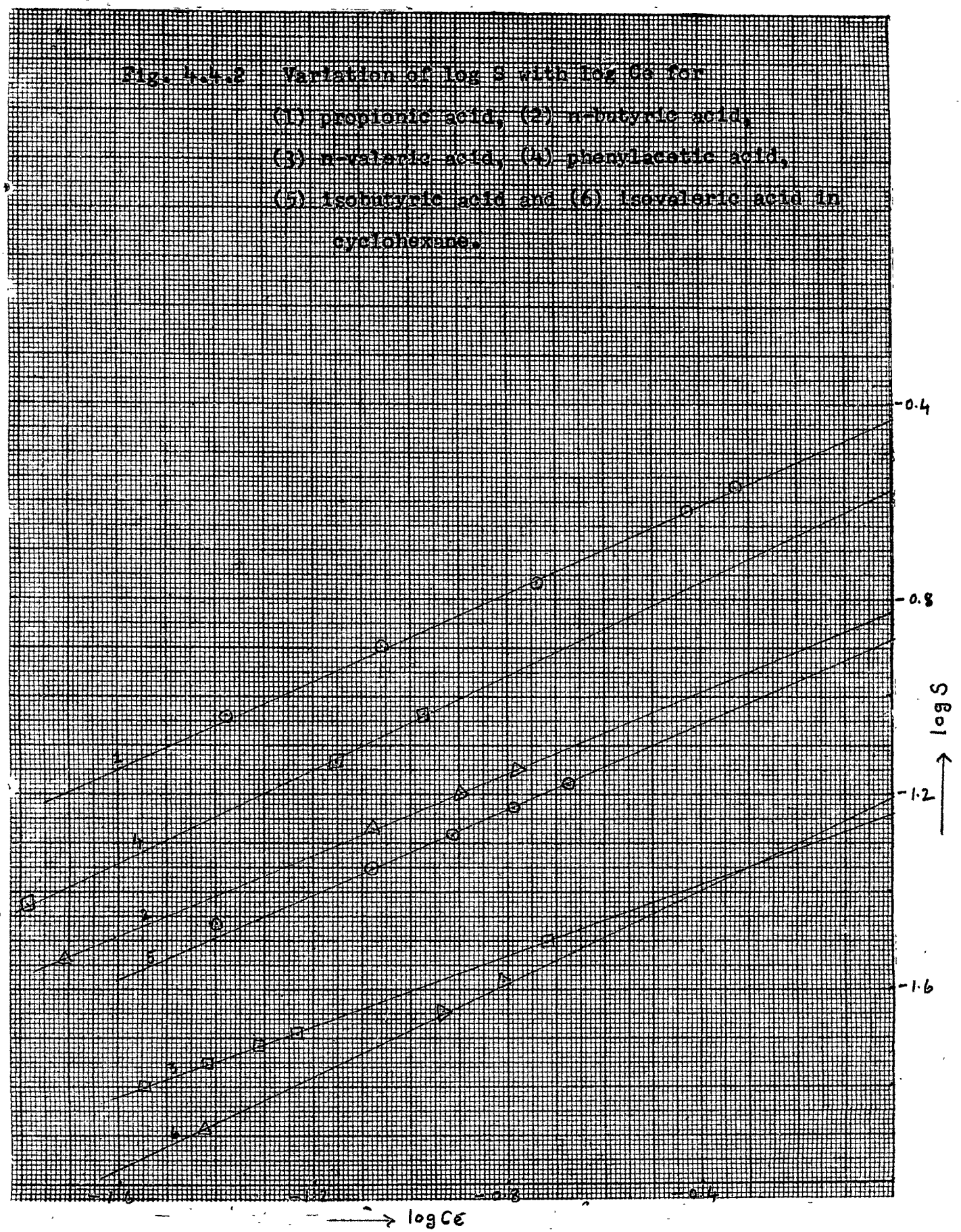


Table 4.4.3

Sorption of monocarboxylic acids with the resin X4 in benzene

Acid	10^2 Ce	10^2 S	Acid	10^2 Ce	10^2 S
Propionic	8.219	6.893	Phenylacetic	3.206	1.995
	12.44	8.000		9.842	3.020
	16.51	8.960		13.20	3.203
	20.04	9.993		16.61	3.507
n-Butyric	4.228	2.140	Isobutyric	4.267	1.508
	8.506	3.210		8.708	2.072
	12.72	4.280		17.39	2.826
	17.08	4.993		21.91	3.015
	21.43	5.707			
n-Valeric	2.502	0.8368	Isovaleric	2.988	0.6651
	5.048	1.255		6.071	0.9977
	7.654	1.673		9.177	1.330
	10.08	2.091		12.24	1.663
				15.23	1.995

Fig. 4.4.3 Variation of log S with log Ce for (1) propionic acid, (2) n-butyric acid, (3) n-valeric acid, (4) phenylacetic acid, (5) isobutyric acid and (6) isovaleric acid in benzene.

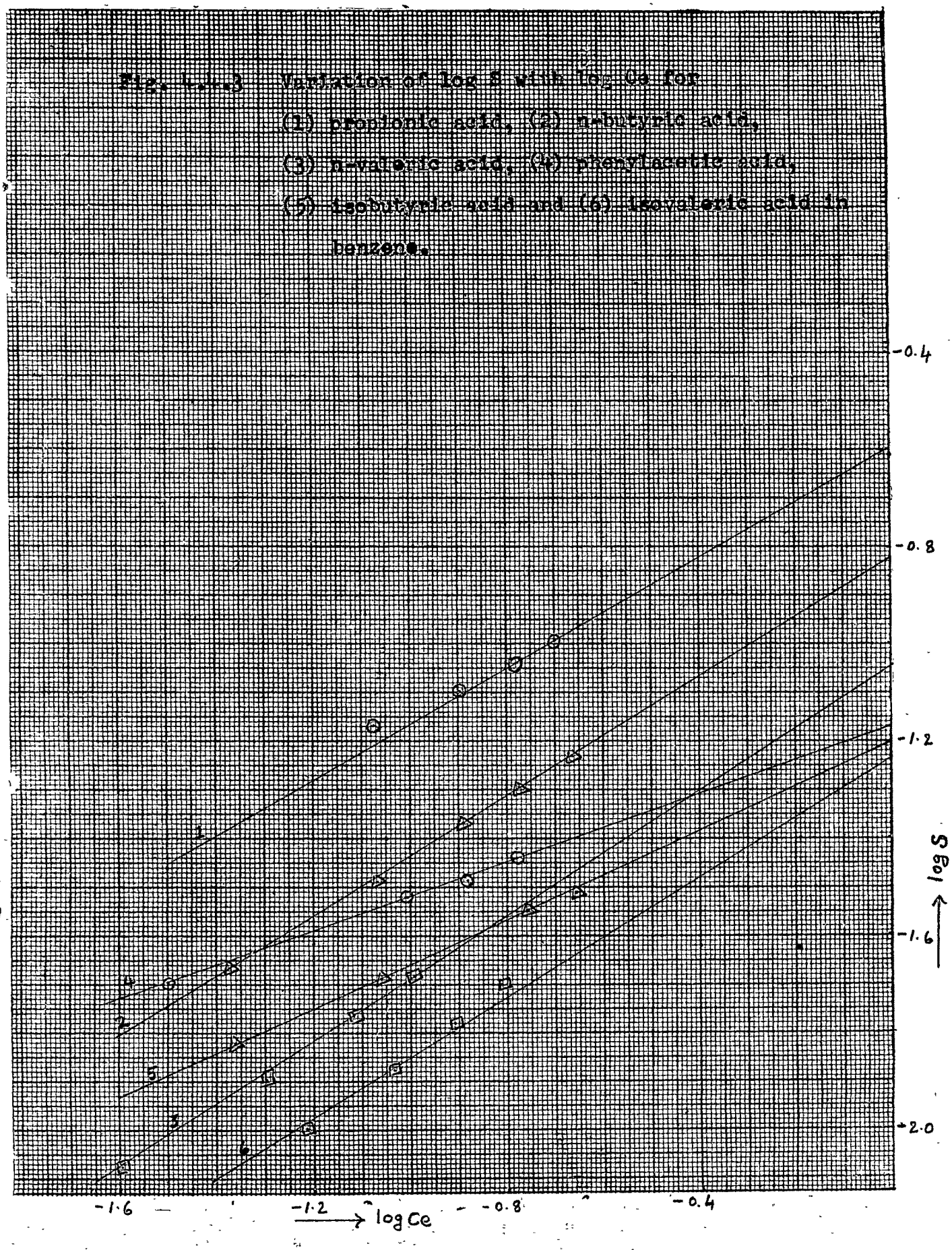


Table 4.4.4

Sorption of monocarboxylic acids with the resin X4 in toluene

Acid	10^2 Ce	10^2 S	Acid	10^2 Ce	10^2 S
Propionic	4.320	4.595	Phenylacetic	3.786	2.371
	8.802	6.893		7.060	2.954
	13.23	8.861		10.45	3.610
	17.66	10.17		12.93	3.802
	22.20	11.16			
n-Butyric	3.788	2.239	Isobutyric	6.806	2.625
	11.82	4.266		11.52	3.231
	15.71	5.012		12.66	3.610
	19.67	5.370		19.44	4.267
n-Valeric	2.729	0.7738	Isovaleric	3.009	0.9772
	4.777	1.330		6.087	1.512
	5.539	1.512		13.12	2.113
	8.322	1.890		16.54	2.512
	11.09	2.269			

Fig. 4.4.4 Variation of log S with log Ce for (1) propionic acid, (2) n-butyric acid, (3) n-valeric acid, (4) phenylacetic acid, (5) isobutyric acid and (6) isovaleric acid in toluene.

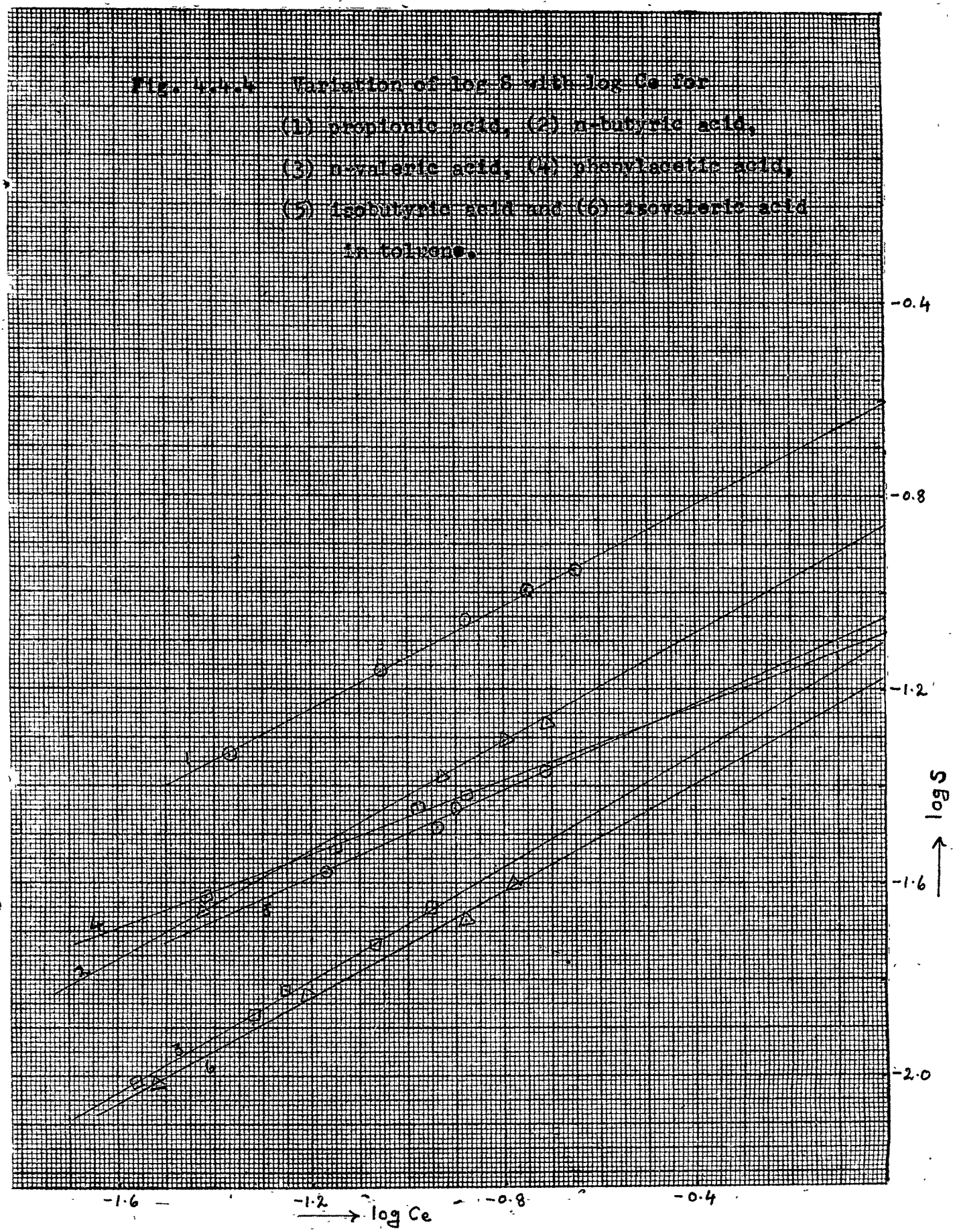


Table 4.4.5

Sorption of monocarboxylic acids with the resin X4 in o-xylene

Acid	10^2 Ce	10^2 S	Acid	10^2 Ce	10^2 S
Propionic	3.884	5.420	Phenylacetic	3.380	2.344
	7.982	7.991		10.47	3.387
	12.17	9.145		14.07	4.403
	16.11	10.84			
n-Butyric	8.292	4.064	Isobutyric	4.386	2.710
	12.63	4.742		8.461	3.387
	16.23	5.081		11.93	3.838
				15.89	4.403
				20.01	4.742
n-Valeric	3.979	1.355	Isovaleric	4.075	1.355
	11.58	2.384		7.982	1.693
	16.42	2.710		11.53	2.239
				17.55	2.710

Table 4.4.6

Sorption of monocarboxylic acids with the resin X4 in m-xylene

Acid	10^2 Ce	10^2 S	Acid	10^2 Ce	10^2 S
Propionic	3.695	5.555	Phenylacetic	3.684	2.399
	7.652	7.244		7.506	3.000
	11.63	9.074		11.23	3.633
	19.45	12.59			
n-Butyric	8.582	4.064	Isovaleric	6.058	1.641
	12.11	4.742		9.152	1.969
	16.25	5.420		12.27	2.297
				14.95	2.664
n-Valeric	4.075	1.259			
	11.62	2.239			
	19.42	2.580			

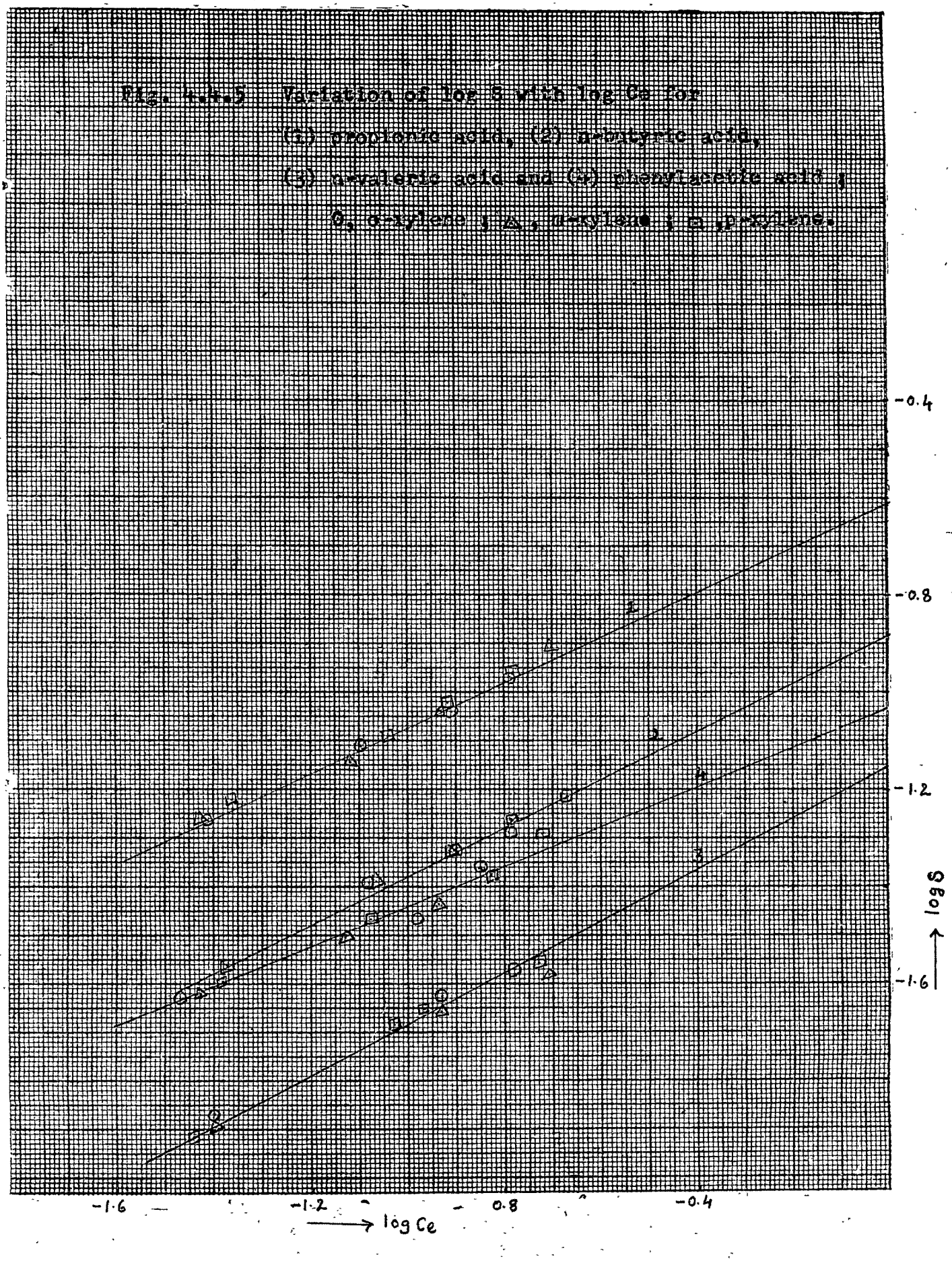


Fig. 4.4.5 Variation of log S with log Ce for (1) propionic acid, (2) n-butyric acid, (3) n-valeric acid and (4) phenylacetic acid ; ○, o-xylene ; △, m-xylene ; □, p-xylene.

Fig. 4.4.6 Variation of log S with log Ce for (1) isobutyric acid and (2) isovaleric acid ; ○, o-xylene ; △, m-xylene ; □, p-xylene.

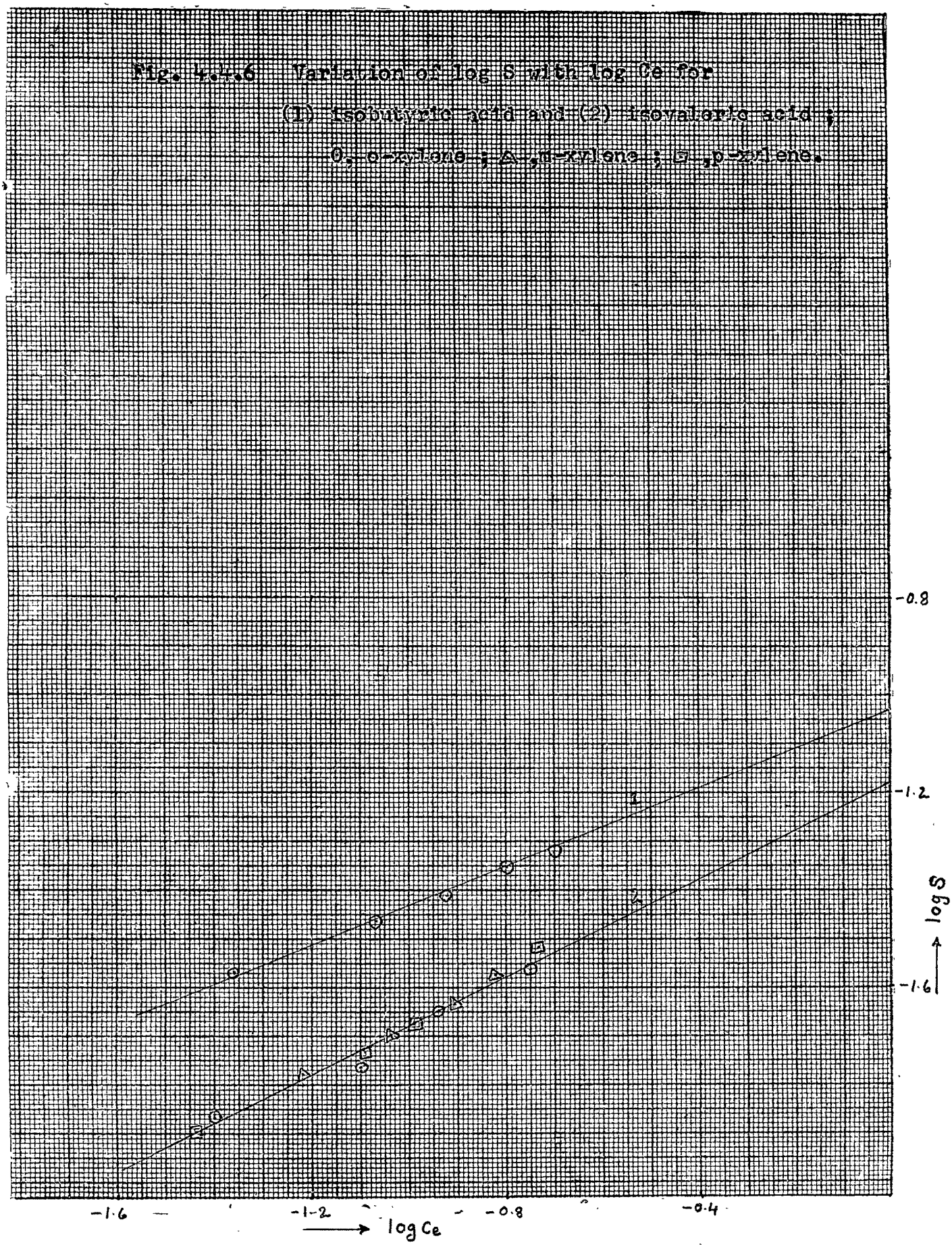


Table 4.4.7

Sorption of monocarboxylic acids with the resin X4 in p-xylene

Acid	10^2 Ce	10^2 S	Acid	10^2 Ce	10^2 S
Propionic	4.314	6.096	Phenylacetic	4.049	2.512
	8.808	8.030		8.341	3.446
	12.03	9.484		14.90	4.135
	16.20	10.96		19.00	5.165
n-Butyric	4.219	2.757	Isovaleric	3.659	1.259
	8.559	3.981		8.072	1.862
	16.25	5.546		10.36	2.067
	21.48	6.203		17.97	3.101
n-Valeric	3.659	1.202			
	9.143	2.067			
	10.80	2.239			
	18.91	2.757			

4.4e Discussion :

When an ion exchanger is placed in a solution of a weak or nonelectrolyte, sorption of the solute occurs till a state of equilibrium is reached. This may take a few seconds to several days.

The sorption equilibrium may be treated in terms of the equation

$$S = B.\ Ce^{a} \qquad (4.03)$$

or $$S / Ce^{a} = B \qquad (4.04)$$

where a is a constant and may be considered to take into account the overall effect of the interactions of the solute and the solvent with the solute, the solvent, the ionogenic groups and the resin matrix and B is the sorption equilibrium constant.

Figures (4.4.1 to 4.4.6) give the plots of log S against log Ce for the sorption of propionic acid, n-butyric acid, n-valeric acid, phenylacetic acid, isobutyric acid and isovaleric acid in organic solvents which include n-hexane, cyclohexane, benzene, toluene, o-xylene, m-xylene and p-xylene. Tables (4.4.8 and 4.4.9) give the values of log B and a obtained from these plots.

The results obtained indicate that the values for o,m-and p-xylenes are essentially same. This implies that the isomeric solvents do not influence the sorption behaviour significantly differently.

