

CHROM. 13,179

MOLECULAR SORPTION ON ION-EXCHANGE RESINS OF ALIPHATIC MONO- AND DICARBOXYLIC ACIDS

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SUMMARY

Molecular sorption behaviour of twenty-four aliphatic mono- and dicarboxylic acids has been studied with styrene-divinylbenzene copolymer-based sulfonic acid cation-exchange resins of nominal degree by crosslinking 4, 8 and 12 in an aqueous medium. The mechanism of sorption phenomena is discussed and a sorption coefficient is proposed as a product of the group term, a summation of the increments contributed by each additional group and the ground term, a function of the sorptive system, provided the molecular size is not too large to be excluded from the resin phase by sieve action. From this an equation is derived to calculate the sorption coefficient. The column elution study of these carboxylic acids has been carried out with the cation-exchange resin of nominal degree by crosslinking 4 in hydrogen form in an aqueous medium. The elution curves were fairly symmetrical under suitable conditions and could be described as Gaussian curves. The sorption elution behaviour is discussed in terms of peak elution volume, peak height and width of the chromatogram and correlated with the sorption coefficient. The separation possibility of mixtures of these carboxylic acids is discussed in terms of resolution.

INTRODUCTION

Carboxylic acids form a class of organic compounds¹⁻⁴ which include a wide variety of substances and are of direct interest to organic and bio-organic chemists because of their occurrence in nature, physiological activity and uses in pharmacy and industry. This has naturally stimulated the development of various chromatographic techniques⁵⁻²⁰. During the past three decades or so, the molecular sorption on ion-exchange resins has provided a new area of interest for the study of sorption and separation of weak and non-electrolytes²¹⁻⁴². On the one hand this has provided an insight into the theoretical aspect of this subject and on the other hand, it has provided a new technique of separation of closely related compounds such as members of the homologous series, position isomers and geometrical isomers. The process has several advantages which include no chemical regeneration of the resin, simplicity of operation and use of ordinary solvents as eluents which should make the process attractive. These studies have thus provided a new dimension to the versatile art of chromatography.

Earlier⁴³ the molecular sorption and column elution behaviour of substituted coumarins had been studied with styrene-divinylbenzene (DVB) copolymer-based sulfonic acid cation-exchange resin in the hydrogen form. In the present paper, the sorption equilibrium and sorption elution behaviour of twenty-four aliphatic mono- and dicarboxylic acids have been studied.

EXPERIMENTAL

The resins used were styrene-DVB copolymer-based sulfonic acid cation exchangers Dowex 50W (Dow Chemical, Midland, MI, U.S.A.) of 100-200 mesh and nominal degree of crosslinking (X) of 4, 8 and 12 (X denotes the percent of combined DVB in the styrene copolymer used as resin matrix for preparing the sulfonate), further referred to as X4, X8 and X12. These were thoroughly washed, conditioned with three cycles of regeneration with 10% HCl (C.P.) and exhaustion with 5% NaCl (C.P.) and finally regenerated with a very large excess of 10% HCl (A.R.), washed free of acid, filtered, air dried and stored in glass-stoppered bottles. Their capacity, determined by limiting the exchange with normal barium chloride solution and moisture, achieved by heating to a constant weight at $101 \pm 2^\circ\text{C}$, was estimated⁴⁴. The capacity in milliequivalents (mequiv.) per gram of oven dry resin was, X4, 4.87; X8, 4.79; and X12, 4.80. The carboxylic acids used (Table II) were of C.P. or A.R. grade and were divided into six homologous series. The solutions of these acids were prepared in distilled water and estimated by titration with standard sodium hydroxide solution using suitable indicators.

The sorption equilibrium studies were carried out by contacting the carboxylic acid solutions of different concentrations and known volumes (50 ml), with the weighed amounts (*ca.* 1 g) of the air dried resin in well stoppered flasks with frequent shaking to attain equilibrium (about 24 h). The initial concentration (C_0) and the final equilibrium concentration (C_e) in moles/l were estimated. Preliminary work indicated that further increase in the contact time or small variation in room temperature (*ca.* 30°C) did not measurably alter the amount sorbed.

Before carrying out a column elution run, a definite quantity of air dried resin X4 was weighed, soaked in distilled water in a beaker and transferred carefully into a Pyrex glass column. The resin bed length (L), bed volume (V_b), total capacity of the resin in the column (C) and disc or dead volume (V_d) were measured. Bed length and bed volume for 100 mequiv. of the resins were 36.13 cm and 87.13 ml, respectively.

Prior to performing an elution run, the resin column was back washed with distilled water at a sufficient speed to loosen the resin and to remove air bubbles. The resin was then allowed to settle under gravity to achieve a size classification within the column.

For carrying out the elution run, the liquid level was first brought to the resin bed level. Then a known feed volume (V_f), containing W mM of a solute depending on its solubility were added carefully from the top of the column, so that the surface layer of the resin bed was minimally disturbed. The solution was allowed to sink into the resin bed by opening the pinch cock at the lower end of the column. The effluent was collected in a measuring flask (V_s ml) and it was marked as sample No. 1. When the liquid level was at the resin bed level, 5 ml of distilled water were added to rinse the inside of the column above the resin bed and it was allowed to sink into the

resin bed. Then the column was connected to an overhead reservoir of distilled water and the continuous elution was carried out at the rate of 2 ml/min. The effluent was collected in measuring flasks (V_s ml) and numbered as 2, 3, 4, etc. The solute content (W_s mequiv.) in each sample was estimated. After the run was completed, the column was washed and back washed with distilled water and allowed to settle under gravity to get it ready for the next run.

RESULTS AND DISCUSSION

Sorption equilibrium study

The sorption coefficient is a fundamental parameter in chromatographic work and should be related to the behaviour of the solute in the column and its appearance in the effluent. It is determined by the interplay of various interactions which should include dispersion, dipole, steric and hydrogen bonding. These in turn, would depend on the variables of the resin-solute-solvent systems^{20,45,46}. Hence, a complex behaviour is to be expected and the study of one variable at a time should lead towards a better understanding of the phenomenon.

For a linear sorption isotherm of solute-resin systems we have

$$\frac{C_0 - C_e}{C_r} = B \cdot C_e \quad (1)$$

where C_0 and C_e are initial and equilibrium concentrations of the solute in moles/l, respectively, C_r is the number of equivalents of the resin per liter of the solution and B is the sorption coefficient. Hence,

$$B = \frac{C_0 - C_e}{C_r \cdot C_e} \quad (2)$$

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

Alternatively, we may consider the sorption equilibrium as:



where R and S denote resin and solute respectively. The sorption equilibrium constant B is given by eqn. 2. The sorption coefficients were determined at room temperature for twenty-four carboxylic acids with resins X4, X8 and X12 in hydrogen form in aqueous medium.

Table I gives an illustrative calculation of the sorption coefficient of *n*-valeric acid with resin X4 in hydrogen form. The experimental values of sorption coefficients obtained in this way are given in Table II and are in agreement with the values obtained earlier for some of these acids^{47,48}.

It is postulated that the sorption coefficient