Table 4.4.8

Values of α and log B obtained from figures (4.4.1 to 4.4.3)

Solvent	n-Hexane		Cyclohexane		Benzene	
Acid	α	log B	α	log B	α	log B
Propionic	0.43	-0.44	0.45	-0.43	0.57	-0.59
n-Butyric	0.41	-0.82	0.41	-0.83	0.605	-0.825
n-Valeric	0.37	-1.19	0.37	-1.23	0.63	-1.05
Phenylacetic	0.46	-0.50	0.47	-0.58	0.355	-1.165
Isobutyric	0.48	-0.88	0.44	-0.88	0.46	-1.20
Isovaleric	0.43	-1.23	0.47	-1.21	0.62	-1.23

Table 4.4.9

Values of α and log B obtained from figures (4.4.3 to 4.4.6)

Solvent	Benzene		Toluene		Xylene	
Acid	α	log B	α	log B	α	log B
Propionic	0.57	-0.59	0.525	-0.60	0.47	-0.605
n-Butyric	0.605	-0.825	0.56	-0.85	0.50	-0.88
n-Valeric	0.63	-1.05	0.58	-1.10	0.53	-1.15
Phenylacetic	0.355	-1.165	0.38	-1.08	0.41	-1.03
Isobutyric	0.46	-1.20	0.44	-1.05	0.40	-1.03
Isovaleric	0.62	-1.23	0.55	-1.17	0.50	-1.18

The values of log B and α for the solvents used may be given by the following equations :

Solvent	Equation	
n-Hexane	$-\text{Log } B = 0.06 + 0.38\ n_c + 0.44\ n_r$	(4.05)
	$\alpha = 0.46 - 0.03\ n_c - 0.00\ n_r$	(4.06)
Cyclohexane	$-\text{Log } B = 0.03 + 0.40\ n_c + 0.55\ n_r$	(4.07)
	$\alpha = 0.49 - 0.04\ n_c - 0.02\ n_r$	(4.08)
Benzene, Toluene, Xylene	$-\text{Log } B = (0.36 - 0.01\ n_{Me}) + (0.23 + 0.02 n_{Me}) n_c + (0.80 - 0.06\ n_{Me})\ n_r$	(4.09)
	$\alpha = (0.54 - 0.05\ n_{Me}) + (0.03 + 0.00 n_{Me}) n_c + (-0.19 + 0.03\ n_{Me})\ n_r$	(4.10)

The values of log B and α calculated according to the above equations (4.05 to 4.10) are in good agreement with the values obtained from the plots of figures (4.4.1 to 4.4.6).

The values of log B and α given for isobutyric acid and isovaleric acid indicate that the contribution of the side chain carbon atom is dependent on the position of the straight chain carbon atom to which the side chain carbon atom is attached.

Since the contribution of n_c to log B and α is

essentially additive for the homologous series in a solvent or a group of closely similar solvents (benzene, toluene and xylene) , it appears that the contribution to the overall free energy change due to the interactions, is essentially additive in such cases. However, when a wider range of solutes is considered in different solvents, constitutive effects also become effective. It also appears that the overall free energy change due to the interactions for the systems studied is practically not influenced by isomeric solvents as indicated from the results with o-, m-and p-xylenes.

The sorption equation (4.04) is similar to a distribution equation. Hence, sorption phenomena may be viewed upon as a distribution equilibrium of the solute between two immiscible phases. The two immiscible phases here are the solvent phase and the " resin " phase, which may be imagined as the second solvent phase.

Hence, the sorption equilibria should show close resemblance to distribution equilibria of the solutes studied in the solvents used. With this in view, the distribution equilibria of such acids between water and organic solvents were studied at room temperatures and are described in the next section.

4.5 Distribution equilibria of some monocarboxylic acids :

4.5a Introduction :

Archibald (22) studied distribution of six straight chain monocarboxylic acids from formic to caproic acid between water and ethyl methyl ketone, tertiary amylalcohol, secondary butylalcohol, normal butylalcohol and normal amylalcohol at 25°C. Angelescu and Dutchievici (23) determined the hydration of several electrolytes by the distribution of aliphatic acids between water and benzene.

Bekturov (24,25) studied the effect of temperature on distribution coefficients of acetic acid and formic acid between water and organic solvents such as benzene, carbon tetrachloride and chloroform. The K ($K = C_w / C_o$) for formic acid in all systems increased with decrease in the formic acid concentration progressively at 0°, more slowly at 25° and very slowly at 60°. An increase in temperature decreases the K for the mixture with the same total concentration of formic acid, because the solubility of latter increases much more rapidly in an organic solvent than in water. The K for low acetic acid concentration in first 2 systems decreases with an increase of temperature from 0° to 60° and was practically independent of temperature at high concentration below 25°. Above 25°, the K for acetic acid concentration also decreases in the 1st and was unchanged in 2nd system. The K for low acetic acid concentration slowly increases with temperature.

The effect of temperature on the distribution

coefficient of propionic, n-butyric, isobutyric and isovaleric between water and benzene was very small and the direction of the change in coefficients was different at different concentrations. In no case was direct proportionality noticed between the changes in the distribution coefficient and temperature. A definate relation between Cw/Co and temperature for one interval of Cw/Co cannot be used in another interval of concentration of the same system.

Moelwyn-Hughes (26) studied the distribution of acetic acid between benzene and water over a wide temperature range at low concentration range. He assumed that the acid forms dimer in benzene layer and considered the following two equilibria :

$$A_1,w \rightleftharpoons A_1,b \quad ; \quad K_1 = A_1,b \; / \; A_1,w \qquad (4.11)$$

$$A_2,b \rightleftharpoons 2A_1,b \quad ; \quad K_2 = (A_1,b)^2 / A_2,b \qquad (4.12)$$

$$\text{or} \qquad Cb / Cw = K_1 + (2K_1^2 / K_2) Cw \qquad (4.13)$$

Moelwyn-Hughes and his coworkers (27) also showed that when a monobasic acid ionises to an extent α in H_2O and forms a dimer in 2nd solvent (s) with which the aqueous solution is in equilibrium, the total concentrations Cw and Cs, in the water and in the 2nd solvent are related to each other as follows :

$$\frac{Cs}{Cw(1-\alpha)} = K_1 + \frac{2K_1^2}{K_2} \; Cw \; (1 - \alpha) \qquad (4.14)$$

This equation satisfactorily accounts for the distribution of acetic acid between water and hexane,benzene,carbon tetrachloride,carbon disulfide and nitrobenzene and of propionic acid between water and petroleum ether, carbon tetrachloride,benzene,chloroform,trichlorobenzene and nitrobenzene. The increase in internal energy attending the dissociation of the dimer which is 14.5 KCal, in vapor phase is about 9 in typical unionising media such as benzene, hexane and petroleum ether and about 6 in ionising solvents such as chloroform,trichlorobenzene and nitrobenzene. The results for 2 acids and 8 solvents were consistant with the view that the force of attraction between the constituents of the dimers is principally if not entirely,electrostatic.

Togliavini and Manfredo (28) gave a brief comment on literature data, especially for the system of water-benzene with acetic acid, propionic acid, morpholine, trimethylamine and pyridine ; and tertiary butylalcohol, ethylalcohol,isopropylalcohol,methylalcohol,butylalcohol, and propylalcohol. The temperature effect on the distribution of above substances between water and benzene and their action on the miscibility of the latter is perticularly discussed.

Sandell (29) studied the distribution of a number of organic compounds between water and organic solvents with the help of paper chromatography. Paper chromatography of aromatic compounds showed that the chromatographic process is mainly a distribution procedure and can be used

to evaluate the distribution coefficients.

Mittra (30) studied the effect of some comman inorganic electrolytes on distribution of acetic acid between water and benzene.

Tokareva and Koziov (31,32) studied the distribution of acetic acid between water and organic solvents such as diethyl ether, ethylacetate,benzene, xylene,toluene and dichloroethane and showed the effect of concentration (0.5 - 10 %) and temperature (20^{0}, 40^{0}, 60^{0} and at boiling). In diethyl ether, dethylacetate and butylacetate,the acetic acid appears as a monomer and in benzene,xylene,toluene and dichloroethane as dimer.

The distribution of propionic and butyric acid between water and diethyl ether,ethylacetate and benzene at 20^{0}, 40^{0},60^{0} and at boiling was also studied in same concentration range. In the expression for solvent / water distribution, $K = X^{1/n} / Y$ where n was 2.184 for propionic acid and 1.795 for butyric acid in the benzene-water system. The acids were not associated. K increases with temperature in diethyl ether and benzene but decreases in ethyl acetate.

Vignes (33) studied the equlibrium distribution of acetone,acetic acid,propionic acid and butyric acid between water and various organic solvents and expressed the distribution coefficient and interfacial tension with an empirical relation.

Kuznetsov and his coworkers (34) studied the

equilibrium distribution of acetic acid,propionic acid and butyric acid between water and organic solvents at $5\text{-}20 \pm 0.1^{0}$ over a wide range of concentration.

$$K = a.C_{org.}^{x} \qquad (4.15)$$

Within limited concentration range x was constant and it was same for acetic acid,propionic acid and butyric acid with benzene as extracting solvent since the log Corg. against.log K plots were parallel lines. For benzene $x = 0.45$ and $a = 3.68 \times 10^{15} M^{-7.82}[1 + 0.005 (20-t)]$ where M is molecular weight of acid and t is the temperature.

It was considered to be of interest to compare the results of sorption equilibria given in section (4.4) with results of the distribution equilibria for the acids between water and organic solvents. The following gives the study of distribution equilibria of propionic acid, n-butyric acid,n-valeric acid, n-caprioic acid,phenylacetic acid,isobutyric acid and isovaleric acid between water and organic solvents (n-hexane,cyclohexane, benzene,toluene, o-xylene,m-xylene and p-xylene) at room temperature (28 ± 2^{0}).

4.5 b Experimental :

Chemicals : The chemicals used were of A.R. or C.P.grade.

Solvents : The solvents used were of C.P.grade and were distilled before use.

Procedure : Acid solution,either in water or in organic solvents, of known volume was mixed with known volume of

other solvent in well stoppered separating funnels, with frequent shaking, at room temperature (28 ± 2^{0}). After over night, the equilibrium concentration in water layer and in organic layer was estimated by titrating aliquots with standard sodium hydroxide solution. Preliminary work had indicated that this period was sufficient for the establishment of distribution equilibrium.

4.5c Nomenclature :

Co, Cw = equilibrium concentration of the acid in organic layer and in water layer respectively, in gram equivalents per liter.

K = $Co^{1/2} / Cw$

K_1, K_2 = equilibrium constants.

4.5d Results :

The results are described in tables (4.5.1 to 4.5.8) and figures (4.5.1 to 4.5.7).

Table 4.5.1

Distribution of monocarboxylic acids between water and n-hexane

Acid	10^2 Cw	10^2 Co	Co/Cw	$Co^{1/2}$ / Cw
Propionic	5.094	0.0674	0.01323	0.5100
	7.570	0.1582	0.0209	0.5256
	11.27	0.3560	0.0316	0.5291
n-Butyric	6.561	1.363	0.2077	1.779
	9.086	2.625	0.2889	1.782
	13.98	5.951	0.4107	1.746
n-Valeric	3.079	4.669	1.516	7.018
	3.963	7.672	1.936	6.988
	5.148	13.02	2.529	7.009
n-Caproic	0.5552	2.701	4.864	29.59
	0.8632	6.462	7.519	29.45
	1.295	14.81	11.44	29.72

Table 4.5.1 (Continued)

Acid	10^2 Cw	10^2 Co	Co/Cw	$Co^{1/2}$ / Cw
Phenylacetic	1.469	0.2524	0.1718	3.420
	2.791	0.7066	0.2532	3.011
	5.118	2.088	0.6469	2.823
Isobutyric	6.033	1.716	0.2845	2.172
	8.405	3.256	0.3874	2.147
	12.52	6.992	0.5584	2.112
Isovaleric	3.383	4.316	1.276	6.140
	4.391	7.193	1.638	6.106
	5.962	13.45	2.246	6.131

Table 4.52

Distribution of monocarboxylic acids between water and cyclohexane

Acid	10^2 Cw	10^2 Co	Co / Cw	$Co^{1/2}$ / Cw
Propionic	5.00	0.0750	0.0150	0.5476
	11.32	0.3957	0.0350	0.5558
	18.00	0.9759	0.0540	0.5488
n-Butyric	6.512	1.414	0.2171	1.826
	9.036	2.675	0.2961	1.810
	13.88	6.310	0.4545	1.809
n-Valeric	2.902	4.846	1.669	7.634
	3.600	7.200	2.000	7.452
	4.897	13.27	2.711	7.463
n-Caproic	0.5098	2.776	5.447	32.68
	0.7823	6.512	8.333	32.60
	1.173	14.71	12.54	32.68

Table 4.5.2 (Continued)

Acid	10^2 Cw	10^2 Co	Co / Cw	$Co^{1/2}$ /Cw
Phenylacetic	1.818	0.5984	0.2742	3.885
	3.352	1.603	0.4783	3.778
	5.916	4.890	0.8264	3.738
Isobutyric	5.932	1.767	0.2979	2.259
	8.228	3.433	0.4171	2.251
	12.16	7.345	0.6039	2.228
Isovaleric	3.256	4.442	1.364	6.473
	4.215	7.370	1.748	6.444
	5.705	13.73	2.407	6.498

Table 4.5.3

Distribution of monocarboxylic acids between water and benzene

Acid	10^2 Cw	10^2 Co	Co/Cw	$Co^{1/2}$ / Cw
Propionic	6.969	0.8071	0.1158	1.289
	10.24	1.450	0.1417	1.176
	16.36	3.199	0.1955	1.093
n-Butyric	4.697	3.188	0.6765	3.795
	6.403	5.534	0.8696	3.673
	9.177	10.59	1.154	3.546
n-Valeric	1.566	5.658	3.614	15.19
	1.985	8.915	4.493	15.05
	2.681	15.44	5.757	14.65
n-Caproic	0.4197	7.295	17.38	64.39
	0.5723	13.13	22.96	63.40
	0.7365	20.97	28.47	62.21

Table 4.5.3 (Continued)

Acid	$10^2 Cw$	$10^2 Co$	Co/Cw	$Co^{1/2} / Cw$
Phenylacetic	0.9759	2.818	2.887	17.20
	1.489	6.105	4.098	16.58
	2.216	12.85	5.801	15.45
Isobutyric	3.953	2.912	0.7407	4.318
	5.348	4.991	0.9346	4.177
	7.642	9.501	1.244	4.034
Isovaleric	1.937	5.503	2.839	12.11
	2.496	8.668	3.472	11.80
	3.263	14.21	4.353	11.55

Table 4:5.4

Distribution of monocarboxylic acids between water and toluene

Acid	$10^2 Cw$	$10^2 Co$	Co/Cw	$Co^{1/2}/Cw$
Propionic	4.234	0.3331	0.07874	1.363
	8.275	0.9179	0.1109	1.158
	16.11	2.660	0.1652	1.013
n-Butyric	3.360	1.473	0.4384	3.612
	5.803	3.739	0.6151	3.331
	9.696	9.463	0.9804	3.174
n-Valeric	1.480	4.412	2.980	14.18
	2.310	9.947	4.308	13.65
	3.512	21.72	6.185	13.27
n-Caproic	0.4487	7.129	15.89	59.48
	0.6050	12.67	20.93	58.82
	0.7668	19.45	25.37	57.51

Table 4.5.4 (Continued)

Acid	$10^2 Cw$	$10^2 Co$	Co / Cw	$Co^{1/2} / Cw$
Phenylacetic	1.274	2.901	2.279	13.38
	2.019	7.176	3.394	12.96
	2.949	14.09	4.780	12.73
Isobutyric	2.813	1.295	0.4606	4.047
	4.595	3.032	0.6598	3.789
	6.266	5.215	0.8333	3.643
	7.709	7.519	0.9804	3.558
Isovaleric	1.187	1.924	1.621	11.69
	1.966	4.826	2.455	11.17
	3.132	11.34	3.619	10.75

Table 4.5.5

Distribution of monocarboxylic acids between water and o-xylene

Acid	10^2 Cw	10^2 Co	Co / Cw	$Co^{1/2}$ / Cw
n-Butyric	5.371	2.702	0.5020	3.054
	7.466	4.622	0.6192	2.879
	10.78	9.196	0.8547	2.812
n-Caproic	0.4384	5.618	12.82	54.09
	0.5902	10.05	17.03	53.70
	0.7821	17.06	21.81	52.82
Isobutyric	5.048	2.749	0.5447	3.284
	6.898	4.810	0.6974	3.180
	8.557	7.041	0.8264	3.100
Isovaleric	2.248	4.930	2.194	9.901
	2.907	7.870	2.708	9.709
	3.448	10.91	3.164	9.615

Table 4.5.6

Distribution of monocarboxylic acids between water and m-xylene

Acid	10^2 Cw	10^2 Co	Co/ Cw	$Co^{1/2}$ / Cw
Propionic	7.206	0.5723	0.0800	1.051
	10.74	1.028	0.0962	0.9434
	17.30	2.260	0.1306	0.8696
n-Butyric	5.282	2.589	0.4897	3.043
	7.254	4.650	0.6410	2.972
	10.62	9.145	0.8621	2.848
n-Valeric	1.829	5.394	2.949	12.70
	2.356	8.541	3.625	12.46
	3.178	14.95	4.704	12.17
n-Caproic	0.4696	6.619	14.09	54.80
	0.6485	12.01	18.53	53.45
	0.8422	19.49	23.14	52.45

Table 4.5.6 (Continued)

Acid	10^2 Cw	10^2 Co	Co / Cw	$Co^{1/2}$ / Cw
Phenylacetic	1.365	2.465	1.806	11.50
	2.062	5.179	2.513	11.04
	2.965	10.13	3.414	10.73
Isobutyric	4.511	2.356	0.5225	3.403
	4.906	2.722	0.5550	3.362
	6.738	4.743	0.7040	3.232
	8.343	6.887	0.8264	3.145
Isovaleric	2.272	5.169	2.276	10.01
	2.915	8.247	2.830	9.901
	3.814	13.67	3.581	9.709

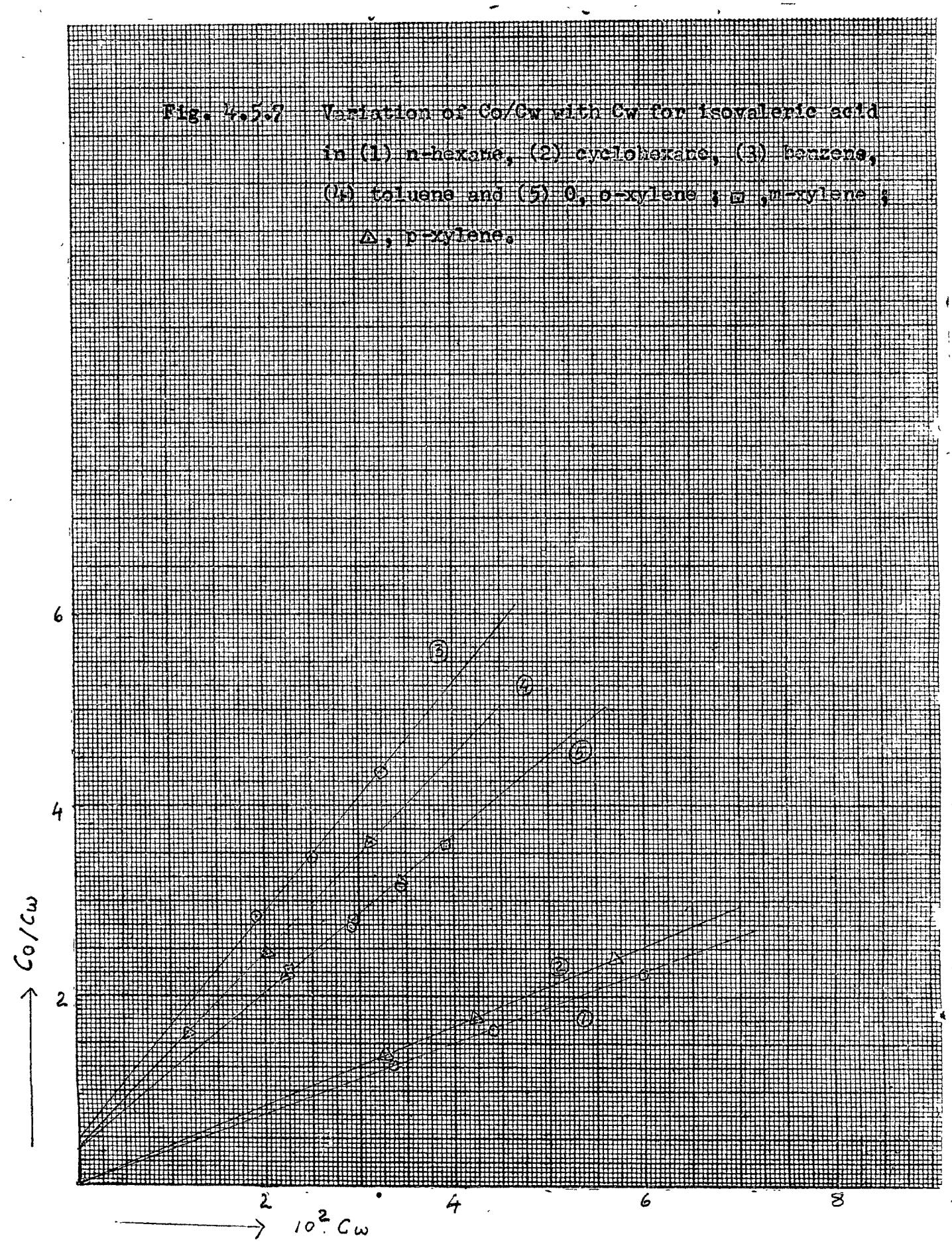


Fig. 4.5.7 Variation of Co/Cw with Cw for isovalenic acid in (1) n-hexane, (2) cyclohexane, (3) benzene, (4) toluene and (5) ○, o-xylene ; □, m-xylene ; △, p-xylene.

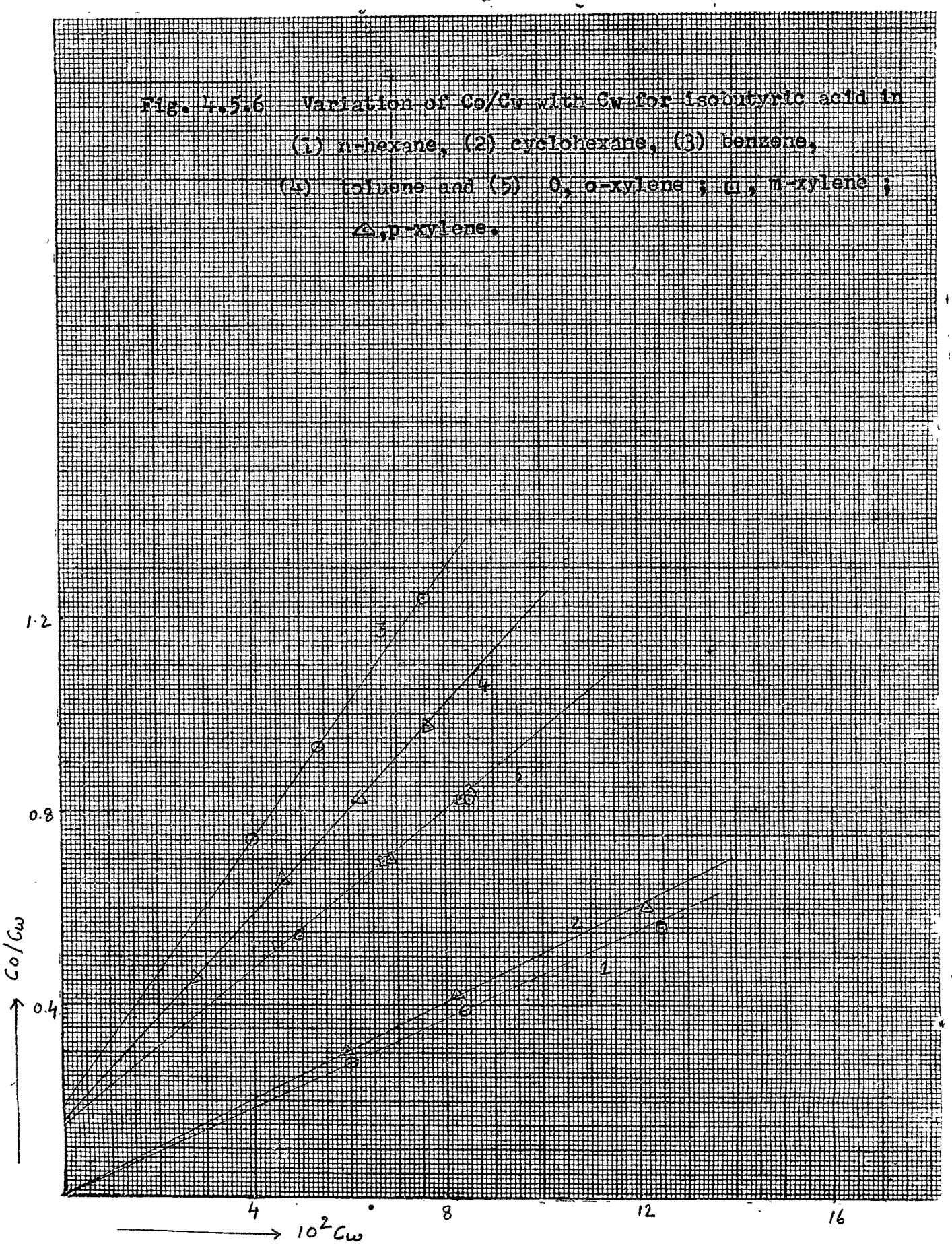


Fig. 4.5.6 Variation of Co/Cw with Cw for isobutyric acid in (1) n-hexane, (2) cyclohexane, (3) benzene, (4) toluene and (5) ○, o-xylene ; □, m-xylene ; △, p-xylene.

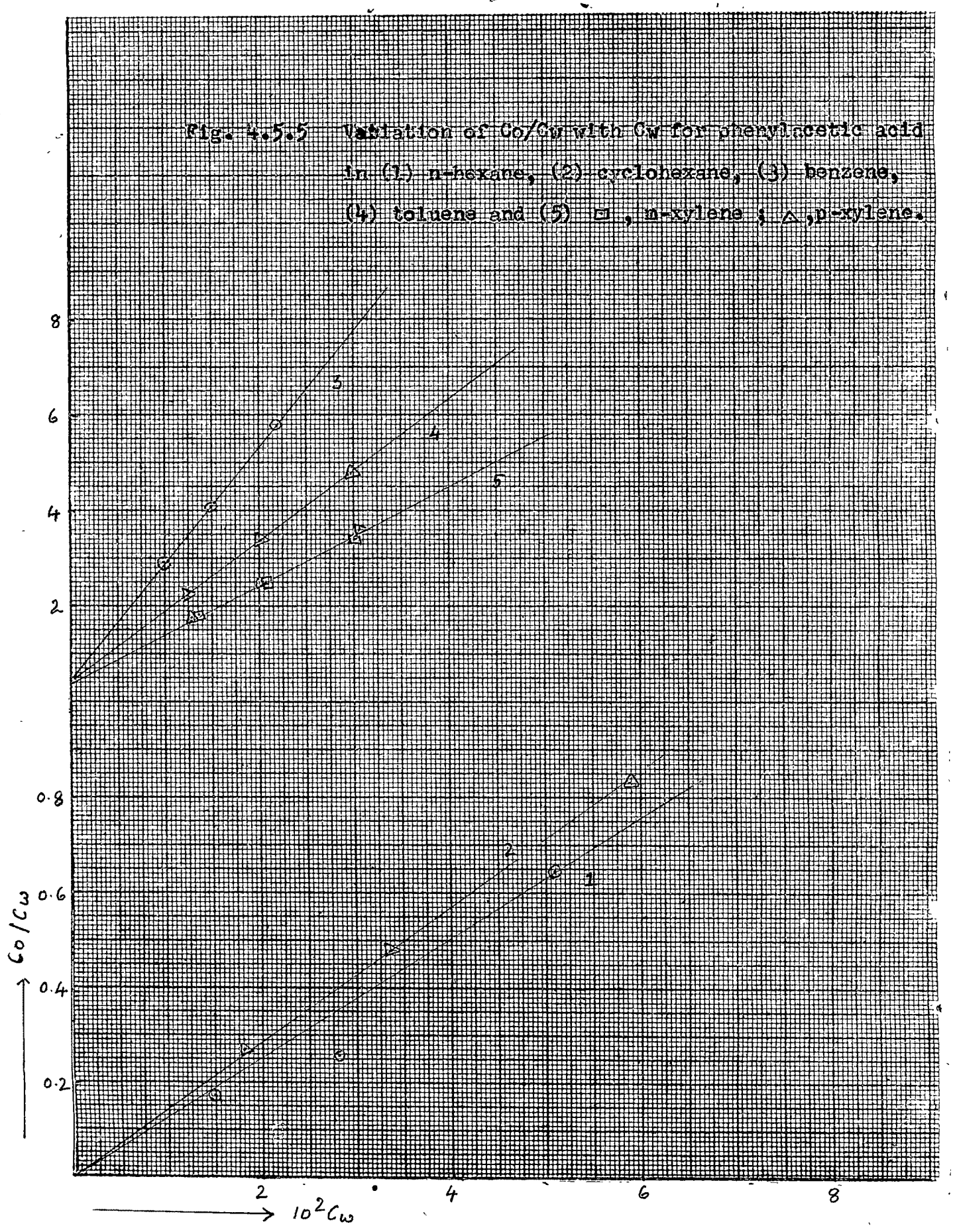


Fig. 4.5.5 Variation of C_o/C_w with C_w for phenylacetic acid in (1) n-hexane, (2) cyclohexane, (3) benzene, (4) toluene and (5) ⊡, m-xylene ; △, p-xylene.

Fig. 4.5.4 Variation of Co/Cw with Cw for n-caproic acid in (1) n-hexane, (2) cyclohexane, (3) benzene, (4) toluene and (5) ⊙, o-xylene ; ⊡, m-xylene ; △, p-xylene.

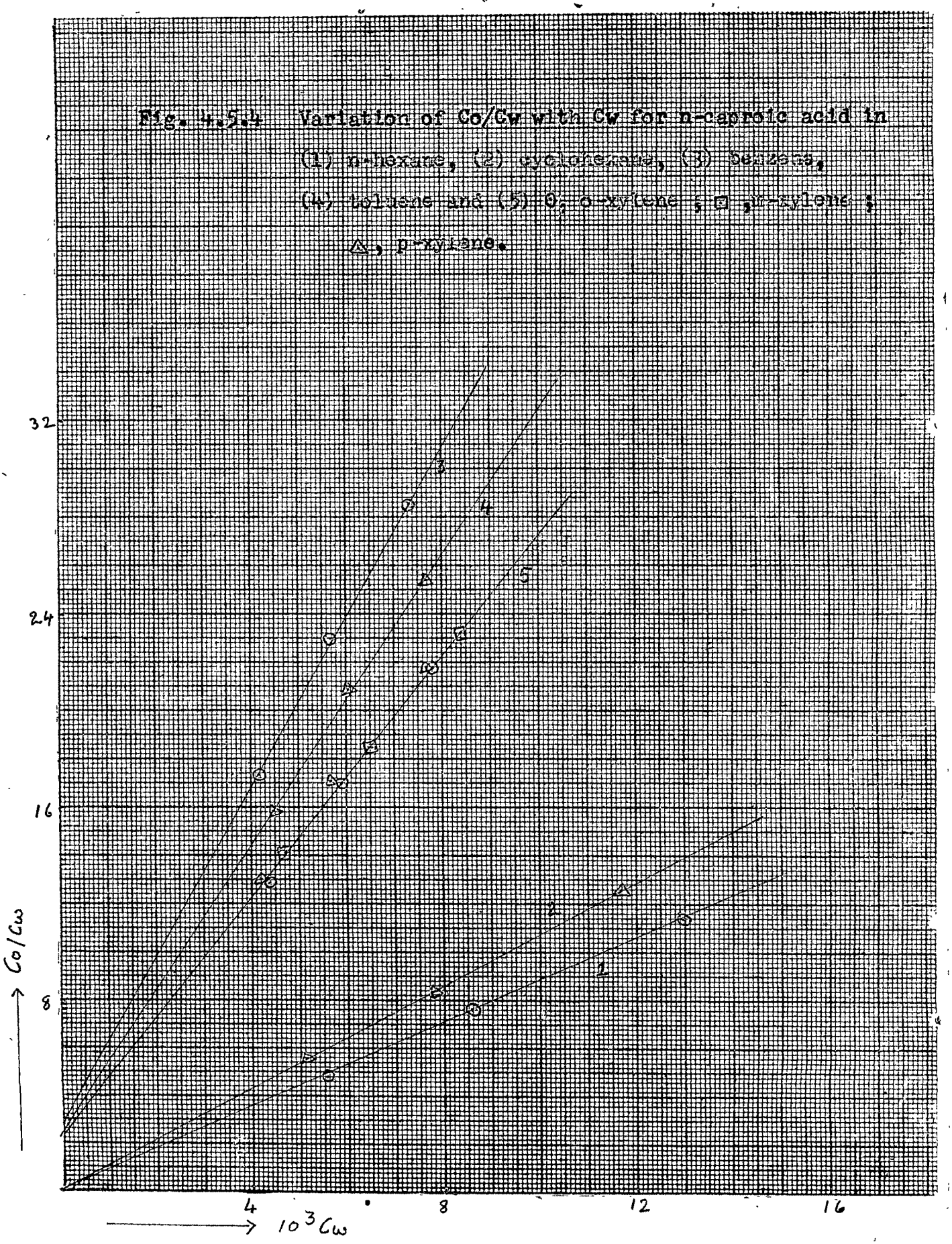


Fig. 4.5.3 Variation of Co/Cw with Cw for n-valeric acid in (1) n-hexane, (2) cyclohexane, (3) benzene, (4) toluene and (5) m-xylene.

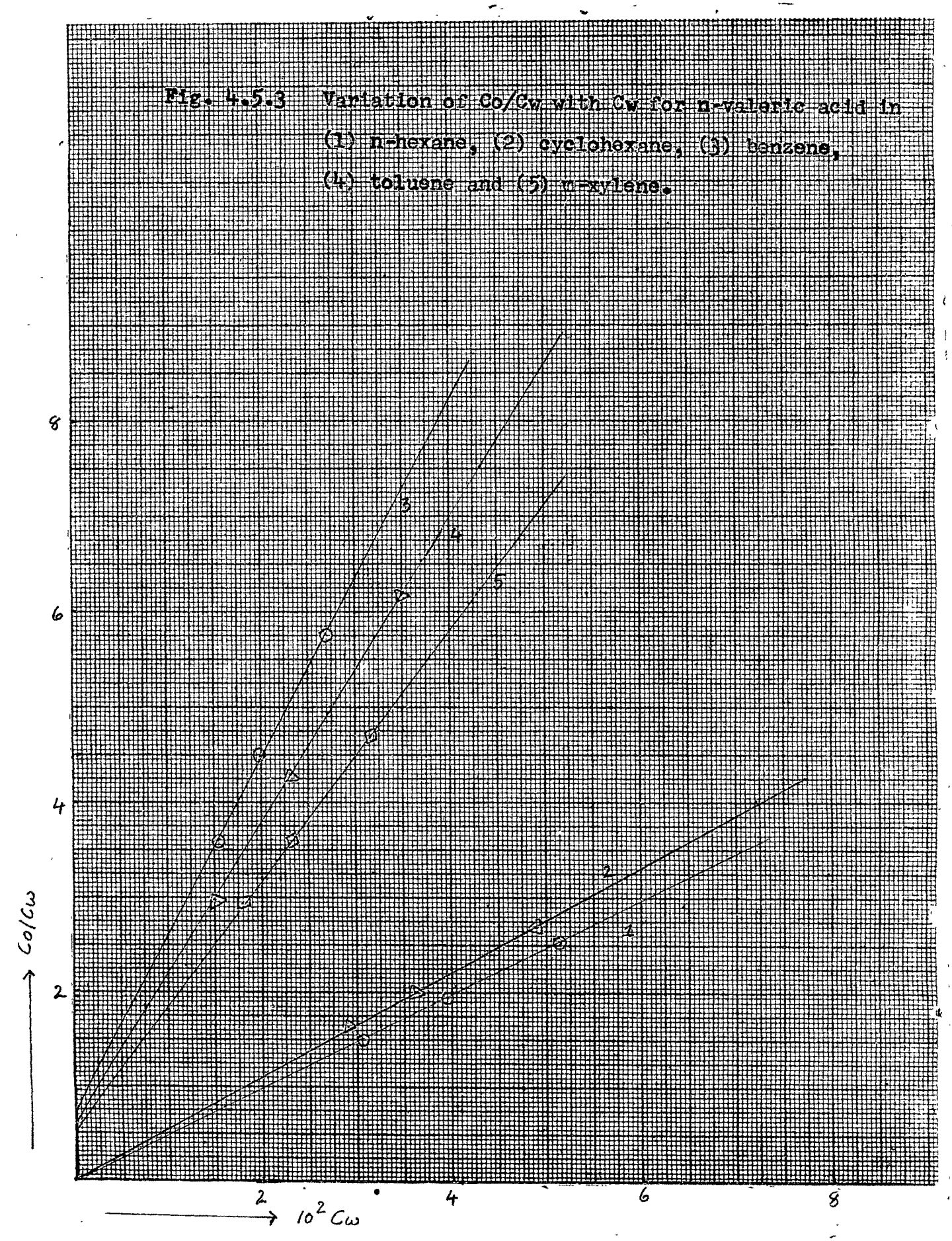


Fig. 4.5.2 Variation of C_o/C_w with C_w for n-butyric acid in (1) n-hexane, (2) cyclohexane, (3) benzene, (4) toluene and (5) o,o-xylene ; □ ,m-xylene ; △, p-xylene.

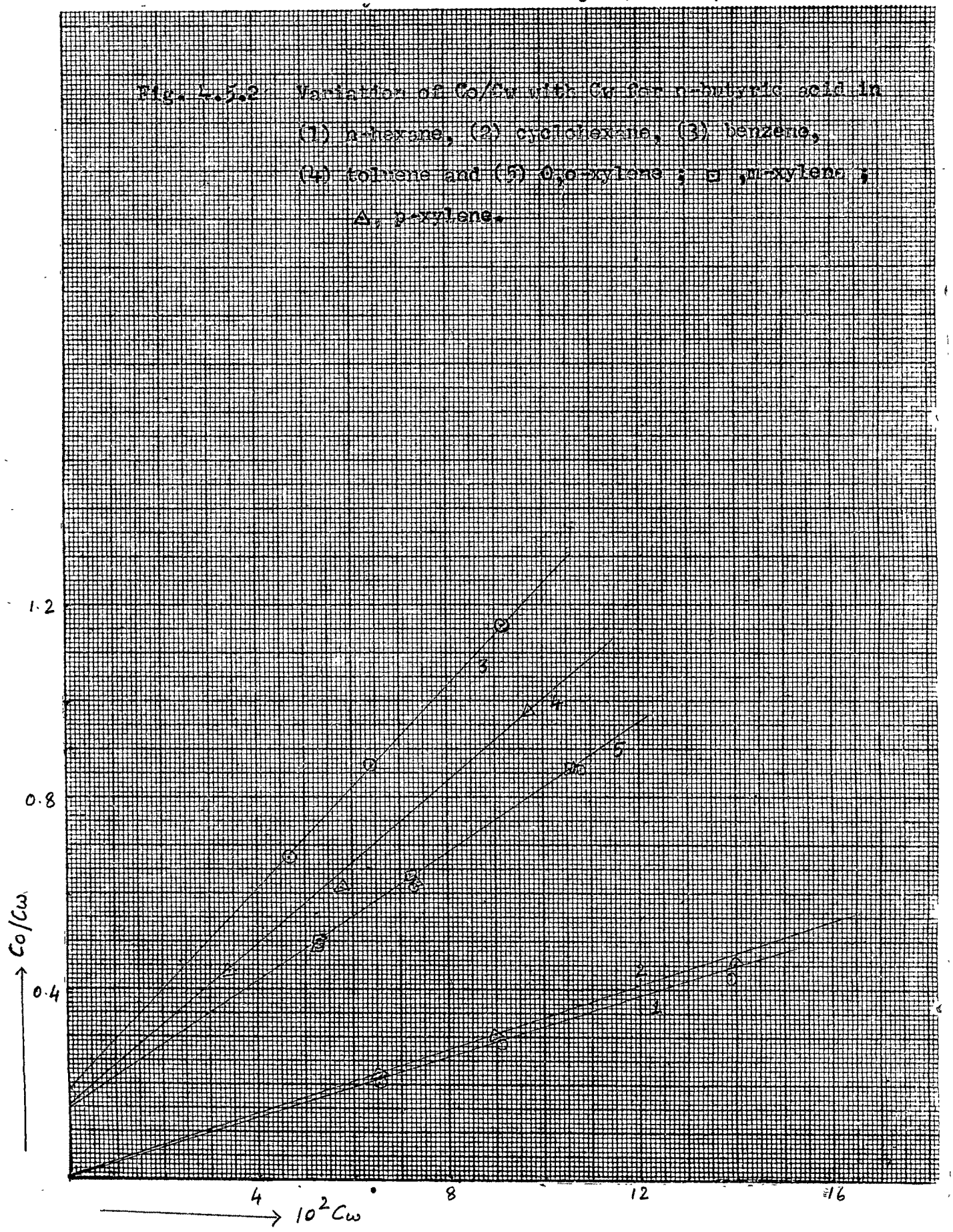


Fig. 4.5.1 Variation of C_o/C_w with C_w for propionic acid in (1) n-hexane, (2) cyclohexane, (3) benzene, (4) toluene and (5) m-xylene.

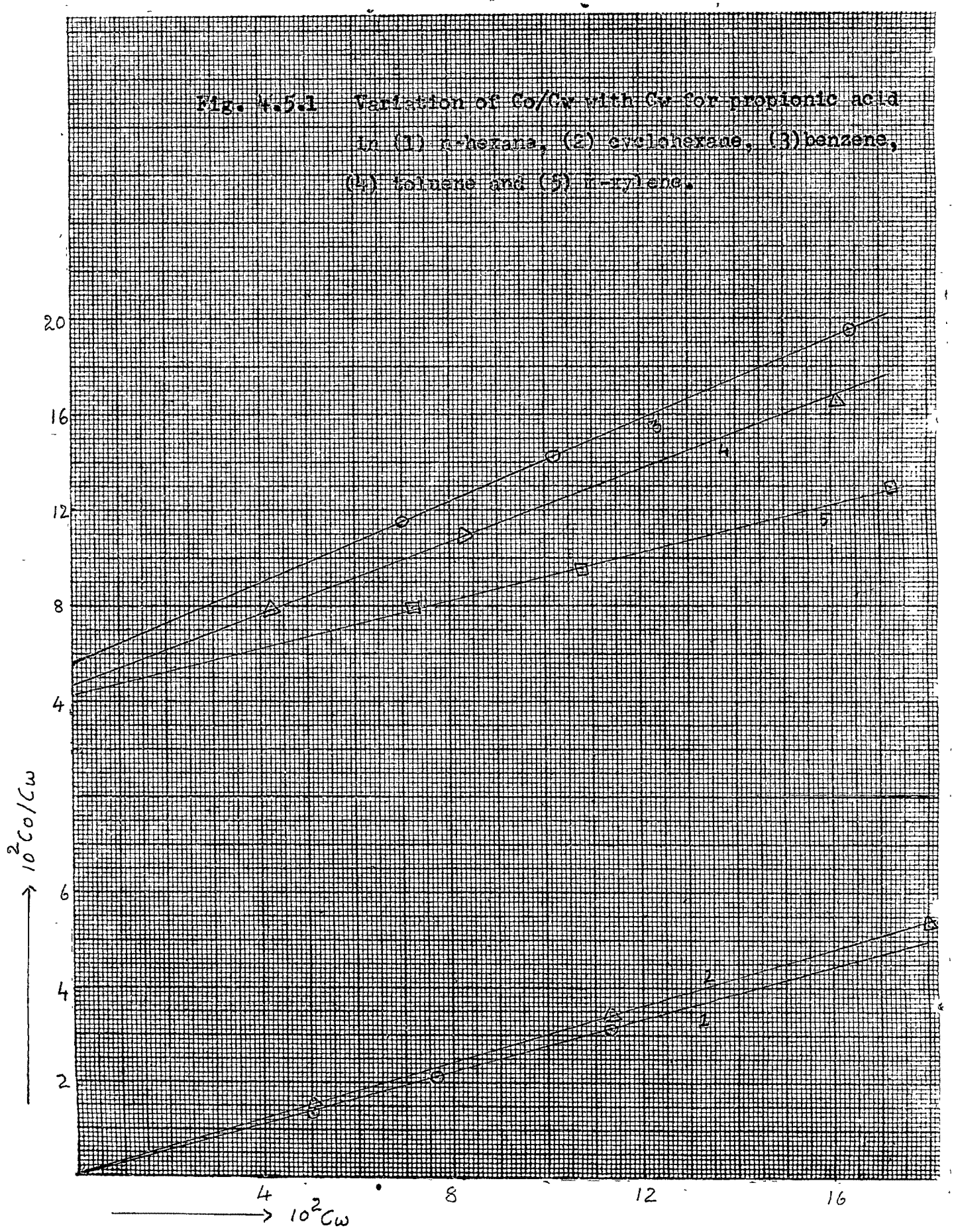


Table 4.5.7

Distribution of monocarboxylic acids between water and p-xylene

Acid	10^2 Cw	10^2 Co	Co / Cw	$Co^{1/2}$ / Cw
n-Butyric	5.371	2.702	0.5020	3.054
	7.442	4.645	0.6239	2.896
	10.74	9.243	0.8621	2.831
n-Caproic	0.4219	5.499	13.05	55.58
	0.5736	9.837	17.15	54.69
	0.7584	16.62	21.91	53.73
Phenylacetic	1.289	2.323	1.802	11.82
	2.019	5.119	2.535	11.20
	3.072	11.21	3.650	10.89
Isobutyric	5.048	2.749	0.5447	3.284
	6.874	4.835	0.7032	3.199
	8.486	7.111	0.8403	3.214
Isovaleric	2.236	4.942	2.210	10.00
	2.883	7.894	2.738	9.804
	3.413	10.94	3.207	9.709

4.5e Discussion :

For the distribution of the organic acids studied between water and an immiscible organic solvent, the following equilibria may be considered :

$$A_1,w \rightleftharpoons[K_1] A_1,o \qquad (4.16)$$

$$A_2,o \rightleftharpoons[K_2] 2A_1,o \qquad (4.17)$$

where K_1 is the distribution equilibrium constant and K_2 is the dissociation constant of A_2 into $2A_1$.

Hence,

$$Co/Cw = K_1 + (2K_1^2 / K_2)\ Cw \qquad (4.18)$$

In case, the second term of the equation (4.18) is much larger than the first term, then as a first approximation,

$$Co^{1/2} / Cw = (2/K_2)^{1/2} \cdot K_1 = K \qquad (4.19)$$

where K is a constant (it is assumed that K_2 is not very substantially altered from acid to acid studied).

Figures (4.5.1 to 4.5.7) give the plots of Co/Cw against Cw for the acids and solvents studied.

It is observed that when the immiscible solvent is n-hexane or cyclohexane, the plots are linear and pass practifally through the origin. This indicates that for such solvents, the value of K_1 is considerably lower than that of the second term in equation (4.18). Hence, the equation (4.19) is applicable and table (4.5.8) gives the values of log K calculated from the slopes of these plots.

In Figures the values of Co/Cw and pH

Table 4.5.8

Values of log K , log K_1 and K_2 obtained from figures (4.5.1 to 4.5.7)

Solvent	n-Hexane	Cyclohexane	Benzene		Toluene		Xylene (o; m- or p-)	
Acid	log K	log K	log K_1	$10^3 K_2$	log K_1	$10^3 K_2$	log K_1	$10^3 K_2$
Propionic	-0.2688	-0.2543	-1.2518	7.466	-1.3279	5.970	-1.3768	7.053
n-Butyric	+0.2525	+0.2657	-0.7212	6.910	-0.7959	6.094	-0.8239	6.720
n-Valeric	+0.8451	0.8702	-0.1249	6.049	-0.1871	5.347	-0.2596	4.618
n-Caproic	+1.4722	1.5126	+0.4771	5.201	+0.3979	4.207	+0.3617	4.283
Phenylacetic	+0.5503	0.5761	-0.3010	2.066	-0.3468	2.755	-0.3979	3.137
Isobutyric	0.3314	0.3495	-0.7212	5.232	-0.7959	4.741	-0.8239	5.49
Isovaleric	0.7841	0.8116	-0.3010	4.767	-0.3468	3.970	-0.398	3.98

In figures (4.5.1 to 4.5.7) the values of Co/Cw are plotted against Cw for the acids studied when the organic solvent is benzene, toluene, o-xylene, m-xylene or p-xylene. From these plots, the values of intercepts on y-axis and slopes are obtained and from these the values of log K_1 and K_2 are calculated and are given in table (4.5.8).

The values of log K, when the organic solvent used is n-hexane or cyclohexane and log K_1 when the organic solvent used is benzene, toluene or o-, m- or p-xylene, may be given by the following equations :

Solvent	Equation	
n-Hexane	$-\log K = 0.875 - 0.58\ n_c - 1.42\ n_r$	(4.20)
Cyclohexane	$-\log K = 0.875 - 0.585\ n_c - 1.45\ n_r$	(4.21)
Benzene, Toluene, Xylene	$-\log K_1 = (1.86 + 0.08\ n_{Me}) - (0.58 + 0.005\ n_{Me})\ n_c - (1.55 + 0.03\ n_{Me})\ n_r$	(4.22)

The values of log K or log K_1 calculated from the above equations (4.20 to 4.22) are in good agreement with the values obtained experimentally.

The results in the table (4.5.8) giving values of log K_1 indicate that the values are essentially same for o-, m- and p-xylene. This implies that the change of an organic solvent for the isomeric solvent does not significantly alters the value of log K_1.

The results for isobutyric acid and isovaleric acid indicate that the contribution of the side chain carbon atom depends on the position of the straight chain carbon atom to which the side chain carbon atoms is attached.

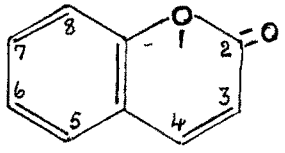
It appears that for a homologous series in an organic solvent (or a group of closely related organic solvents)-water system, the value of log K or log K_1 is essentially a linear function of n_c . This should imply that the over all free energy change is, in such cases, essentially a linear function of n_c . However, when a wider range of acids are studied in different solvents, the constitutive effects also become significant.

A comparison of the results for the distribution of the acids between the organic solvent and water from this section and the results of the sorption studies of the acids by the ion exchanger in organic solvents given in the previous section indicates that there is a close similarity between the two sets of results. One may hence, view the sorption phenomenon also as a distribution of the solute between two immiscible phases, where one immiscible phase is " resin" phase instead of water phase.

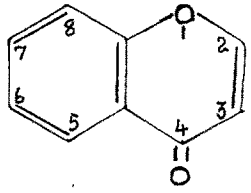
4.6 Sorption of coumarins

4.6.1 Introduction : (35,36)

The fusion of a pyrone ring with a benzene nucleus gives rise to a class of heterocyclic compounds known as benzopyrones, of which two distinct types are recognized : (1) benzo-α-pyrones commanly called coumarins and (2) benzo-γ-pyrones, called chromones, the latter differing from the former only in position of the carbonyl group in the heterocyclic ring.



Benzo-α-pyrone



Benzo-γ-pyrone

Representatives of these groups of compounds are found to occur in the vegitable kingdom, either in the free or in the combined state. Coumarin, the parent substance of the benzo-α-pyrone group, was first isolated from tonkabeans in 1820. Several coumarin derivatives have been found to be widely distributed in the plant kingdom. Particularly the plant belonging to the natural orders of orchidaceae Leguminoceae, Rutaceae, Umbelliferae and Labiatae are rich sources of naturally occuring coumarins.

Synthetic uses of coumarins :

Coumarin and its derivatives are substances of potential value for synthetic purposes. Their easy accessibility opens the way through suitable reactions to the synthetic preparation of other heterocyclic compounds,

such as coumarones, furanocoumarins (or furocoumarins) chromons-α-pyrone, flavano-α-pyrones and chromones as well as natural products containing such ring systems.

Physiological action of coumarins :

Coumarins have been found to be physiologically effective for animals as well as man. It has been observed that coumarin acts as a narcotic for rabbits,frogs, earthworms and many other animals. It is a sedative and hypnotic for mice. It has toxic effect on man as well as dog.

Some hydroxy coumarins possessing the power of absorbing ultraviolet light are extensively used as medicinals in skin diseases. Some coumarins in the plant play the important role of protecting the plant from harmful effect of the short-wave rediation.

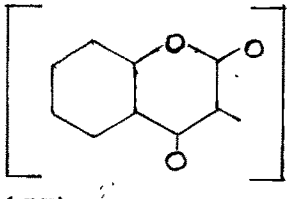
4.6.2 Ultraviolet absorption spectra of coumarins

4.6.2 a Introduction :

Tasaki (37) studied the absorption spectra of the substituted coumarins in alcoholic solution. Coumarin, hydroxy-and methoxycoumarins, dihydroxycoumarin, esculin, esculetin, acetylcoumarin, diacetylesculatin and methylenedihydroxyphenyl coumarin were studied. Coumarin showed two absorption maxima. When one or two hydroxy groups were introduced into the benzene nucleus of coumarin the substance showed only one absorption maximum.

Mangini and Passerini (38) have reported the ultraviolet absorption maxima and log ϵ for coumarin (I) its 3-,4-, 5-, 6-, 7-, 8-Me, 3-, 4-, 6-, 7-Cl and 3-, 4-, 6-, 7-MeO derivatives in ethanol, C_6H_{14}, 60 % $HClO_4$ or H_2SO_4 (1 : 10^5). I and the 3-, 5-, 6-, 7- and 8-Me derivatives showed maxima at 282-86 mμ, logϵ 3.95-4.02 ; the 4-Me derivative at 287 mμ log ϵ 3.55 .

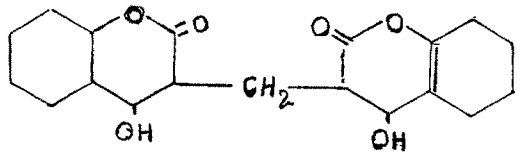
Examination of ultraviolet spectra by Chmielewska and Ciecierska (39) showed that the three substituted derivatives of 4-hydroxycoumarin in 96 % ethanol were completely ionized with the formation of an



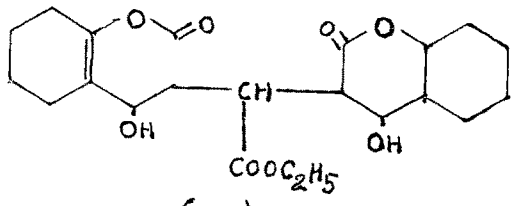
ion, Dicoumarol (I)

and Pelenten (II) under similar conditions did not form ions

of this type. The results, though not sufficient to prove the ketal structure of I and II, were considered to show that in ethanol both I and II given below, must occur in tautomeric form.



(I)



(II)

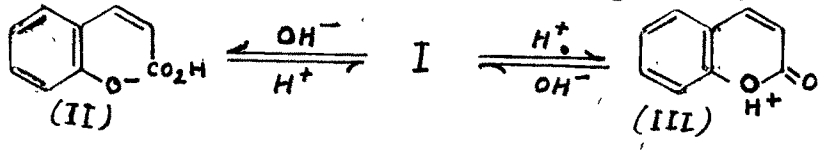
5-, 6- and 7-hydroxy (I), methoxy-(II), methyl-(III) and acetoxycoumarins (IV) and 5,7-, 6,7- and 7,8-dihydroxy(V), dimethoxy (VI), dimethyl (VII), and diacetoxy (VIII) coumarins were prepared by Nakabayashi, Tokoroyama, Miyazaki and Isono (40) and the ultraviolet absorption spectra were determined in 95% ethanol (III), (IV), (VI), and (VIII) showed spectra similar to that of coumarin, irrespective of the position or number of the substitutents ; (I), (II), (IV) and (VI) on the other hand showed complicated spectra according to the position and number of substitutents present. On the assumption that the two absorption bands of coumarin at 270 and 312 mμ, were those of benzene around 200 and 240-260 mμ that had shifted to these regions the ultraviolet absorption$ spectra of these coumarins derivatives were qualitatively explained according to the latest theory regarding light absorption.

Jacobson and Amstutz (41) recorded ultraviolet absorption spectra of a series of thirteen new coumarins and

concluded that neither addition of the 4-methyl group nor of the 6-alkyl groups have significant effect on the spectra.

Goodwin and Pollock (42) studied the ultraviolet absorption spectra of a series of coumarin derivatives for use as a clue to the identification of unknown fractions isolated from the roots. They concluded that saturation of the double bond at the 3,4-position in the coumarin neclues greatly reduces absorption at wavelength larger than 300 mμ, secondly 4-Me substitution has very little effect upon the absorption and thirdly there is a great similarity between the absorption spectra of hydroxy derivatives and their ethers.

Cingolani (43) studied the ultraviolet absorption spectra in ethanol, 0.1 NaOH and 60 % $HClO_4$ solution of coumarin (I), and its following derivatives, 3-Me, 3-Me-6-MeO, 3-Me-7-MeO, 3-Me-8-MeO, 3-Me-6, 7-diMeO, 3-Me-6, 8-diMeO, 4-Me, 4-Me-6-MeO, 7-MeO, 4-Me-5,7-diMeO, 4-Me-6,7-diMeO and 4-Me-7,8-diMeO and have given interpretation in terms of electronic structures. Variations of spectra in acid and alkaline solutions agree with the possibility that coumarins could ionize as bases or acids (by ring opening). Spectra in alcoholic solution were attributed to I, in 0.1 N NaOH to II and 60 % $HClO_4$ to III. I, 3-Me-I and 4-Me-I gave similar spectra in alcohol with a strong band at 265-275, and a weak band at 325-75 mμ. The position of MeO in the ring influences the spectra. 6-MeO derivatives caused bathochromic shifts in the 1st band below 250 mμ. ; 8-MeO derivatives caused hypsochromic shifts. The maxima band of all 3-Me-I derivatives were shifted to greater λ in contrast



(II) (III)

with 4-Me-I derivatives. The position of the Me caused a shift to greater λ. This was evident when with the lactone form of 3-Me-I derivatives and explained by admitting that the equillibrium for 3-Me-I is shifted toward quinoid form, where as with 4-Me-I it was shifted to nonquinoid form.

Cingolani (44) examined the ultraviolet absorption spectra in ethanol, in 0.1 N NaOH, and after acidification of alkaline solution for coumarin and the following derivatives :- 4-Me-8-OH, 8-OH, 4-Me-5, 8-$(OH)_2$, 3-Me, 4-Me, 4-Me-6-OH-5,7-$(MeO)_2$ and 4-Me-5-OH. The curves are characteristic enough for any of these compounds to be identified in an unknown solution, especially if the behaviour in alkaline solution is examined, since the lactone ring opens and the hydroxy cinnamic acid formed isomerizes at different rates according to structures. After isomerization the original lactone can only be recovered by acidification if a 5-OH group is present. In ethanol the 275 and 310 mμ. bands of coumarin were shifted to longer λ by 6-OH or 6-Me, and to shorter λ by 5-or 8-OH or Me alone. Both 5 and 8 substituents together give bands for Me at 228, 293 and 343 mμ. 7-OH or Me gives a single band at 310-30 mμ.

Ganguly and Bagchi (45) studied the ultraviolet absorption maxima and log ϵ for coumarin (I), 3-Me(I), 3,4-diMe (I), 4,8-diMe(I) and 4,6-diMe(I) in 95 % ethanol solution. Absorption measurement in region 220-340 mμ showed that it is possible to distinguish between them on the basis

of absorption characteristics. A methyl group present w either in the benzene or in the pyrone ring fails to show any significant change in the absorption properties of the parent compound.

Sen and Bagchi (46) studied the ultraviolet absorption spectra of coumarin (I), 7-OH(I), 7-OH-4-Me(I), 6-OH-4-Me(I), 4-OH(I), 4-OH-3-Me(I), 3-OH(I) and 5-OH-4-Me(I) in ethanol. Absorption spectra of coumarin a substituted by hydroxy groups in the aromatic as well as in the heterocyclic neclues in different positions showed bathochromic shift in the position of one or more of the principal bands.

Shah and Bafna (47) studied the ultraviolet absorption spectra of methyl-, methoxy-, and hydroxy-coumarins in methanol in the range 250-350 mμ. The absorption maxima were almost same for hydroxy- and methoxycoumarins, if t he substituent was in 5,6,7 or 8 position ; however, the substituents position (5 or 8), 6 or 7 could be distinguished. It was possible to distinguish isomeric monomethyl- and dimethylcoumarins from a study of their ultraviolet absorption data.

From the above it appears that the ultraviolet absorption provides a convenient and useful method for the estimation of coumarins in dilute solution. The effect of change of medium from water to methanol or ethanol on maxima and log ϵ values appears to be relatively small; however, this was further investigated by studing the ultraviolet absorption spectra of some substituted coumarins

in 10 % methanol and methanol. These are described below.

4.6.2 b Experimental :

Chemicals : The substituted coumarins were obtained from Prof. S.M.Sethna's laboratory and were recrystallised from ethanol and checked for melting point. 10 % methanol (by volume) and pure methanol were used.

Procedure : The stock solution of coumarins were first prepared by dissolving known weights of coumarins in known volumes of pure methanol and the concentrations were calculated from weights. The stock solutions were then suitable diluted in pure methanol for solution in pure methanol and with aqueous methanol so that final solution contained 10 % methanol (by volume) as a solvent for solution in 10 % methanol. The ultraviolet absorption spectra were studied with a Beckman Model DU Spectrophotometer using 10 mm. quartz cells in the range 250 mμ - 350 mμ. The values of the extinction coefficients, ϵ , were calculated by dividing the observed optical density, D, by the concentration of coumarins in gram moles per liter.

4.6.2 c Results :

Table (4.6.2.1a and 4.6.2.1b) and figure (4.6.2.1) give the ultraviolet absorption spectrum of 7-methoxycoumarin in methanol and in 10 % methanol.

Tables(4.6.2.2aand 4.6.2.2b) and figure (4.6.2.2) give the ultraviolet absorption spectrum of 6-methoxy-4-methyl-coumarin in methanol and in 10 % methanol.

Tables(4.6.2.3aaand 4.6.2.3b) and figure (4.6.2.3) give the ultraviolet absorption spectrum of 7,8-dimethoxy-coumarin in methanol and in 10 % methanol.

Tables (4.6.2.4a and 4.6.2.4b) and figure (4.6.2.4) give the ultraviolet absorption spectrum of 7,8-dihydroxy-4-methylcoumarin in methanol and in 10 % methanol.

Table (4.6.2.5) gives the valuess of λ maxima and logϵ in 10 % methanol, methanol and ethanol obtained from figures (4.6.2.1 to 4.6.2.4) and from (39).

Table 4.6.2.1a

Ultraviolet absorption spectrum of 7-methoxycoumarin in 10 % methanol

Wave length (mμ)	ε	Wave length (mμ)	ε
250	2887	310	12340
252	2787	315	13680
254	2587	318	14290
256	2229	320	14430
260	2090	322	14530
264	2389	323	14530
268	3026	324	14530
272	3722	325	14530
276	4479	327	14230
280	5375	330	13540
284	6110	335	11740
288	6868	340	9714
292	7665	345	7266
296	8360	350	4739
300	9158	355	2488
305	10710	360	1195

Fig. 4.6.2.1 Ultraviolet absorption spectrum of 7-methoxy-coumarin in (a) 10^{-4} methanol and (b) methanol.

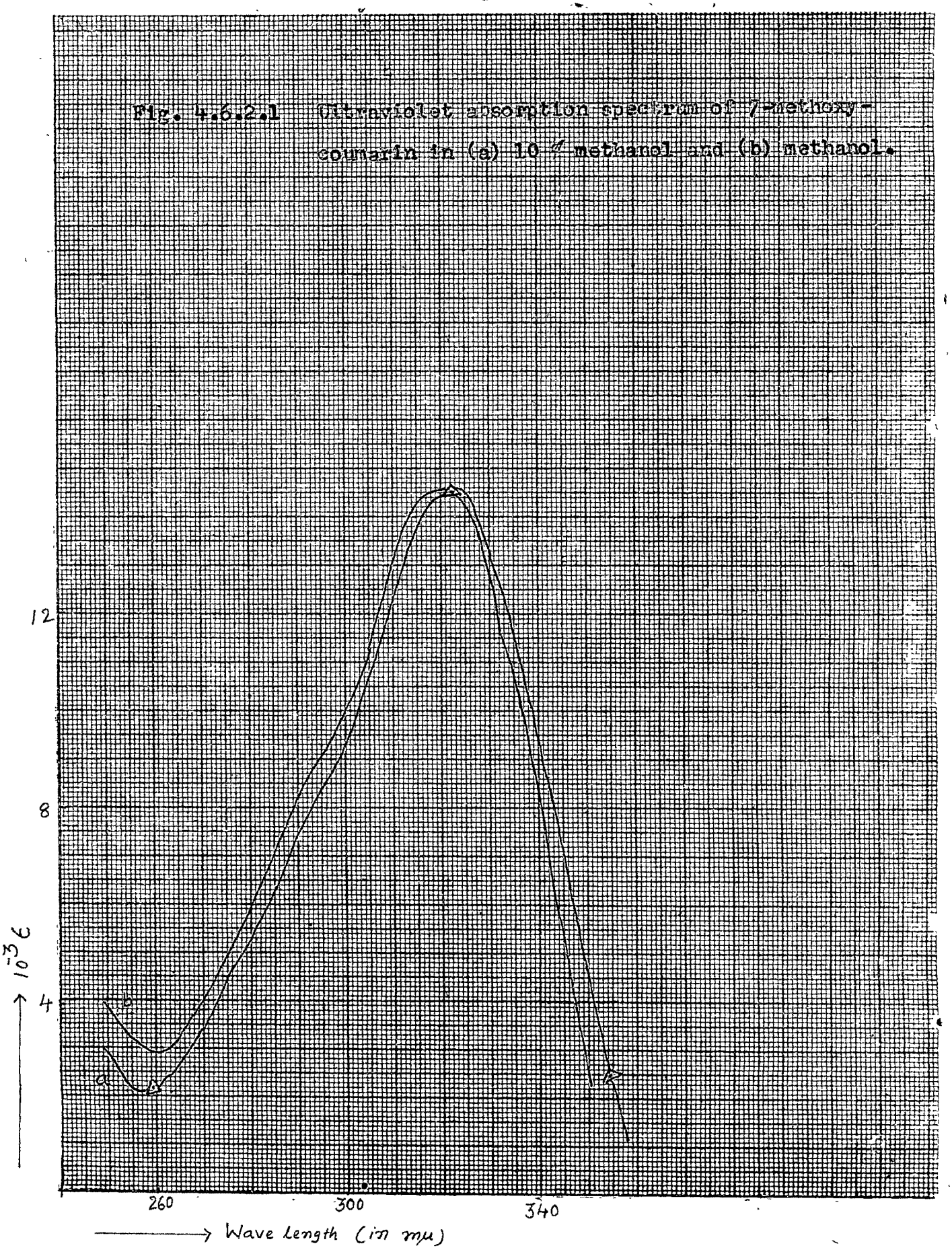


Table 4.6.2.1b

Ultraviolet absorption spectrum of 7-methoxycoumarin in methanol

Wave length (mμ)	ε	Wave length (mμ)	ε
250	3942	302	10350
254	3583	306	11740
258	2986	310	13040
262	2887	314	13930
266	3344	316	14170
268	3623	318	14490
272	4220	320	14490
276	5017	322	14490
280	5872	324	14430
284	6769	326	14230
288	7565	330	12750
292	8561	334	11250
296	9158	338	9356
298	9515	344	6471
300	9954	350	22885

Table 4.6.2.2a

Ultraviolet absorption spectrum of 6-methoxy-4-methyl-coumarin in 10 % methanol.

Wave length (mμ)	ε	Wave length (mμ)	ε
250	4469	298	3324
254	5448	302	2770
258	6648	306	2733
262	8403	310	3102
266	9972	314	3600
270	11090	318	4062
272	11450	322	4525
273	11540	326	4875
274	11600	330	5078
275	11630	332	5301
276	11630	334	5262
278	11090	336	5262
280	10800	338	5262
282	9936	340	5207
284	9510	342	5078
286	8496	344	4894
290	6500	346	4709
294	4801	350	4247

Fig. 4.6.2.2 Ultraviolet absorption spectrum of 6-methoxy-4-methylcoumarin in (a) 10% methanol and (b) methanol.

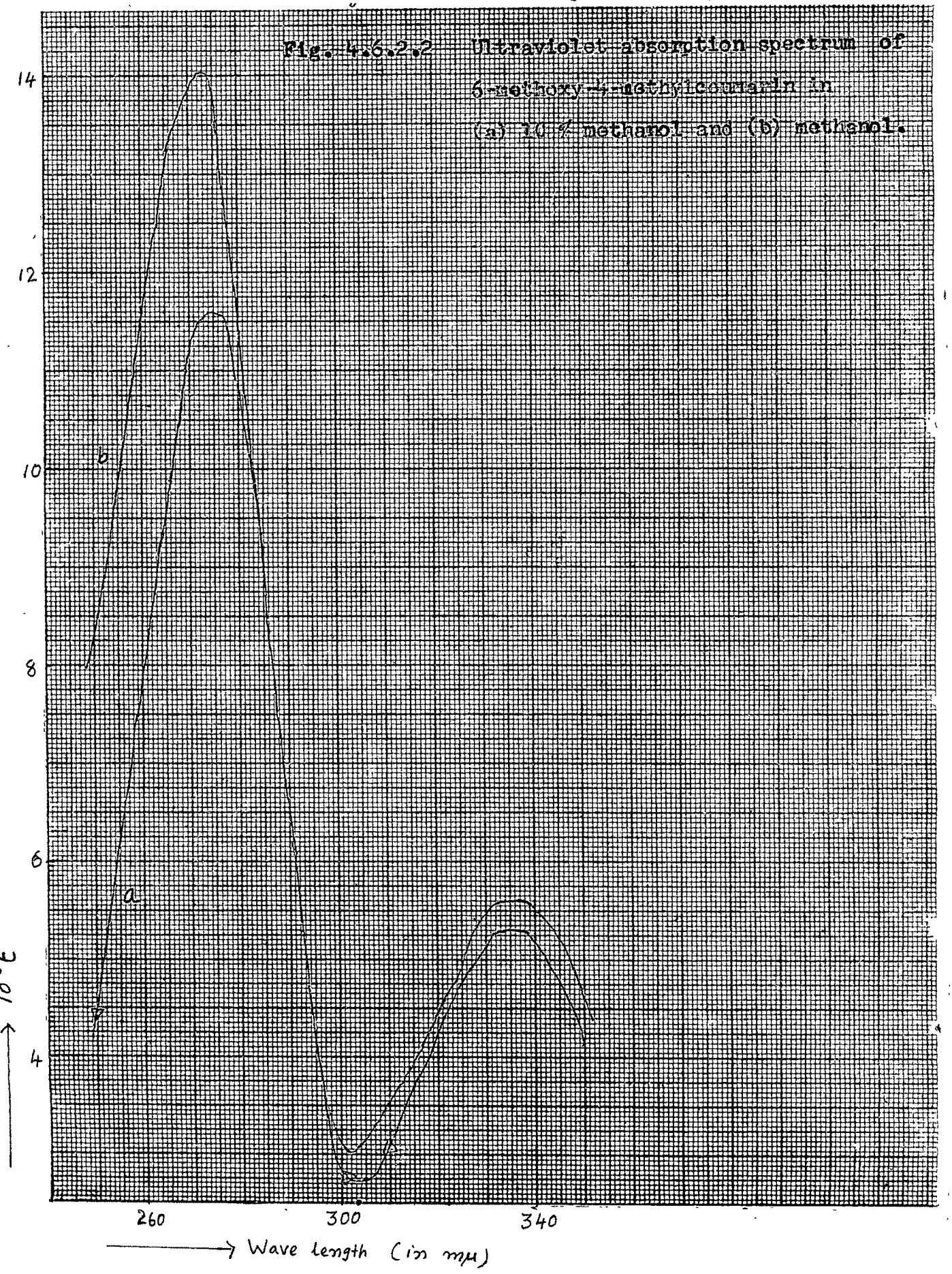


Table 4.6.2.2b

Ultraviolet absorption spectrum of 6-methoxy-4-methyl-coumarin in methanol

Wave length (mμ)	ε	Wave length (mμ)	ε
250	8279	300	3098
254	9348	304	3098
258	10690	308	3338
262	12010	312	3685
266	13360	316	4005
268	13490	320	4407
270	13750	324	4807
272	14030	328	5288
274	14030	330	5288
276	13490	332	5608
278	12550	334	5608
280	11480	336	5608
282	10420	338	5608
284	9614	340	5608
286	8680	342	5448
290	6463	344	5340
294	4326	346	5207
298	3418	350	4673

Table 4.6.2.3a

Ultraviolet absorption spectrum of 7,8-dimethoxy-coumarin in 10 % methanol

Wave length (mμ)	ε	Wave length (mμ)	ε
248	4566	304	11820
250	4657	308	12770
252	4790	312	13100
254	4812	314	13320
255	4859	316	13440
256	4859	318	13660
258	4433	320	13660
260	3761	322	13660
264	2910	324	13320
268	3022	326	12980
272	3626	328	12310
276	4523	330	11640
280	5552	332	10860
284	6671	336	9290
288	7723	340	7836
292	8843	344	6045
296	9851	348	4119
300	10790	350	3358

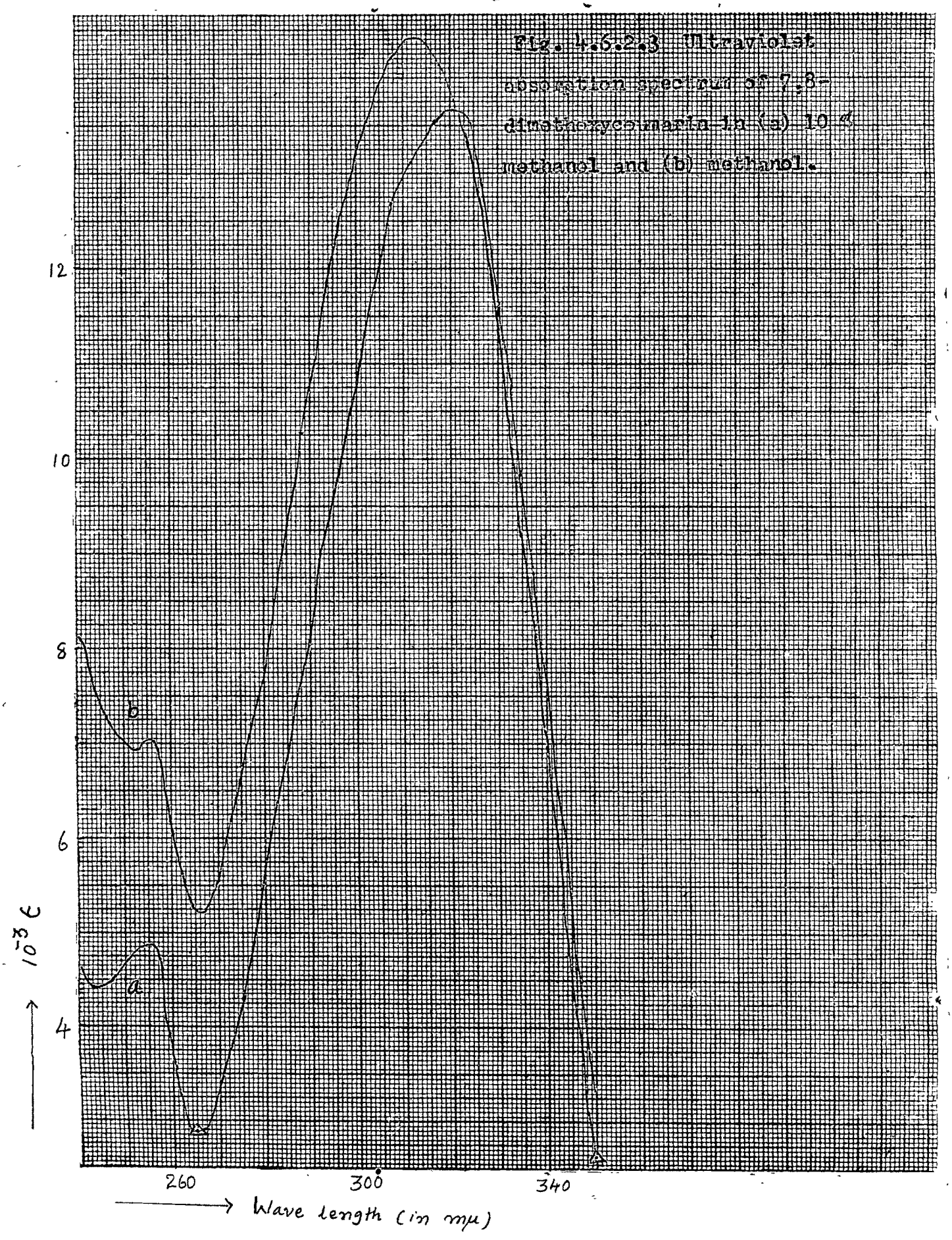


Fig. 4.6.2.3 Ultraviolet absorption spectrum of 7,8-dimethoxycoumarin-1a (a) 10 % methanol and (b) methanol.

Table 4.6.2.3b

Ultraviolet absorption spectrum of 7,8-dimethoxy-coumarin in methanol

Wave length (mμ)	ε	Wave length (mμ)	ε
248	7206	284	8997
250	7055	288	10160
252	6963	292	11280
254	7025	296	12390
256	7055	300	13090
258	6717	305	13930
260	6255	310	14350
262	5669	315	14270
264	5299	320	13870
266	5207	325	12880
268	5330	330	11190
270	5669	335	9243
272	6070	340	7086
274	6471	345	4622
276	6933	350	2558
280	7836		

Data taken from the unpublished work of Shri R.S.Shah of this laboratory.

Table 4.6.2.4a

Ultraviolet absorption spectrum of 7,8-dihydroxy-4-methylcoumarin in 10 % methanol

Wave length (mμ)	ε	Wave length (mμ)	ε
250	6368	304	9031
252	6844	308	9696
254	7224	312	10460
256	7700	316	10830
258	7889	318	11130
260	7889	320	11210
262	7319	322	11210
264	6558	324	10930
268	4468	326	10640
272	3764	328	10270
276	3936	330	9982
280	4505	332	9506
284	5037	334	9031
288	5665	336	8555
292	6330	340	7129
296	7129	344	5703
300	8081	348	4372
302	8592	350	3764

Fig. 4.6.2.4 Ultraviolet absorption spectrum of 7,8-dihydroxy-4-methylcoumarin in (a) 10 % methanol and (b) methanol.

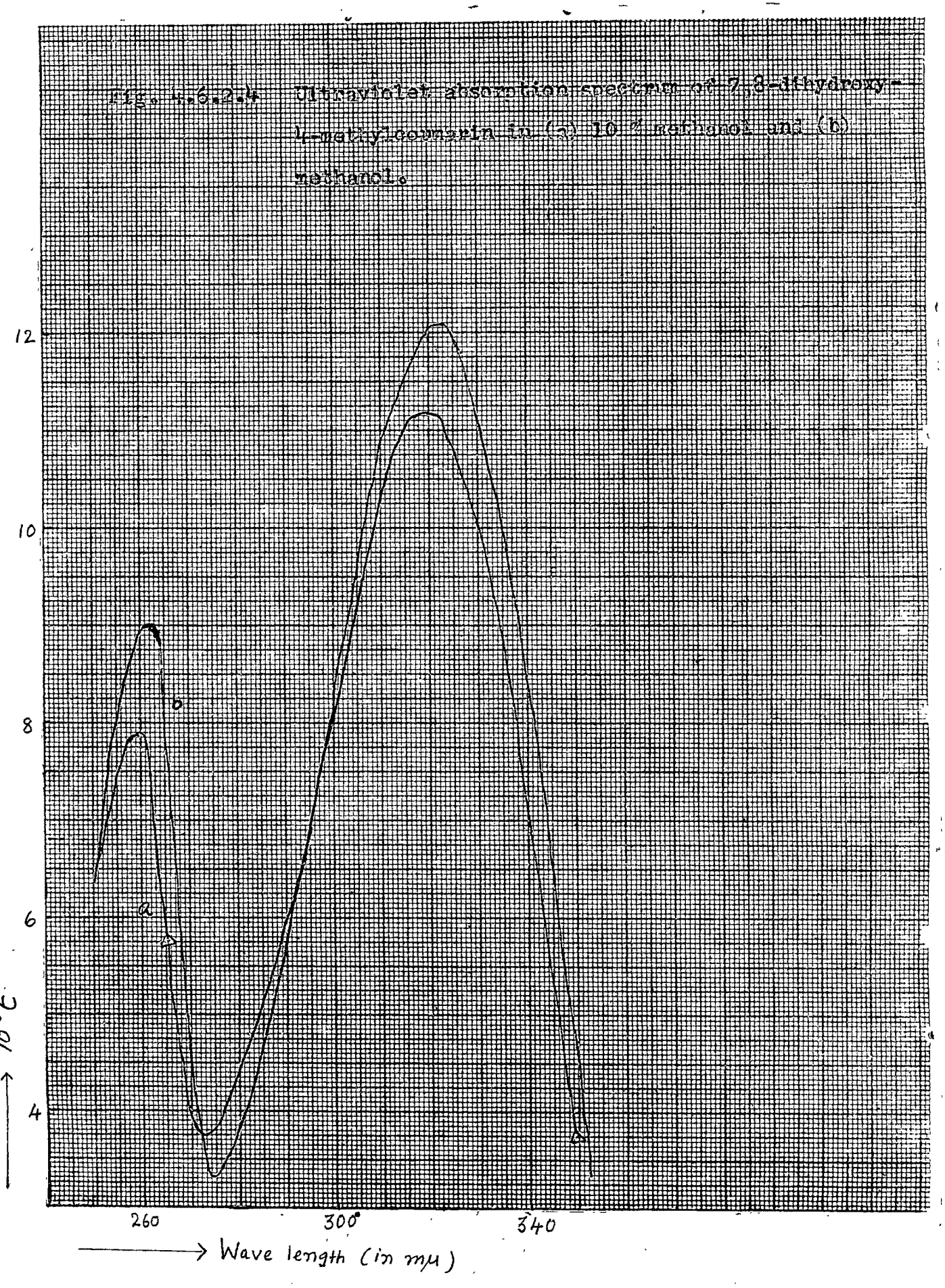


Table 4.6.2.4b

Ultraviolet absorption spectrum of 7,8-dihydroxy-4-methylcoumarin in methanol

Wave length (mμ)	ε	Wave length (mμ)	ε
250	6377	286	4967
252	7099	288	5426
254	7839	290	5848
256	8333	292	6306
258	8684	294	6834
260	8966	296	7311
262	8984	300	8368
264	8620	305	9690
266	7450	310	10800
268	5856	315	11530
270	4422	320	12070
272	3612	325	11940
274	3294	330	11110
276	3418	335	9970
278	3593	340	8403
280	3893	345	6290
282	4263	350	4298
284	4615		

Data taken from unpublished work of Shri R.S.Shah of this laboratory.

4.6.2 d Discussion :

Table (4.6.2.5) gives the values of λmax. and log ϵ for 7-methoxycoumarin, 6-methoxy-4-methylcoumarin, 7,8-dimethoxycoumarin and 7,8-dihydroxy-4-methylcoumarin in 10 % methanol and methanol. The values for ethanol are taken from (39) . The figures (4.6.2.1 to 4.6.2.4) indicate that the effect of change of solvent on the maxima is relatively small but there is a definate small shift. log ϵ value is also affected to a small but definate extent. The general shape of the spectrum is not significantly altered under these condition.

In view of the above, the estimation in aqueous methanols and in water were carried out by preparing a standard solution of perticular compound in the particular solvent medium and comparing its optical density with that of same compound in same solvent in which the concentration is to be determined at a suitable wave length, prefereably at or near the λmax. It was not considered essential to measure the entire spectrum of each of the compounds studied in each of the solvents used for analytical purpose, which was the main objective.

Table 4.6.2.5

Values of λmax. and log ε obtained from figures (4.6.2.1 to 4.6.2.4)

Solvent	10% methanol		methanol		ethanol(39)	
Substance	λmax.	log ε	λmax.	log ε	λmax.	log ε
7-MeO(I)	322-25	4.1623	318-22	4.1611	252	3.3210
					318-23	4.1700
6-MeO-4-Me(I)	274-76	4.0657	272-74	4.1426	273	4.05
	334-38	3.7212	332-40	3.7488	340	3.70
7,8-diMeO(I)	254-56	3.6865	254-56	3.8455		
	318-22	4.1353	310-15	4.1582		
7,8-diOH-4-Me(I)	258-60	3.8970	260-62	3.9535		
	320-22	4.0499	322	4.0822		

4.6.3 Sorption equilibrium studies :

4.6.3a Introduction :

In previous sections (4.3 and 4.4) sorption of monocarboxylic acids of $R-CH_2COOH$ type on sulfonic acid cation exchange resins in aqueous solution and in organic solvents was described.

In this section sorption of coumarin on sulfonated styrene-divinylbenzene copolymer type sulfonic acid cation exchange resins of relative degree of crosslinking as 4,8 and 12 in water and aqueous methanols and ten substituted coumarins on a same type resin of relative degree of crosslinking as 4 in aqueous methanols is described.

4.6.3b Experimental :

Resins : The resins used were from the samples used in the previous section (4.3)

Chemicals : The coumarins were obtained from Prof. S.M. Sethna's laboratory and were recrystallised from ethanol and checked for melting points.

Solutions : The solutions were prepared in 10 %, 20 %, 30 % and 40 % methanol (by volume : 10 cc. methanol + 90 cc. water, 20 cc. methanol + 80 cc. water, 30 cc. methanol + 70 cc. water and 40 cc. methanol + 60 cc. water).

Procedure : The procedure was same as in the previous section (4.3). Estimation of coumarin and substituted coumarins was done by ultraviolet absorption with Beckman Model DU spectrophotometer using 10 mm. quartz cells.

4.6.3c Nomenclature :

The symbols used are same as these used in the section (4.3)

4.6.3d Results :

Tables (4.6.3.01 to 4.6.3.03) and figure (4.6.3.1) give the sorption of coumarin with the resins X4, X8 and X12 in water and in aqueous methanols.

Tables (4.6.3.04 to 4.6.3.13) and figures (4.6.3.2 to 4.6.3.6) give the sorption of ten substituted coumarins with the resin X4 in aqueous methanols.

Table (4.6.3.14) gives the values of B obtained from figure (4.6.3.1) and a and b obtained from figure (4.6.3.7) for coumarin.

Table (4.6.3.15) gives the values of log β and γ obtained from figure (4.6.3.7) and equations (4.25 and 4.26).

Table (4.6.3.16) gives the values of B obtained from figures (4.6.3.2 to 4.6.3.6) and a and b from the figures (4.6.3.8 and 4.6.3.9) for ten substituted coumarins.

Table 4.6.3.01

Sorption of coumarin on the resin X4 in aqueous methanols

Solvent (% methanol)	10^4 Ce	10^4 S	Solvent (% methanol)	10^4 Ce	10^4 S
0	0.7591	4.736	30	1.005	1.432
	1.423	11.84		1.952	4.230
	2.123	17.28		2.872	5.921
	2.774	24.06		3.804	7.548
	3.479	29.70		4.741	10.02
10	0.8416	4.269	40	1.140	0.8849
	1.617	9.499		2.145	1.952
	2.361	13.93		3.100	3.904
	3.233	19.00		4.254	4.555
	4.042	22.64		5.273	4.945
20	0.8820	3.045			
	1.810	6.702			
	2.590	10.41			
	3.629	12.36			
	4.373	17.05			

Table 4.6.3.02

Sorption of coumarin on resin X8 in aqueous methanols

Solvent (% methanol)	10^4 Ce	10^4 S	Solvent (% methanol)	10^4 Ce	10^4 S
0	0.7509	4.851	20	0.9738	2.082
	1.464	11.27		19.52	4.555
	2.214	16.00		28.25	7.158
	2.910	22.14		38.04	9.348
	3.768	27.77		47.32	12.36
10	0.8820	3.644	30	1.047	1.432
	1.722	7.352		2.113	2.277
	2.572	10.412		3.077	3.904
	3.456	14.29		4.547	5.271
	4.227	18.26		5.168	5.856

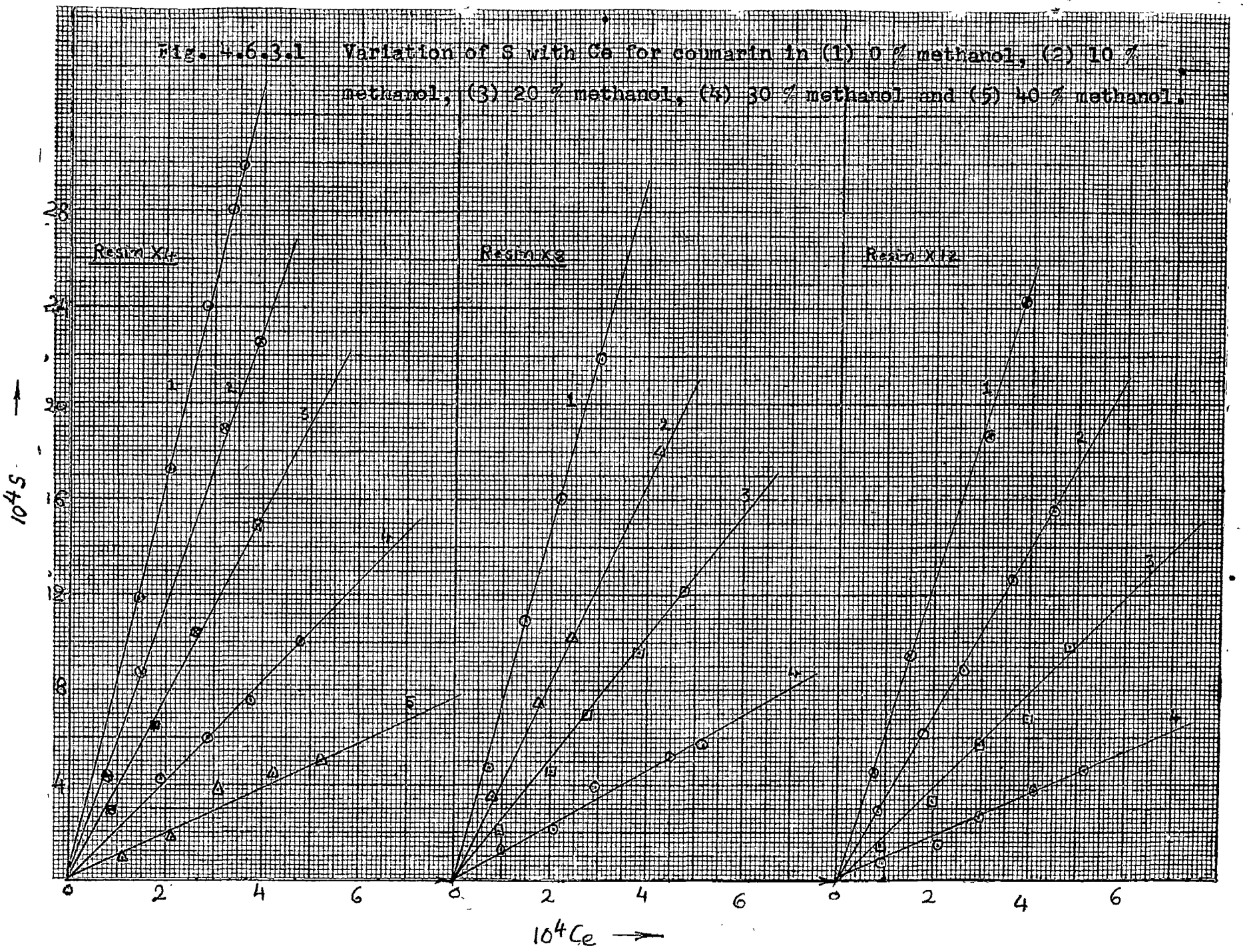


Fig. 4.6.3.1 Variation of S with Ce for coumarin in (1) 0 % methanol, (2) 10 % methanol, (3) 20 % methanol, (4) 30 % methanol and (5) 40 % methanol.

Table 4.6.3.03

Sorption of coumarin on the resin X12 in aqueous methanols

Solvent (% methanol)	10^4 Ce	10^4 S	Solvent (% methanol)	10^4 Ce	10^4 S
Water	0.7591	4.736	20	1.020	1.432
	1.514	10.56		2.012	3.384
	2.313	14.59		2.985	5.856
	3.135	18.94		3.969	7.028
	3.841	24.58		4.888	10.15
10	0.9279	2.993	30	1.084	0.9109
	1.792	6.377		2.159	1.627
	2.656	8.915		3.004	2.928
	3.572	12.65		4.259	4.100
	4.410	15.62		5.250	4.687

Table 4.6.3.04

Sorption of 7-hydroxycoumarin on the resin X4 in aqueous methanols

Solvent (% methanol)	10^4 Ce	10^4 S	Solvent (% methanol)	10^4 Ce	10^4 S
10	0.7845	4.111	30	2.257	3.045
	1.539	8.037		3.289	6.850
	2.309	11.60		4.513	7.085
	3.018	15.25			
	3.984	20.09			
20	0.8921	2.587	40	0.9888	0.4599
	1.754	5.602		1.977	1.035
	2.631	7.491		2.966	2.283
	3.418	10.96		3.901	2.943
	4.485	14.21		4.943	4.262

Fig. 4.6.3.2 Variation of S with Ce for 7-hydroxycoumarin (A) and 8-hydroxycoumarin (B) in (1) 10 % methanol, (2) 20 % methanol, (3) 30 % methanol and (4) 40 % methanol.

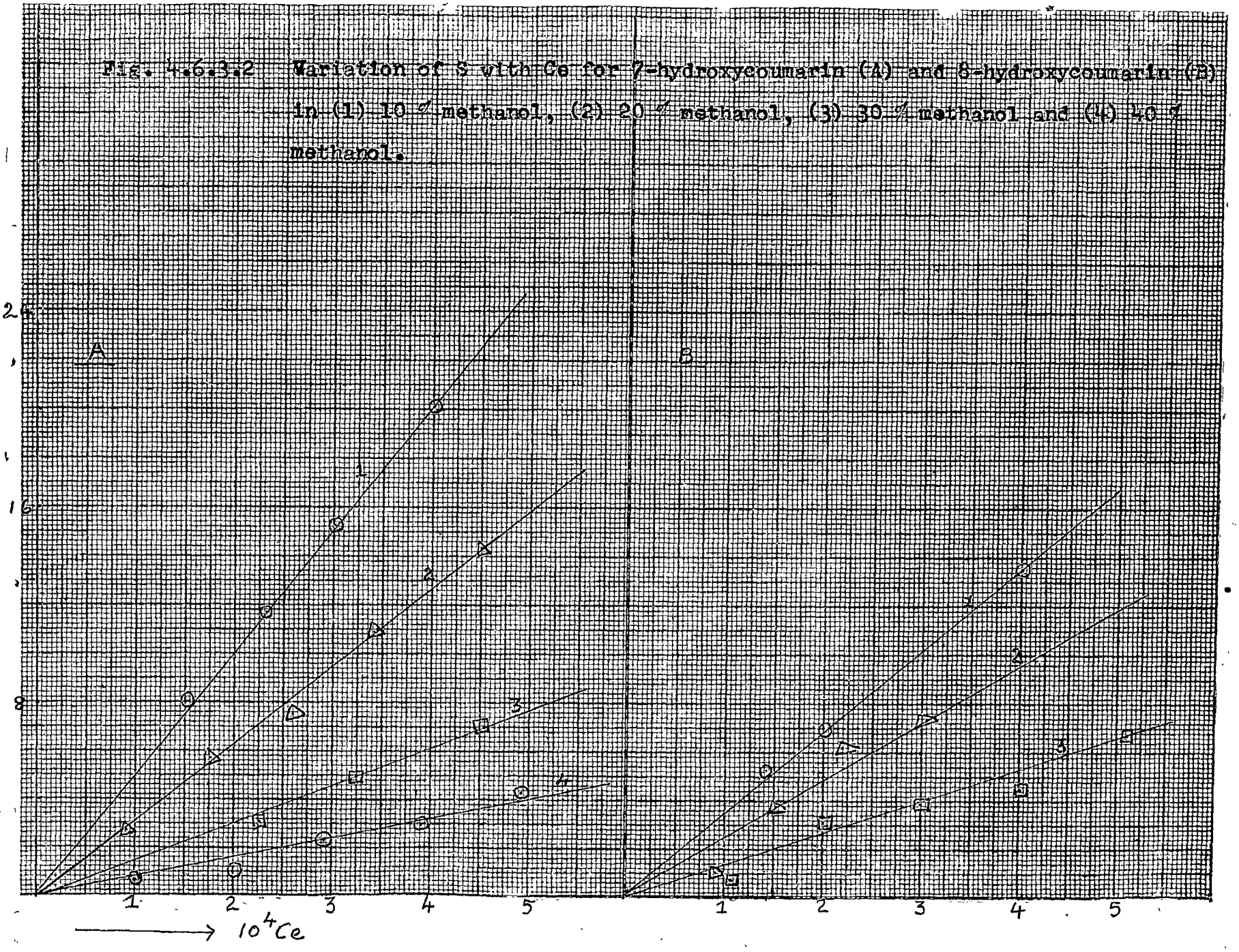


Table 4.6.3.05

Sorption of 8-hydroxycoumarin on the resin X4 in aqueous methanols

Solvent (% methanol)	10^4 Ce	10^4 S	Solvent (% methanol)	10^4 Ce	10^4 S
10	1.410	5.218	30	1.076	0.6905
	2.053	6.898		2.006	3.121
	4.064	13.44		3.047	3.784
				4.093	4.422
				5.139	6.640
20	0.8147	0.9915			
	1.531	3.718			
	2.210	6.197			
	3.032	7.251			

Table 4.6.3.06

Sorption of 6-hydroxy-4-methylcoumarin on the resin X4 in aqueous methanols

Solvent (% methanol)	10^4 Ce	10^4 S	Solvent (% methanol)	10^4 Ce	10^4 S
10	0.7381	4.605	30	0.9448	1.195
	1.450	9.831		1.898	4.40
	2.208	15.75		2.777	5.735
	2.846	20.16		4.555	10.52
	3.532	25.89			
20	0.8435	2.863			
	1.603	6.845			
	2.425	10.82			
	3.203	13.44			
	3.954	18.05			

Fig. 4.6.3.3 Variation of S with Ce for 6-hydroxy-4-methylcoumarin (A) and 7,8-dihydroxy-4-methylcoumarin (B) in (1) 10 % methanol, (2) 20 % methanol and (3) 30 % methanol.

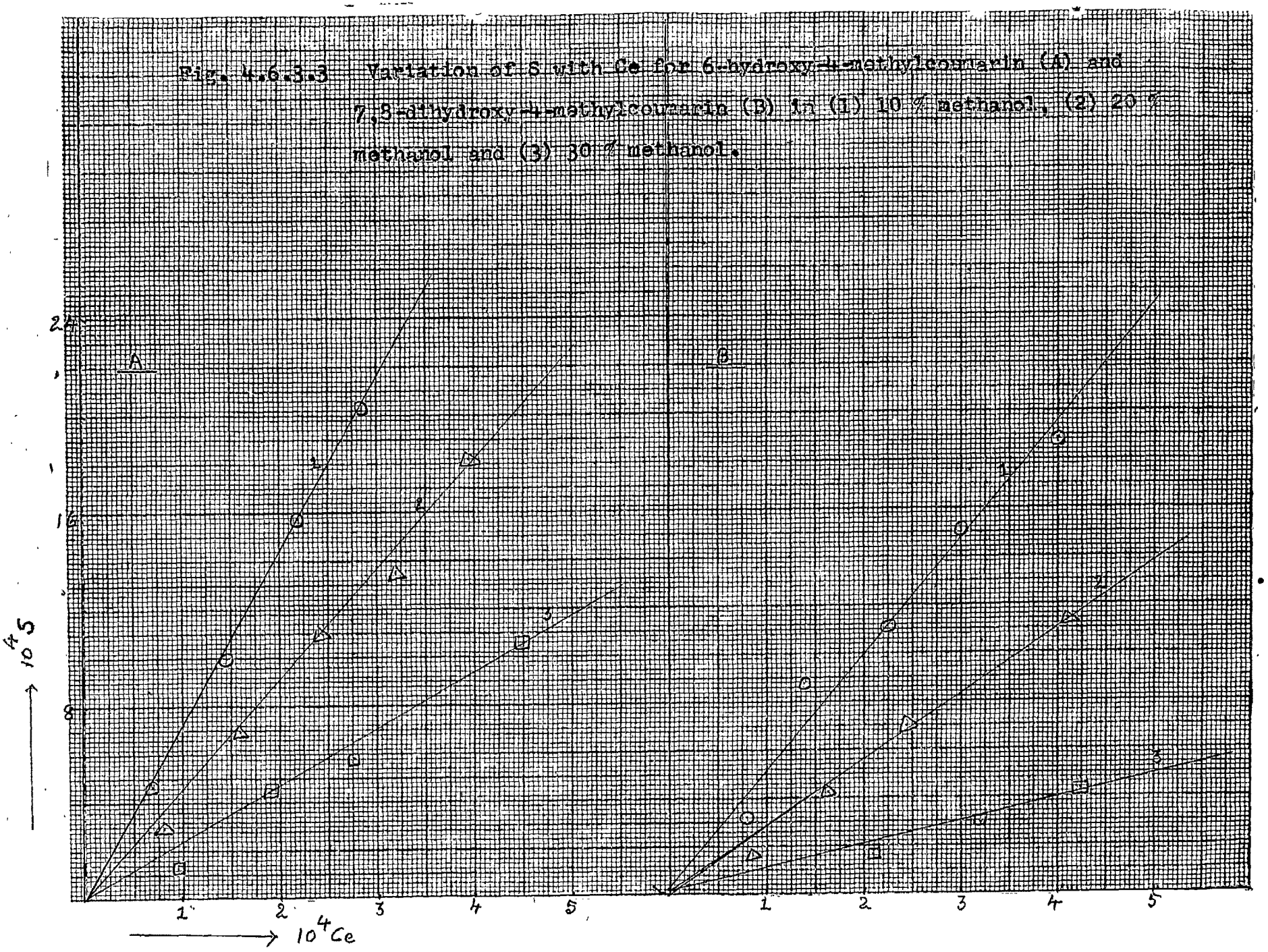


Table 4.6.3.07

Sorption of 7,8-dihydroxy-4-methylcoumarin on the resin X4 in aqueous methanols

Solvent (% methanol)	10^4 Ce	10^4 S	Solvent (% methanol)	10^4 Ce	10^4 S
10	0.8037	2.986	30	2.113	1.481
	1.415	8.584		3.193	2.773
	2.253	10.97		4.268	4.742
	3.026	15.04			
	3.917	18.66			
20	0.8535	1.540			
	1.653	4.030			
	2.435	6.756			
	4.101	11.26			

Table 4.6.3.08

Sorption of 7-methylcoumarin on the resin X4 in aqueous methanols

Solvent (% methanol)	10^4 Ce	10^4 S	Solvent (% methanol)	10^4 Ce	10^4 S
10	0.6215	5.919	30	0.7821	2.201
	1.223	12.71		1.576	5.375
	1.808	18.53		3.118	10.24
	2.446	26.69		3.795	12.65
	3.072	30.23			
20	0.7411	4.300	40	2.880	4.427
	1.518	9.486		3.885	6.956
	2.120	13.59		4.777	8.853
	2.946	18.34			
	3.679	23.15			

Fig. 4.6.3.4 Variation of δ with Ce for 7-methylcoumarin (A) and 3,4-dimethylcoumarin (B) in (1) 10 % methanol, (2) 20 % methanol, (3) 30 % methanol and (4) 40 % methanol.

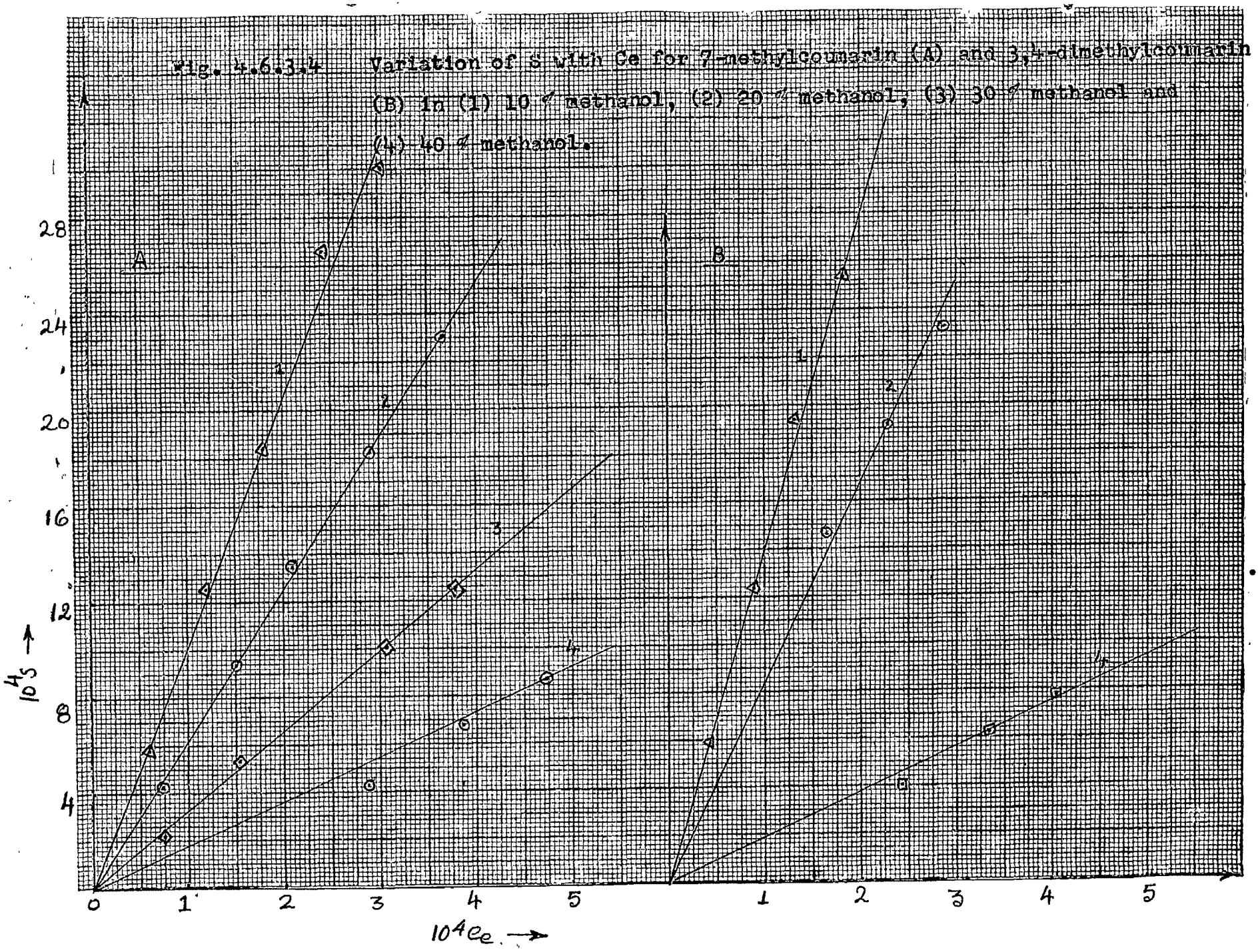


Table 4.6.3.09

Sorption of 3,4-dimethylcoumarin on the resin X4 in aqueous methanols

Solvent (% methanol)	10^4 Ce	10^4 S	Solvent (% methanol)	10^4 Ce	10^4 S
10	0.4835	6.027	40	2.465	4.109
	0.9185	12.53		3.368	6.287
	1.354	19.45		4.042	7.807
	1.845	25.39			
	2.224	32.05			
20	0.5319	5.342			
	1.644	14.72			
	2.297	19.23			
	2.900	23.28			

Table 4.6.3.10

Sorption of 7-methoxycoumarin on the resin X4 in aqueous methanols

Solvent (% methanol)	10^4 Ce	10^4 S	Solvent (% methanol)	10^4 Ce	10^4 S
10	0.5765	6.492	30	0.7778	3.148
	1.150	13.18		1.563	6.640
	1.702	19.18		2.257	9.346
	2.282	26.57		3.125	12.83
	2.882	32.96		3.876	15.93
20	0.6668	4.820	40	1.417	2.951
	1.326	9.984		2.014	4.427
	1.962	14.51		4.220	8.853
	2.675	19.65		5.765	11.80
	3.278	24.89			

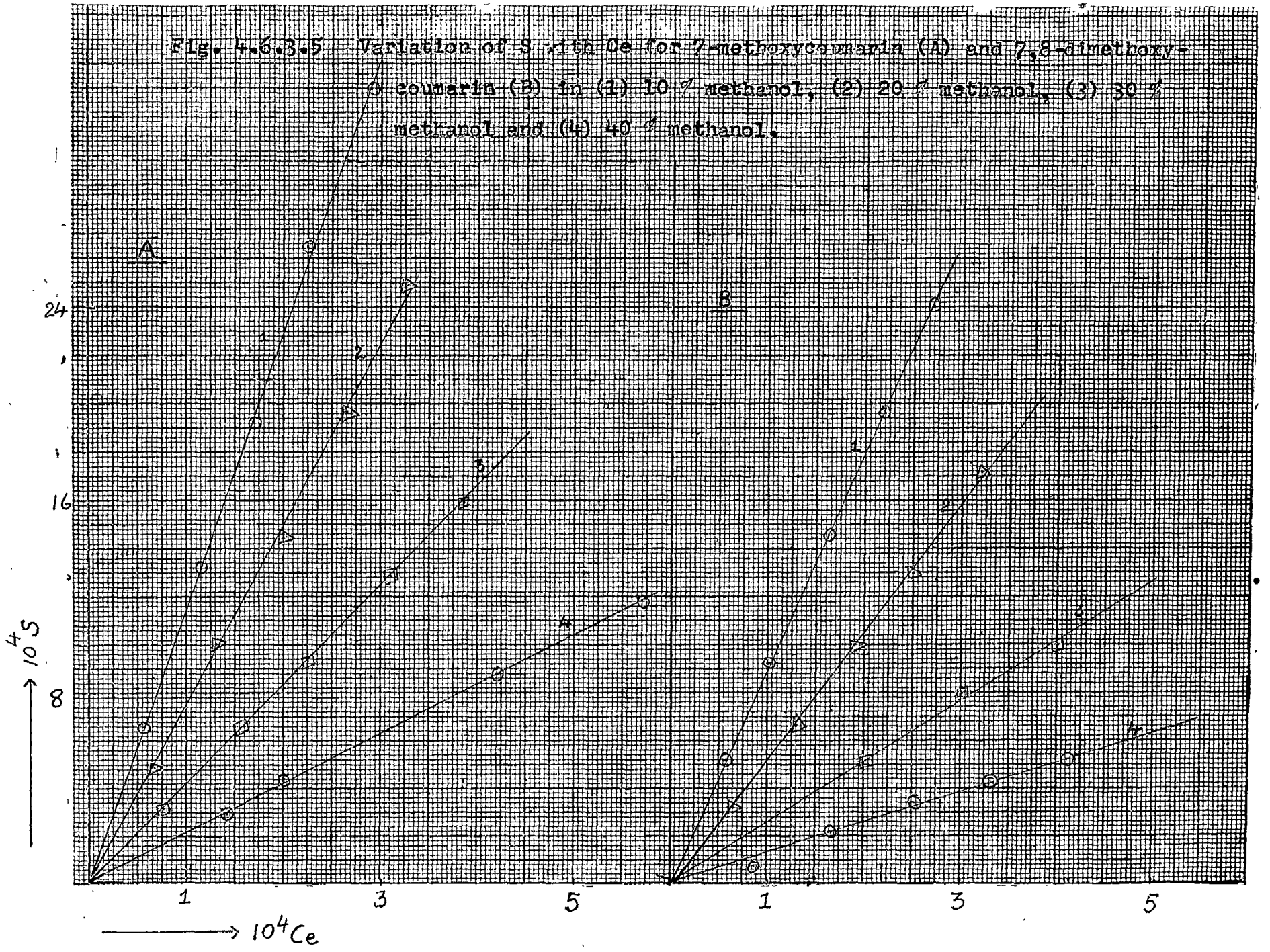


Fig. 4.6.3.5 Variation of S with Ce for 7-methoxycoumarin (A) and 7,8-dimethoxy-coumarin (B) in (1) 10 % methanol, (2) 20 % methanol, (3) 30 % methanol and (4) 40 % methanol.

Table 4.6.3.11

Sorption of 7,8-dimethoxycoumarin on the resin X4 in aqueous methanols

Solvent (% methanol)	10^4 Ce	10^4 S	Solvent (% methanol)	10^4 Ce	10^4 S
10	0.5559	5.101	30	2.031	5.249
	1.082	9.344		3.068	8.032
	1.601	14.59		4.039	9.972
	2.168	19.74			
	2.705	24.14			
20	0.6522	3.255	40	0.8598	0.7348
	1.297	6.719		1.675	2.205
	1.927	9.972		2.482	3.412
	2.581	12.94		3.282	4.346
	3.173	17.22		4.135	5.249

Table 4.6.3.12

Sorption of 6-methoxy-4-methylcoumarin on the resin X4 in aqueous methanols

Solvent (% methanol)	10^4 Ce	10^4 S	Solvent (% methanol)	10^4 Ce	10^4 S
10	0.5927	7.068	30	2.320	8.590
	1.191	14.11		3.525	13.03
	1.742	21.72		4.332	15.35
	2.355	29.35			
	2.859	32.89			
20	0.7364	5.023	40	3.004	4.564
	1.451	10.13		4.094	6.074
	2.152	15.53		4.852	7.364
	2.885	20.05			
	3.621	25.40			

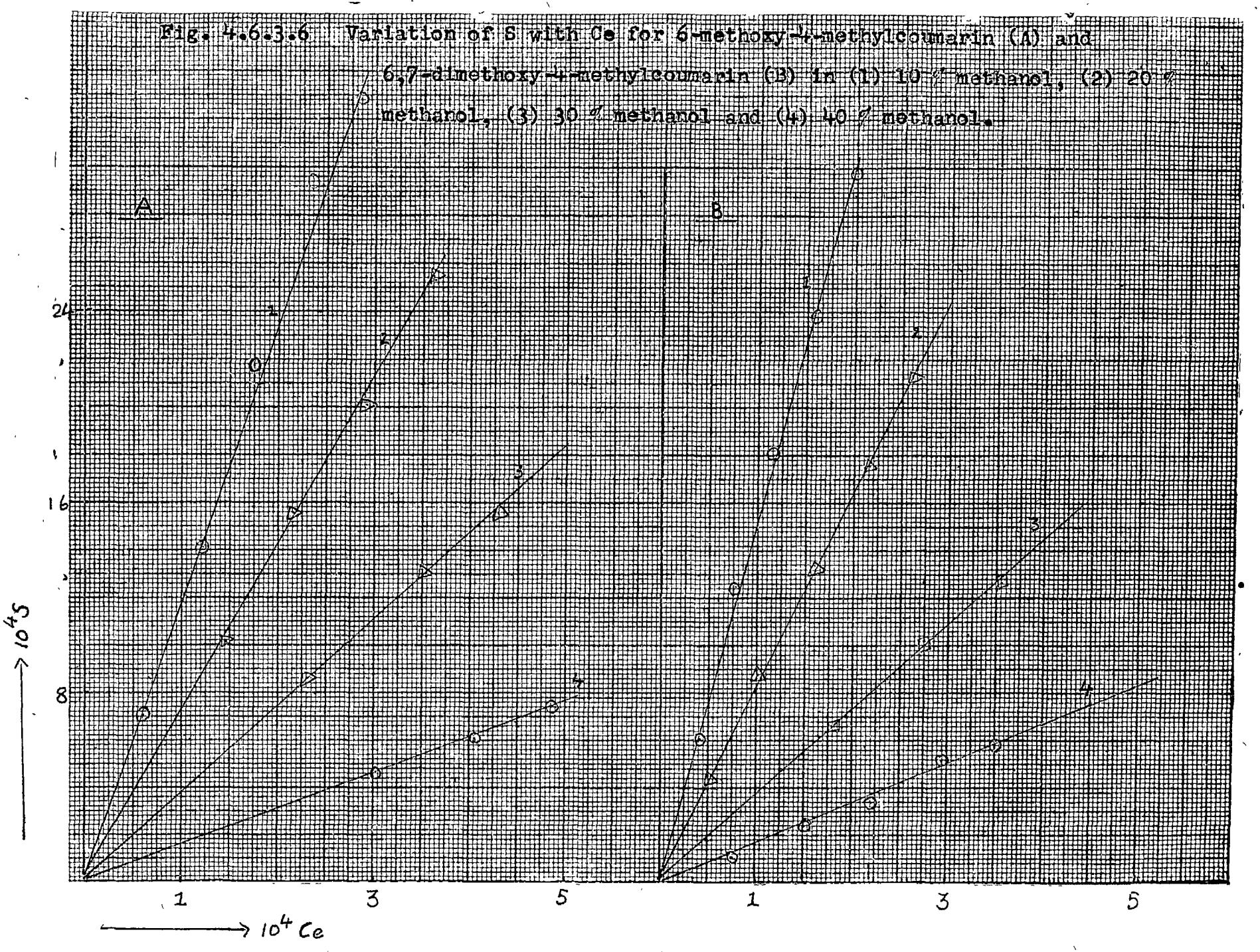


Fig. 4.6.3.6 Variation of S with Ce for 6-methoxy-4-methylcoumarin (A) and 6,7-dimethoxy-4-methylcoumarin (B) in (1) 10 % methanol, (2) 20 % methanol, (3) 30 % methanol and (4) 40 % methanol.

Table 4.6.3.13

Sorption of 6,7-dimethoxy-4-methylcoumarin on the resin X4 in aqueous methanols

Solvent (% methanol)	10^4 Ce	10^4 S	Solvent (% methanol)	10^4 Ce	10^4 S
10	0.4116	6.059	30	1.836	6.573
	0.7749	12.38		2.760	10.08
	1.171	18.04		3.551	12.57
	1.619	23.87			
	2.018	29.73			
20	0.5326	4.344	40	0.7506	1.074
	1.069	8.746		1.513	2.287
	1.583	13.23		2.227	3.293
	2.142	17.49		2.942	5.144
	2.623	21.14		3.511	5.716

4.6.3e Discussion :

The sorption of weak and nonelectrolytes on ion exchange resins may in a more general way, be given by

$$S.X^{\gamma} / Ce^{\alpha} = B.X^{\gamma} = \beta \qquad (4.23)$$

where B, α, β and γ are constants. B may be regarded as sorption equilibrium constant for a given resin, α may be considered to take into account the overall effect due to interactions such as those of the solute and the solvent with the solute, the solvent, the ionogenic groups and the resin matrix. γ may be considered to take into account the overall effect due to the extent of solvent content of the fully swollen resin under the prevailing conditions, the solubility of the solute in the solvent in the resin relative to that in the solvent outside, in which the resin is immersed and the shape and size of the solute molecule relative to the pore width of the resin and the spacing of the ionogenic groups in the resin matrix.

In the previous section (4.3) on the sorption of monocarboxylic acids of $R\text{-}CH_2COOH$ type on sulfonic acid cation exchange resins, α and γ were each equal to unity and log BX or log B was an additive property of n_c , n_b and n_r .

In the section (4.4) on the sorption of monocarboxylic acids of $R\text{-}CH_2COOH$ type on a resin of the same type in organic solvents, α was less than unity ; log B and α were here also additive property of n_c for a homologous series.

In the study of sorption of coumarin on three cation exchange resins X4, X8 and X12 in water, 10 % methanol, 20 % methanol, 30 % methanol and 40 % methanol (by volume) given in this section, α is equal to unity and the value of B decreases with increase in the % methanol content in the solvent.

In figure (4.6.3.7) log B is plotted against log X for water, 10 %, 20 % and 30 % methanol as solvent for the three resins used. The plots are linear and the values of the intercept and slopes give the values of log B and γ according to the equation.

$$\log B = \log\beta - \gamma \log X \qquad (4.24)$$

In the table (4.6.3.15) the values of $\log\beta$ and γ obtained from figure (4.6.3.7) are given. $\log\beta$ and γ may be expressed by the equations,

$$\log\beta = 1.14 - 0.0475 \left(2^{\bar{P}/10} \right) \qquad (4.25)$$

$$\gamma = 0.30 + 0.15 \ (P/10) \qquad (4.26)$$

where P denotes the percentage of methanol in the solvent medium used.

The values of $\log\beta$ and γ calculated according to equations (4.25 and 4.26) are also given in table(4.6.3.15) and the agreement between the experimental and calculated values is good. This indicates that both β and γ are functions of P under the conditions studied. The effect of methanol content on the values of B for the given resins may be expressed by the equation,

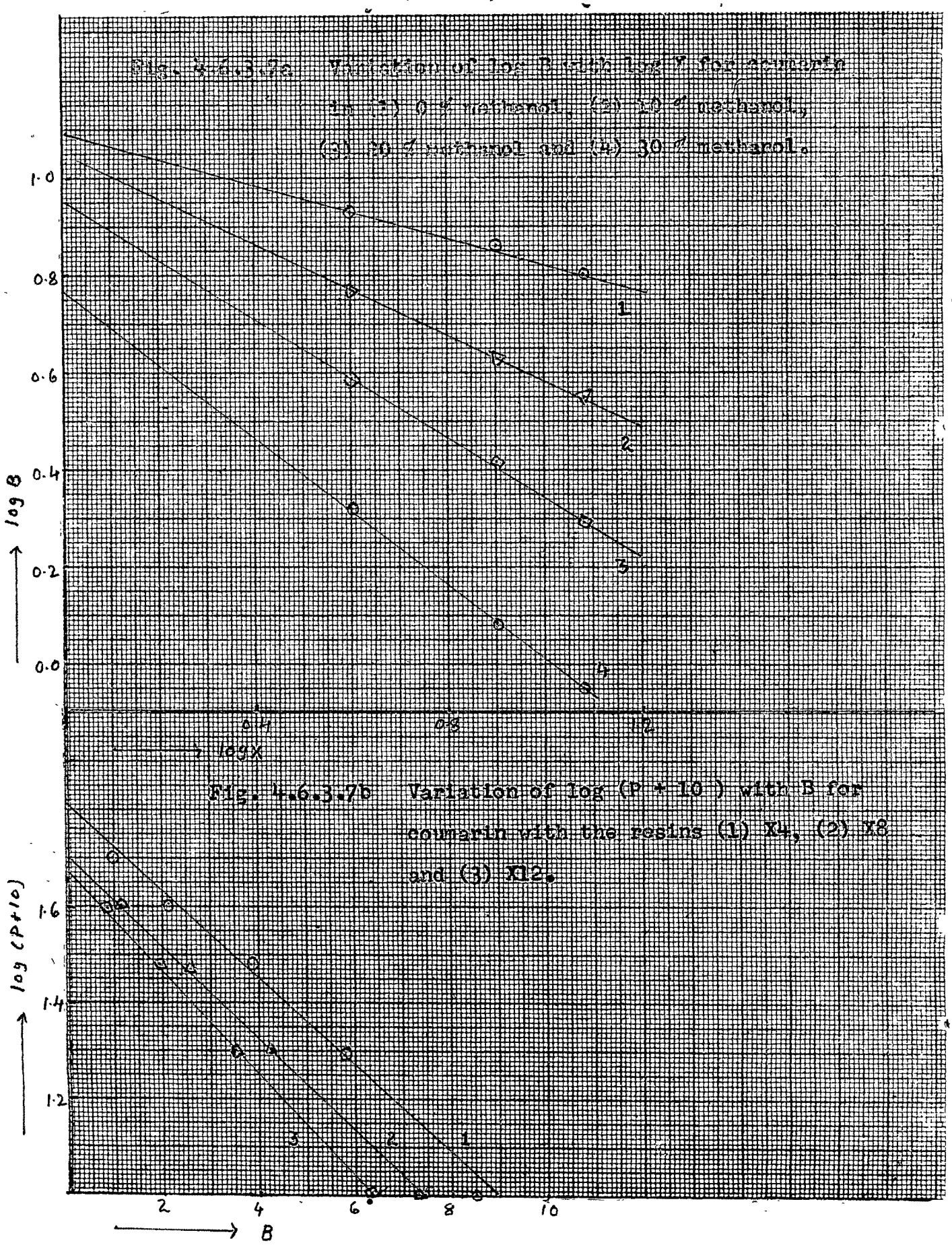


Fig. 4.6.3.7a Variation of log B with log X for acrylic (1) 0 % methanol, (2) 10 % methanol, (3) 20 % methanol and (4) 30 % methanol.

Fig. 4.6.3.7b Variation of log (P + 10) with B for coumarin with the resins (1) X4, (2) X8 and (3) X12.

Table 4.6.3.14

Variation of B with P and X for coumarin

Resin	B when methanol content (by volume) of the solvent is						
	0 %	10 %	20 %	30 %	40 %	a	b
X4	8.50	5.80	3.84	2.1	0.96	1.81	0.090
X8	7.30	4.25	2.6	1.2	-	1.70	0.094
X12	6.35	3.50	2.0	0.9	-	1.67	0.106

Table 4.6.3.15

Experimental and calculated values of log β and γ

P	log β		γ	
	Exp.	Cal.	Exp.	Cal.
0	1.09	1.092	0.27	0.30
10	1.05	1.045	0.47	0.45
20	0.95	0.95	0.60	0.60
30	0.76	0.76	0.75	0.75

Fig. 4.6.3.8 Variation of log (P ÷ 10) with B for (1) 7-hydroxycoumarin, (2) 8-hydroxycoumarin, (3) 6-hydroxy-4-methylcoumarin, (4) 7,8-dihydroxy-4-methylcoumarin, (5) 7-methylcoumarin and (6) 3,4-dimethylcoumarin with the resin X4.

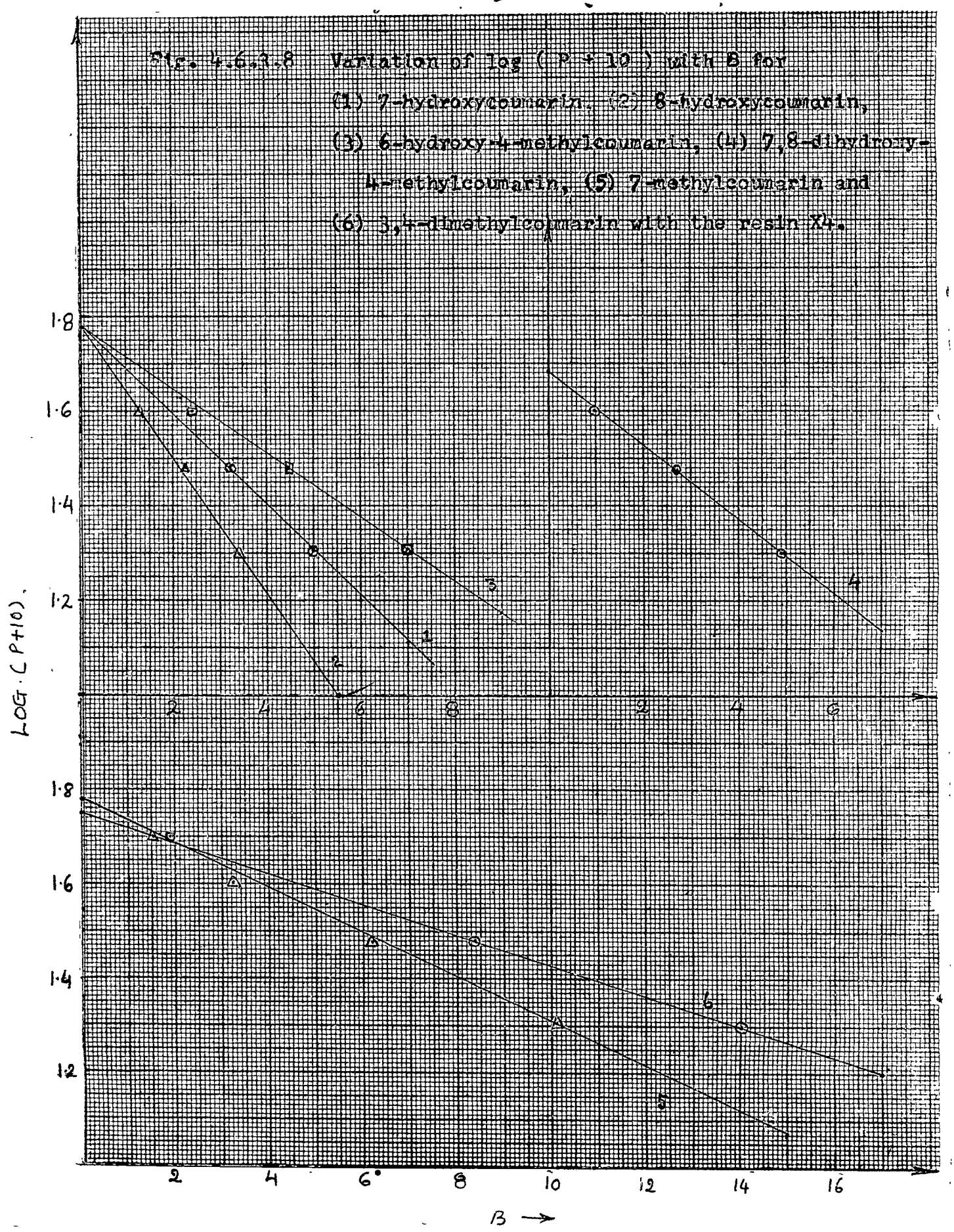


Fig. 4.6.3.9 Variation of log (P + 10) with B for (1) 7-methoxycoumarin, (2) 7,8-dimethoxycoumarin, (3) 6-methoxy-4-methylcoumarin and (4) 6,7-dimethoxy-4-methylcoumarin with the resin XL.

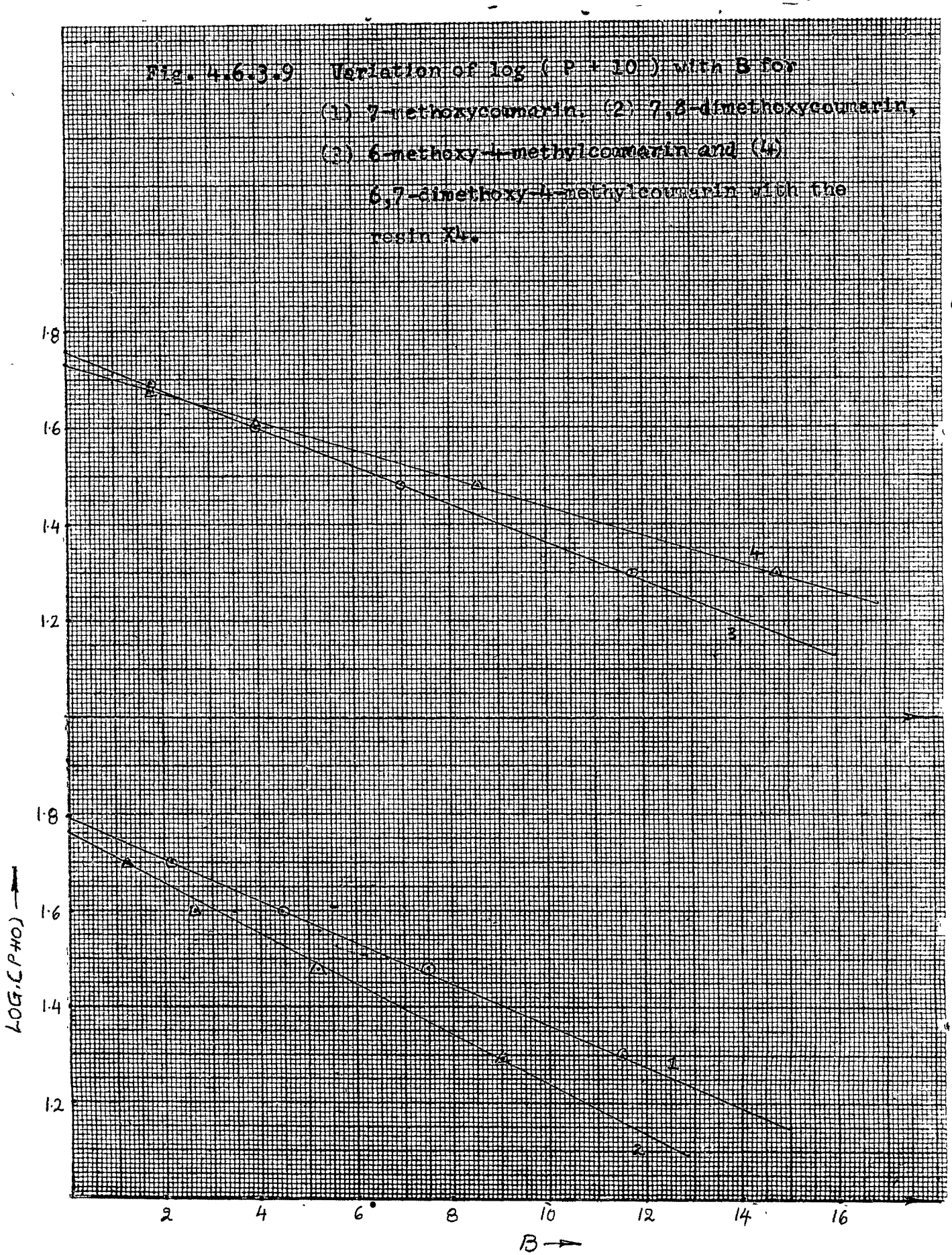


Table 4.6.3.16

Variation of B with P for substituted coumarins

Substance	B when methanol content(by volume) of the solvent is				a	b
	10 %	20 %	30 %	40 %		
Coumarin(I)	5.80	3.84	2.10	0.96	1.81	0.090
7-Me(I)	10.20	6.30	3.30	1.85	1.78	0.048
3,4-diMe(I)	14.00	8.40	-	1.90	1.75	0.032
7-OH(I)	5.00	3.20	1.52	0.80	1.77	0.094
8-OH(I)	3.36	2.36	1.30	-	1.77	0.140
6-OH-4-Me(I)	7.10	4.50	2.32	-	1.77	0.066
7,8-diOH-4-Me(I)	4.84	2.70	0.94	-	1.68	0.078
7-MeO(I)	11.50	7.50	4.16	2.10	1.79	0.042
7,8-diMeO(I)	9.00	5.30	2.54	1.28	1.76	0.052
6-MeO-4-Me(I)	11.70	7.10	3.68	1.52	1.76	0.039
6,7-diMeO-4-Me(I)	14.90	8.10	3.60	1.64	1.73	0.030

$$\log (P + 10) = a - b.B \qquad (4.27)$$

where a and b are constants.

Figure(4.6.3.7) gives the plots of log (P + 10) against B for the sorption of coumarin on the resins X4, X8 and X12 and the values of a and b calculated from the figures are given in table (4.6.3.14). It is observed that as P or % methanol content of the solvent increases, the value of log B decreases, and the value of γ increases toward unity. The values of γ are less then unity and the effect of crosslinking is relatively less in aqueous solution.

For the sorption of ten substituted coumarins studied with the resin X4 in 10 %, 20 %, 30 % and 40 % methanol the values of a is unity. The value of B in each case decfeases with increase in percent methanol content of the solution.

Table (4.6.3.16) gives the values of B obtained from figures (4.6.3.2 to 4.6.3.6) for the coumarins studied. The values are significantly different. Broadly it may be said that the B value for coumarin and hydroxycoumarins are less than those for methyl and methoxycoumarins. This difference is marked and indicates the possibility of the separation of binary mixtures of such coumarins. This is the subject of study in the next section.

Equation (4.27) can also account for the sorption of substituted coumarins on the resin X4 in aqueous methanols.

Figures (4.6.3.8 and 4.6.3.9) give the plots of log (P + 10) against B and the values of a and b obtained

from those figures are given in table (4.6.3.16). It may be noted that the value of a is affected only to a small extent by the nature of the substituent. On the other hand, the effect on the value of b is marked. Again, broadly, the values for coumarin and hydroxycoumarins are significantly different from those for methyl and methoxycoumarins.

4.6.4 : Separation studies :

4.6.4a : Introduction :

In the previous section, the study of sorption equilibria of coumarin on three sulfonated styrene-divinylbenzene copolymer type sulfonic acid resins in water and aqueous methanols and of ten substituted coumarins with the resin X4 in aqueous methanols was described.

In this section, the separation of some binary mixtures of coumarin and substituted coumarins with a sulfonic acid resin of relative degree of crosslinking as four is described.

4.6.4b Experimental :

Materials : The chemicals and the resin Dowex 50 W-X4 (-100, + 200 mesh) used were from the samples used in the previous section and the solutions were prepared in 10 % methanol (by volume).

Procedure : A column containing 46 gms. of air dry resin, Dowex 50 W-X4 was set up. The column data were as follows : moisture content of air dry resin 29.9 % ; capacity of air dry resin, 3.55 meq./gm. ; bed volume, 131 cc. ; bed length, 53 cms. ; flow rate of effluent, 5 cc./min.

The solvent (aqueous methanol, 10 % by volume) level in the column was brought to the resin bed level and 100 cc. of coumarin (or substituted coumarins) solution in aqueous methanol (10 % by volume) were added (W denotes the meq.of solute content in 100 cc. of the added solution).

When the liquid level was again at the bed level, 25 cc. of aqueous methanol were added and then column was connected to an overhead resorvoir of aqueous methanol (10 % by volume). The effluent was collected in measuring containers. The first sample was equal to void volume and numbered as sample number v.v. Then 100 cc. samples were collected and numbered 1,2,3 and so on. Solute content, Ws, was estimated as milliequvalents of solute in 100 cc. sample by ultraviolet absorption with a Beckman Model DU Spectrophotometer, using 10 mm. quartz cells.

In the same way, binary mixtures of coumarins in aqueous methanol (10 %, by volume), 100 cc. were sorbed on resin bed and were eluted with aqueous methanol (10 % by volume) and samples were estimated for solute contents by ultraviolet absorption.

4.6.4c Results :

Tables (4.6.4.1a and 4.6.4.1b) give the column elution of coumarin and ten substituted coumarins with the resin X4. Table(4.6.4.2) and figure (4.6.4.1) give the separation of coumarin from 7-methoxycoumarin and 7-methylcoumarin. Table (4.6.4.3) and figure (4.6.4.2) give the separation of 7-hydroxycoumarin from 7-methoxycoumarin and 7-methylcoumarin. Table (4.6.4.4) and figure (4.6.4.3) give the separation of 6-hydroxy-4-methylcoumarin from 8-hydroxycoumarin and 6-methoxy-4-methylcoumarin.

Table (4.6.4.5) and figure (4.6.4.4) give the separation of 7,8-dihydroxy-4-methylcoumarin from 3,4-dimethylcoumarin and 6,7-dimethoxy-4-methylcoumarin.

Table (4.6.4.6) and figure (4.6.4.5) give the separation of 7,8-dimethoxycoumarin from 3,4-dimethylcoumarin and 6,7-dimethoxy-4-methylcoumarin.

Table 4.6.4.1 a

Column elution of coumarins with the resin X4

	Coumarin	7-OH(I)	8-OH(I)	6-OH-4-Me(I)	7,8-diOH-4-Me(I)
10^2 W =	6.202	5.155	5.008	8.129	6.003
Sample No.			10^2 Ws =		
v.v.	-	-	-	-	-
1-5	-	-	-	-	-
6	-	-	0.0339	-	-
7	-	-	0.7857	-	-
8	-	-	2.5830	-	0.3250
9	0.5054	0.3117	1.4400	-	1.396
10	2.9860	1.4870	0.1651	-	2.4420
11	2.4580	2.1130	-	0.1476	1.3570
12	0.2526	1.0390	-	0.5580	0.3959
13	-	0.2042	-	1.6470	0.0879
14	-	-	-	2.5220	-
15	-	-	-	2.0250	-
16	-	-	-	0.8610	-
17	-	-	-	0.2768	-
18	-	-	-	0.0922	-
19	-	-	-	-	-
20	-	-	-	-	-

Table 4.6.4.1 b

Column elution of coumarins with the resin X4

	7-Me(I)	3,4-diMe(I)	7-MeO(I)	7,8-diMeO(I)	6-MeO-4-Me(I)	6,7-diMeO-4-Me(I)
10^2 W =	5.438	5.577	5.066	5.039	5.667	5.507
Sample No.			10^2 Ws =			
v.v.	-	-	-	-	-	-
1-10	-	-	-	-	-	-
11	-	-	-	0.0504	-	-
12	-	-	-	0.1986	-	-
13	-	-	-	0.6966	-	-
14	-	-	-	1.4230	-	-
15	-	-	-	1.4680	-	-
16	0.1741	-	0.0695	0.8448	-	-
17	0.4303	-	0.1632	0.2816	-	-
18	0.9376	-	0.4099	0.0763	-	-
19	1.3910	-	0.8612	-	0.1040	-
20	1.2860	-	1.2360	-	0.2166	-
21	0.7767	-	1.1390	-	0.4678	-
22	0.3170	0.1770	0.7223	-	0.8455	-
23	0.1250	0.3530	0.3368	-	1.1610	0.0807
24	-	0.6091	0.1285	-	1.1270	0.1614
25	-	0.8993	-	-	0.8318	0.2905

Table 4.6.4.1 b (Continued)

	7-Me(I)	3,4-diMe(I)	7-MeO(I)	7,8-diMeO(I)	6-MeO-4-Me(I)	6,7-diMeO-4-Me(I)
10^2 W =	5.438	5.577	5.066	5.039	5.667	5.507
Sample No.			10^2 Ws =			
26	-	0.9088	-	-	0.5024	0.4601
27	-	0.8702	-	-	0.2772	0.6215
28	-	0.6769	-	-	0.1343	0.7457
29	-	0.4883	-	-	-	0.7586
30	-	0.3094	-	-	-	0.6860
31	-	0.1788	-	-	-	0.5165
32	-	0.1064	-	-	-	0.4019
33	-	-	-	-	-	0.2986
34	-	-	-	-	-	0.2219
35	-	-	-	-	-	0.1550
36	-	-	-	-	-	0.1089
37	-	-	-	-	-	-
38	-	-	-	-	-	-

Fig. 4.6.4.1 Separation of coumarin (a) from 7-methylcoumarin (b) and 7-methoxycoumarin (c) with the resin X_4.

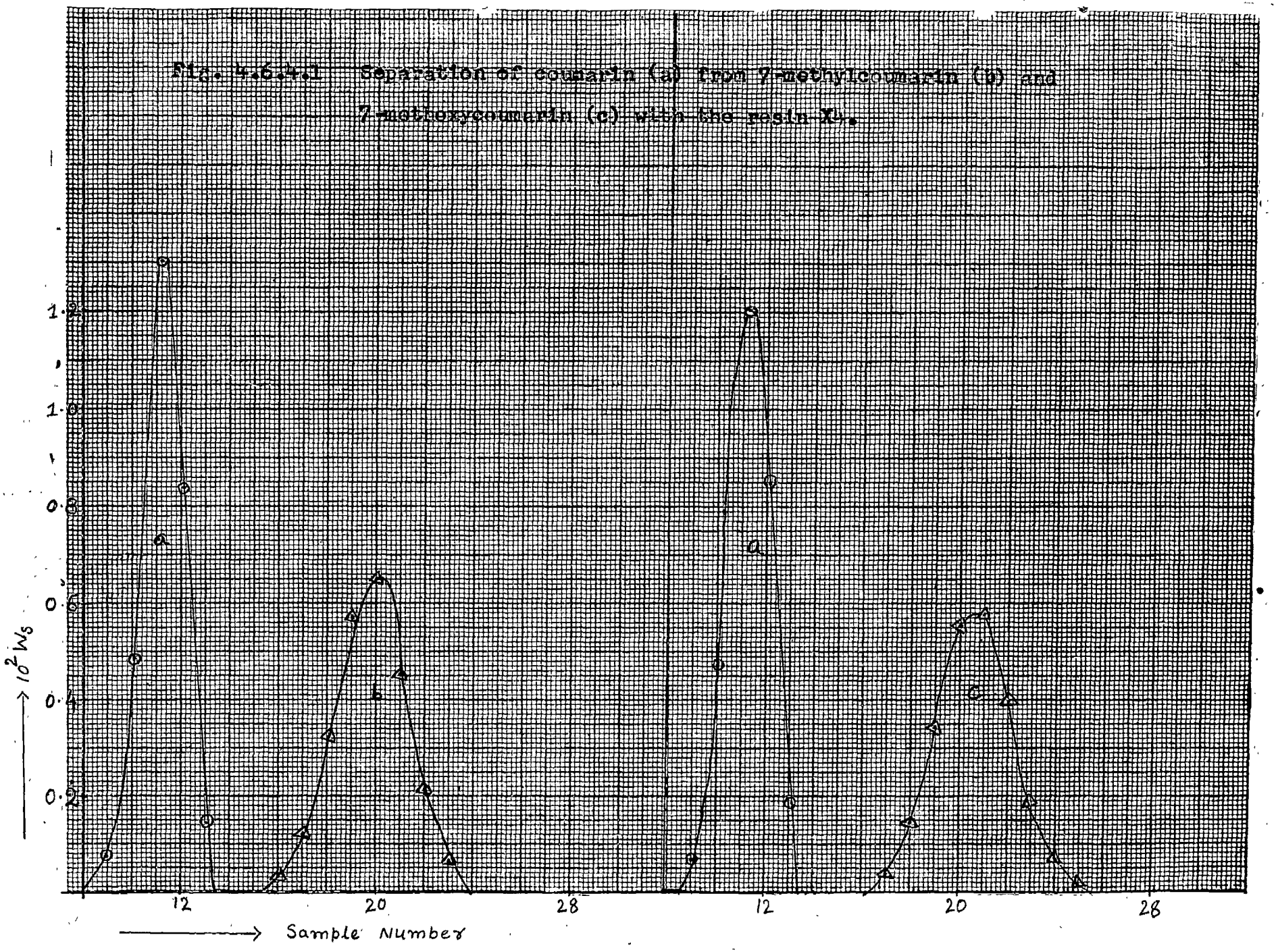


Table 4.6.4.2

Separation of coumarin from 7-methylcoumarin and 7-methoxycoumarin with the resin X4

10^2 W = Sample No.	Coumarin + 7-Methyl(I) 2.888 + 2.510 10^2 Ws =		Coumarin + 7-Methoxy(I) 2.831 + 2.465 10^2 Ws =	
v.v.	-	-	-	-
1-8	-	-	-	-
9	0.0808	-	0.0781	-
10	0.4943	-	0.4823	-
11	1.3090	-	1.2130	-
12	0.8453	-	0.8636	-
13	0.1593	-	0.1947	-
14	-	-	-	-
15	-	-	-	-
16	-	0.0458	-	-
17	-	0.1340	-	0.0514
18	-	0.3304	-	0.1632
19	-	0.5803	-	0.3577
20	-	0.6563	-	0.5765
21	-	0.4643	-	0.5903
22	-	0.2232	-	0.4099
23	-	0.0759	-	0.2048
24	-	-	-	0.0800
25	-	-	-	0.0312
26	-	-	-	-
27	-	-	-	-

Fig. 4.6.12 Separation of 7-hydroxycoumarin (a) from 7-methylcoumarin (b) and 7-methoxycoumarin (c) with the resolution

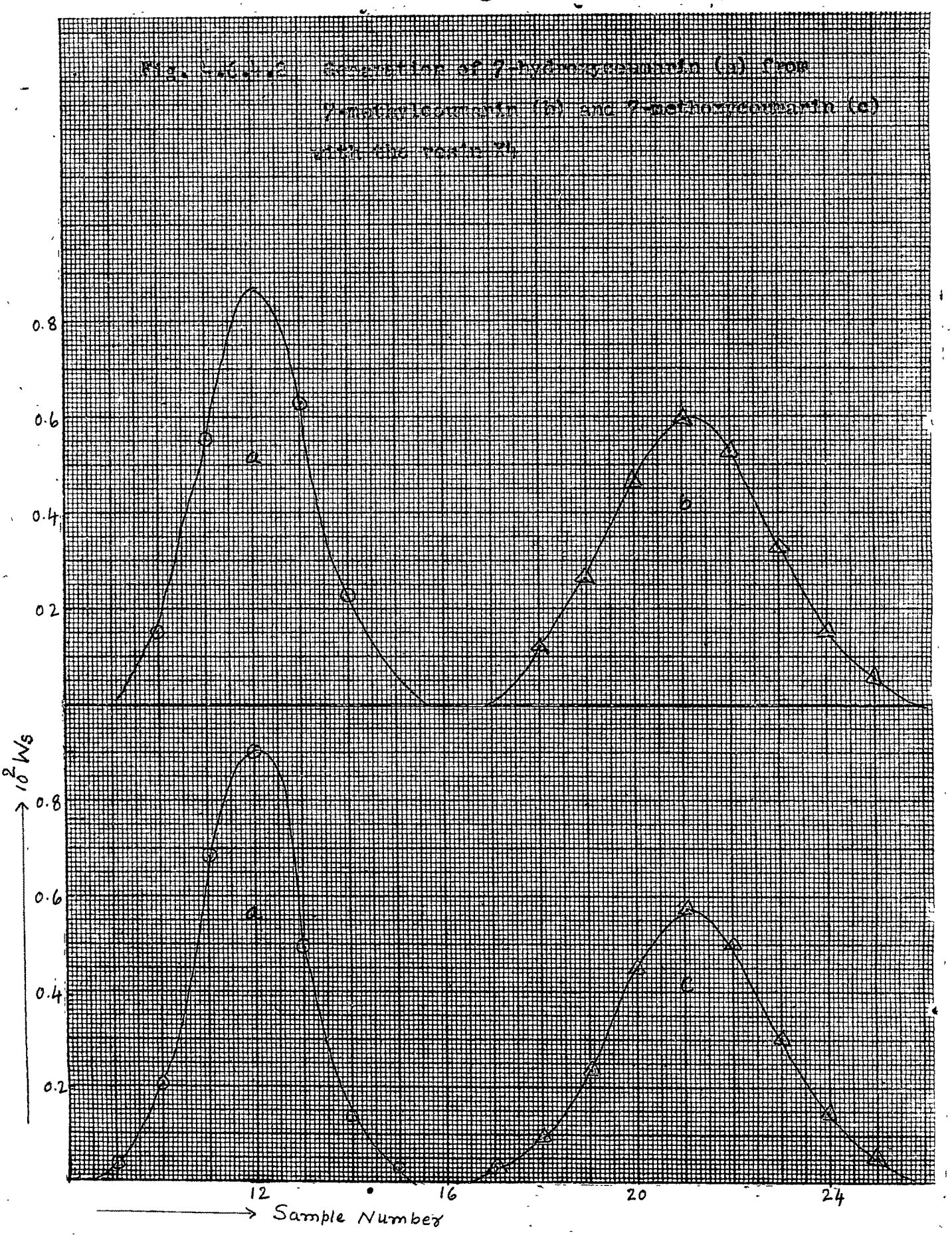


Table 4.6.4.3

Separation of 7-hydroxycoumarin from 7-methylcoumarin and 7-methoxycoumarin with the resin X4

	7-Hydroxy(I) + 7-Methyl(I)		7-Hydroxy(I) + 7-Methoxy(I)	
10^2 W =	2.501	+ 2.562	2.506	+ 2.445
Sample No.	10^2 Ws =		10^2 Ws =	
v.v.	-	-	-	-
1-8	-	-	-	-
9	-	-	0.0358	-
10	0.1504	-	0.2092	-
11	0.5575	-	0.6879	-
12	0.8742	-	0.9028	-
13	0.6305	-	0.5015	-
14	0.2329	-	0.1376	-
15	0.0559	-	0.0322	-
16	-	-	-	-
17	-	-	-	0.0382
18	-	0.1250	-	0.0972
19	-	0.2679	-	0.2431
20	-	0.4733	-	0.4514
21	-	0.5982	-	0.5808
22	-	0.5358	-	0.5070
23	-	0.3348	-	0.3112
24	-	0.1607	-	0.1528
25	-	0.0670	-	0.0639
26	-	-	-	-
27	-	-	-	-

Fig. 4.6.4.3 Separation of 6-hydroxy-4-methylcoumarin (a) from 8-hydroxycoumarin (b) and 6-methoxy-4-methylcoumarin (c) with the resin K4.

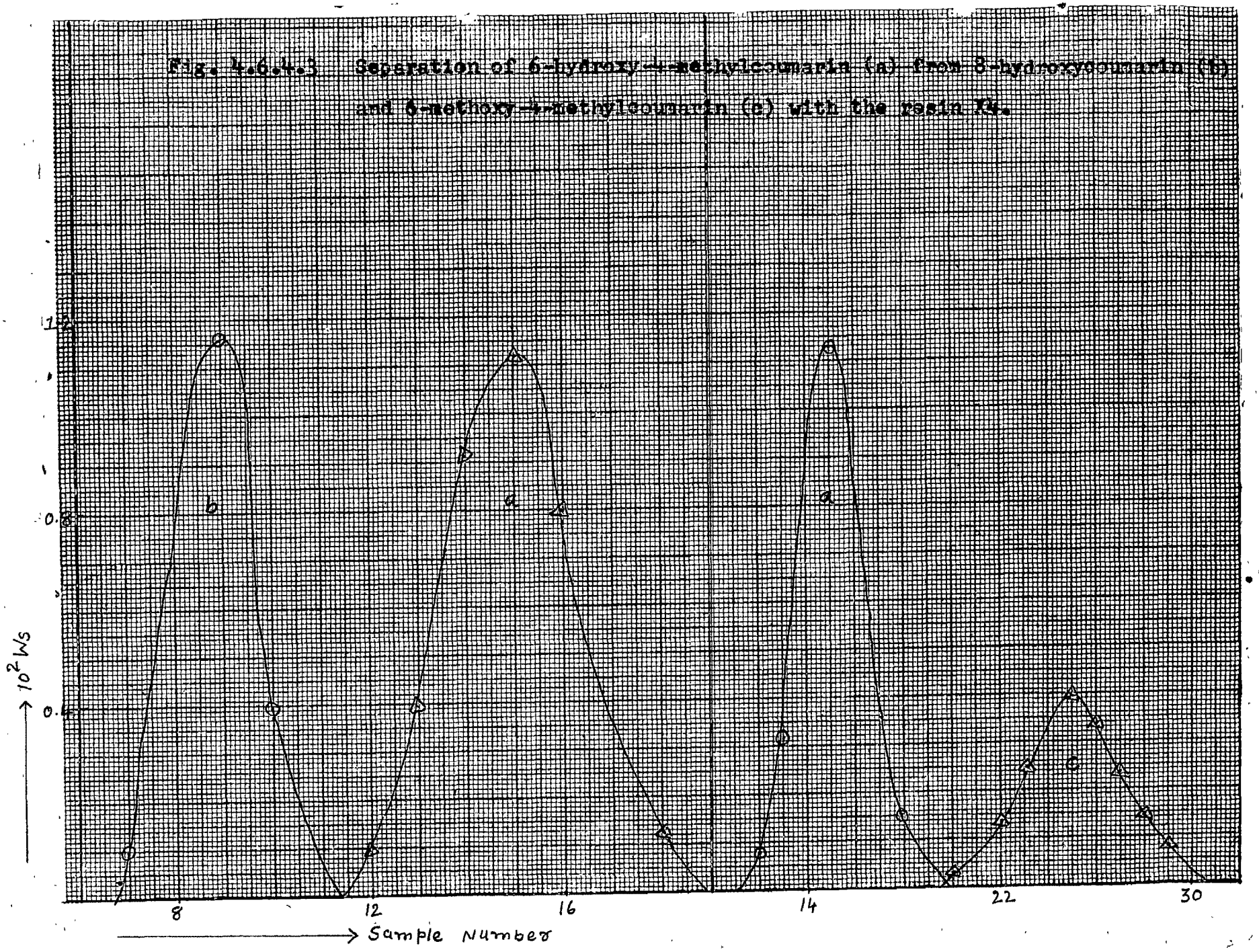


Table 4.6.4.4

Separation of 6-hydroxy-4-methylcoumarin from 8-hydroxycoumarin and 6-methoxy-4-methylcoumarin with the resin X4

	6-Hydroxy-4-methyl(I) + 8-Hydroxy(I)		6-Hydroxy-4-methyl(I) + 6-Methoxy-4-Methyl(I)	
10^2 W =	3.8400	+ 2.503	3.911	+ 2.084
Sample No.	10^2 Ws =		10^2 Ws =	
v.v.	-	-	-	-
1-6	-	-	-	-
7	-	0.1099	-	-
8	-	0.7705	-	-
9	-	1.1650	-	-
10	-	0.4023	-	-
11	-	0.0550	-	-
12	0.1098	-	0.0808	-
13	0.3997	-	0.3207	-
14	0.9226	-	0.8523	-
15	1.1250	-	1.1330	-
16	0.7995	-	0.8874	-
17	0.3559	-	0.4261	-
18	0.1275	-	0.1538	-
19	-	-	0.0571	-
20	-	-	-	0.0433
21	-	-	-	0.0693
22	-	-	-	0.1387
23	-	-	-	0.2496
24	-	-	-	0.3639
25	-	-	-	0.4029
26	-	-	-	0.3465
27	-	-	-	0.2425
28	-	-	-	0.1472
29	-	-	-	0.0797
30	-	-	-	-

Fig. 4.6.4.4 Separation of 7,8-dihydroxy-4-methylcoumarin (a) from 6,7-dimethoxy-4-methylcoumarin (b) and 3,4-dimethylcoumarin (c) with the resin X4.

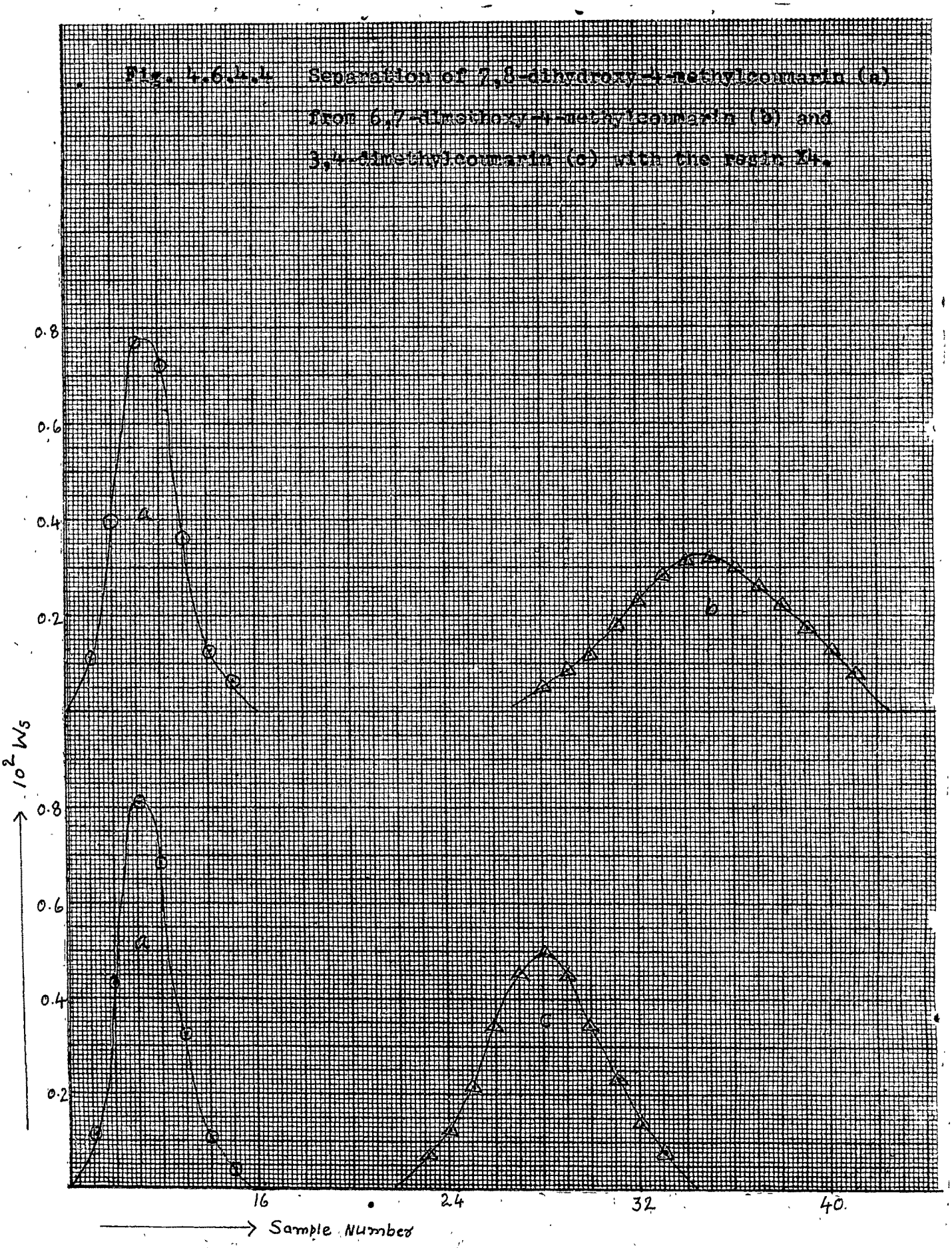


Table 4.6.4.5

Separation of 7,8-dihydroxy-4-methylcoumarin from 3,4-dimethylcoumarin and 6,7-dimethoxy-4-methylcoumarin with the resin X4

	7,8-Dihydroxy-4-methyl(I) + 3,4-Dimethyl(I)		7,8-Dihydroxy-4-methyl(I) + 6,7-Dimethoxy-4-methyl(I)	
10^2 W =	2.506	+ 2.947	2.535	+ 2.761
Sample No.	10^2 Ws =		10^2 Ws =	
v.v.	-	-	-	-
1 to 8	-	-	-	-
9	0.1142	-	0.1107	-
10	0.4304	-	0.3953	-
11	0.8046	-	0.7642	-
12	0.6852	-	0.7202	-
13	0.3224	-	0.3601	-
14	0.1054	-	0.1186	-
15	0.0439	-	0.0659	-
16	-	-	-	-
17	-	-	-	-
18	-	-	-	-
19	-	-	-	-
20	-	-	-	-
21	-	-	-	-
22	-	-	-	-

Table 4.6.4.5 (Continued)

	7,8-Dihydroxy-4-methyl(I)	+ 3,4-Dimethyl(I)	7,8-Dihydroxy-4-methyl(I)	+ 6,7-Dimethoxy-4-methyl(I)
10^2 W =	2.506	+ 2.947	2.535	+ 2.761
Sample No.		10^2 Ws =		10^2 Ws =
23	-	0.0725	-	-
2424	-	0.1233	-	-
25	-	0.2156	-	-
26	-	0.3433	-	-
27	-	0.4496	-	-
28	-	0.4932	-	0.0484
29	-	0.4496	-	0.0807
30	-	0.3452	-	0.1170
31	-	0.2301	-	0.1760
32	-	0.1431	-	0.2316
33	-	0.0822	-	0.2835
34	-	-	-	0.3148
35	-	-	-	0.3228
36	-	-	-	0.2986
37	-	-	-	0.2663
38	-	-	-	0.2300
39	-	-	-	0.1735
40	-	-	-	0.1291
41	-	-	-	0.0888

Fig. 4.6.4.5 Separation of 7,8-dimethoxycoumarin (a) from 6,7-dimethoxy-4-methylcoumarin (b) and 3,4-dimethylcoumarin (c) with the zeolin X4.

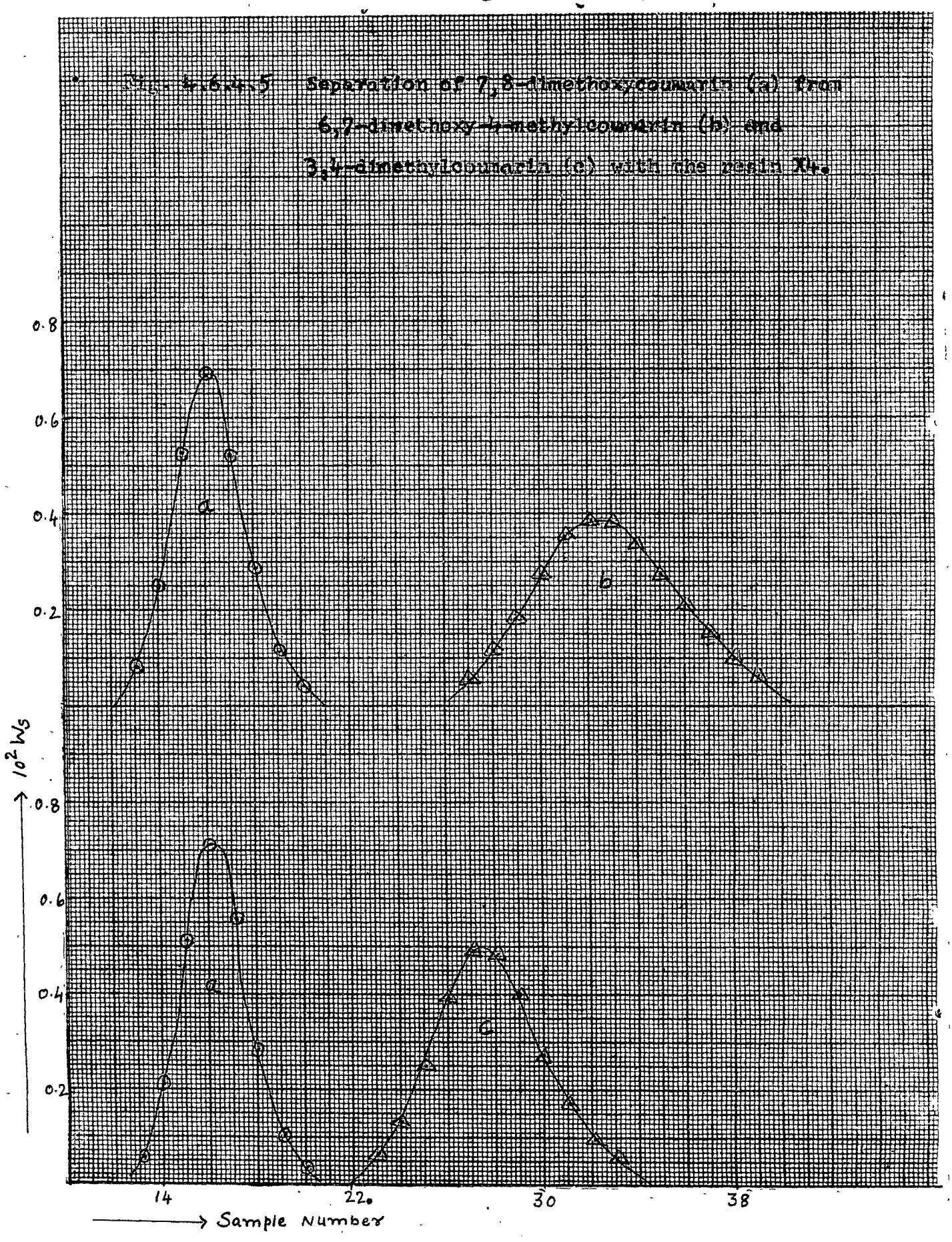


Table 4.6.4.6

Separation of 7,8-dimethoxycoumarin from 3,4-dimethylcoumarin and 6,7-dimethoxy-4-methylcoumarin with the resin X4

	7,8-Dimethoxy(I) + 3,4-Dimethyl(I)		7,8-Dimethoxy(I) + 6,7-Dimethoxy -4-methyl(I)	
10^2 W =	2.464	+ 2.804	2.504	+ 2.904
Sample No.	10^2 Ws =		10^2 Ws =	
v.v.	-	-	-	-
1-12	-	-	-	-
13	0.0533	-	0.0778	-
14	0.2075	-	0.2482	-
15	0.5113	-	0.5262	-
16	0.7115	-	0.6893	-
17	0.5559	-	0.5225	-
18	0.2816	-	0.2854	-
19	0.1005	-	0.1112	-
20	0.0430	-	0.0430	-
21-22	-	-	-	-
23	-	0.0677	-	-
24	-	0.1286	-	-
25	-	0.2514	-	-
26	-	0.3916	-	-
27	-	0.4854	-	0.0670
28	-	0.4815	-	0.1146
29	-	0.3984	-	0.1857
30	-	0.2755	-	0.2745
31	-	0.1692	-	0.3511
32	-	0.0967	-	0.3833
33	-	0.0580	-	0.3793
34	-	-	-	0.3431
35	-	-	-	0.2745
36	-	-	-	0.2098
37	-	-	-	0.1493
38	-	-	-	0.1009
39	-	-	-	0.0710

4.6.4d Discussion :

The observation that B values are different for coumarins, suggested that separation of mixtures should be possible. In tables (4.6.4.1a and 4.6.4.1b) the elution data for each of the compounds studied areegiven. The tables indicate that the elution of coumarin and hydroxy coumarins is relatively quicker then that of methoxy and methyl derivatives, and hence separation of several binary mixtures is possible.

The data also indicate that as the value of B for a compound increases, in general, the elution hand becomes broader and reduced in height.

Tables (4.6.4.2 to 4.6.4.6) and figures (4.6.4.1 to 4.6.4.5) give the data for the separation of 10 binary mixtures as evidence to support the conclusion.

It may be noted here that in the study of sorption of coumarins on the chloride form of a strongly basic anion exchanger, Amberlite IRA-400, Shah and Bafna (48) had shown that the sorption of coumarin is less from methanol than from water solution. Hence, in both cases, the effect of increase in methanol content of the solution seems to be similar, namely, the reduced sorption of coumarin as the methanol content increases in the solution.

It was further observed by them that the order of sorption was dihydroxycoumarin > hydroxycoumarin > methyl and methoxycoumarin and taking advantage of this separation of a mixture containing a dihydroxycoumarin, a hydroxycoumarin

and a methyl or methoxycoumarin could be achieved (49) using different solvents.

In this study the order hydroxycoumarin > methyl or methoxycoumarin, observed for strongly basic anion exchanger is reversed and is methyl or methoxycoumarin > hydroxycoumarin and again separation of such binary mixtures has become possible.

The reversal of this order may be explained as follows: The coumarins are lactones and hence may be considered to behave as very weak acids, the hydroxycoumarins being relatively more acidic than the methyl and methoxy coumarins. Hence with basic anion exchangers, the dipole interaction should be more for dihydroxycoumarins, relatively less for hydroxycoumarins and relatively further less for methyl and methoxycoumarins. Hence the sorption should be in the order,

dihydroxy- > monohydroxy-> methyl or methoxy-

With strongly acidic cation exchangers, the dipole interaction should be less for hydroxycoumarins than for methyl or methoxycoumarins. Hence the sorption should be in the order

hydroxy- < methyl or methoxy-

The reversal of the order may thus be attributed mainly to the dipole interactions ; the London dispersion forces, which are also operating do not appear to be significantly responsible for the marked difference in the sorption. On the other hand, for achomologous series of acids(section 4.3) in water, where the acid strength and hence the dipole interactions are substantially different, the London dispersion forces may be considered to be mainly responsible for the observed difference in the sorption of the acids.

References :

1. Mayneord,W.V. and Roe, E.M.F., Proc.Roy.Soc. (London), A 152, 299 (1955) ; A 158, 634 (1937).
2. Bafna,S.L. and Govindan, K.P. Ind.Eng.Chem., 48, 310 (1956).
3. Govindan, K.P. and Bafna, S.L. J.Sci.Ind.Res.,(India), 16B, 321 (1957).
4. Anderson, R.E. and Hansen, R.D. Ind.Eng.Chem., 47, 71 (1955).
5. Cesarano,C. and Lepscky, C. J.Inorg.Nucl.Chem., 14, 276 (1960).
6. Cerrai, E. and Godoa,F., Nature, 183, 1528 (1959).
7. Chasanov,M.G. and Kunin,R. and McGervey, F.X., Ind.Eng.Chem., 48, 305 (1956).
8. Clark, I.T., Anal.Chem., 30, 1676 (1958).
9. Gregor,H.P., Collins, F.C. and Pope, M., J.Colloid Sci., 6, 304 (1951).
10. Griffin, R.P. and Dranoff., J.J., J.Chem.Soc., 283 (1963).
11. Radzitzky,P.de.,Ind.Chem.Belge.Suppl., 1, 156 (1959).
12. Reichenberg,D. and Wall,W.F., J.Chem.Soc., 3364 (1956).
13. Samuelson, O., Dechema-Monograph, 26, 219 (1956).
14. Sargent, R.N. and Graham,D.L., Ind.Eng.Chem.Process Design Develop., 1, 56 (1962).
15. Simpson,D.W. and Bauman, W.C., Ind.Eng.Chem., 46, 1958 (1954).
16. Tamamushi, B. and Tamki, K., Trans. Faraday Soc., 55, 1013 (1959).

17. Turse,R., Gerdes,W.H. and Rieman,W., Z.Physik.Chem., 33, 219 (1962).

18. Vassiliou,B. and Dranoff,J., A.I.Ch.E.J.8, 248 (1962).

19. Wasmer,H.B., J.Polymer Sci., 36, 461 (1959).

20. Wheaton, R.M. and Bauman,W.C., Ann.N.Y. Acad.Sci., 57, 159 (1953).

21. Wheaton,R.M. and Bauman,W.C., Ind.Eng.Chem., 45, 2281 (1953).

22. Archibald, R.C., J.Am.Chem.Soc., 54, 3178 (1932).

23. Angelescu, E. and Dutchievici, O., Bul.Soc.Chim. Romania, 14, 46 (1932). ; Chem.Abstr., 27, 1258 (1933).

24. Bekturov,A., J.Gen.Chem.(U.S.S.R.), 9, 419 (1939) ; Chem.Abstr., 33, 6686 (1939).

25. Bekturov, A., J.Gen.Chem.(U.S.S.R.), 9, 1717 (1939) ; Chem.Abstr., 34, 3563 (1940)

26. Moelwyn-Hughes, E.A., J.Chem.Soc., 850 (1940).

27. Mansel Davies, Percy Jones, Patnaik,D. and Moelwyn-Hughes, E.A., (Univ.Coll.of Wales, Aberystwyth Engl.) J.Chem.Soc., 1249 (1951)

28. Tagliavini Giuseppe., (Univ.Modena, Italy) and Manfredo Biancani,Atti.Soc.Nat.emat.Modena, 32-33, 102-8 (1954,55) ; Chem.Abstr., 51, 14379 (1957).

29. Sandell, K.Bertil, Monatsh, 89, 36 (1958) ; Chem.Abstr., 52, 19410 i (1958).

30. Mittra, R., J.Indian Chem.Soc., 5, 209 (1928).

31. Tokareva, G.A. and Kozlov, V.N., Trudy Inst. Khim., Akad. Nauk.(S.S.S.R.), Ural,Filial,Sbornik Rabot 2, No.1 19 (1958) ; Chem.Abstr., 53, 7727 (1959).

32. Kozlov, V.N. and Tokareva, G.A., Gidrolizn i Lesokhim. Prom. 15, No.1 9 (1962) ; Chem.Abstr., 56, 14990 (1962).

33. Vignes, A. (Ecole Natl.Super Ind.Chem., Nancy,France) J.Chim.Phys. 57, 966 (1960) ; Chem.Abstr., 55, 13026 (1961).

34. Kuznetsov, F.A., Lilleva,A.K. and Smirnov, N.I., (Lensovet Technol.Inst., Liningrad) Zhur Priklad Khim 34, 1829 (1961) ; Chem.Abstr., 56, 3318 (1962).

35. Sethna, S.M. and Shah, N.M., Chem.Rev., 36, 1 (1945).

36. Sethna, S.M. and Phadke, R., Organic reaction, RogerAdams, 7, 1 (1953).

37. Tasaki,T., Chem.Abstr., 22, 1543 (1928).

38. Mangini, A. and Passerini, R., Chem.Abstr., 46, 3047d (1952).

39. Chmielewska, J. and Ciecierska, D., Chem.Abstr., 47, 9773d (1953).

40. Nakabayashi, T., Tokoroyama, T., Miyazaki, H. and Isono,S., J.Pharm.Soc., Japan, 73, 669 (1953).

41. Jacobson,C and Amstutz,E., J.Org.Chem., 18, 1117 (1953).

42. Goodwin, R. and Pollock,B., Arch.Biochem.Biophys., 49, 1 (1954).

43. Cingolani,E., Chem.Abstr., 49, 5964a (1955).

44. Cingolani,E., Chem.Abstr., 51, 14418e (1957).

45. Ganguli,B. and Bagchi, P., J.Org.Chem., 21, 1415 (1956).

46. Sen,K. and Bagchi, P., J.Org.Chem., 24, 316 (1959).

47. Shah, R.S. and Bafna, S.L., Indian.J.Chem., 1, 400(Sept.1963).

48. Shah,R.S. and Bafna,S.L., J.Indian.Chem.Soc., 42,179(1965).

49. Shah,R.S. and Bafna,S.L., Nature, 208, 76 (1965).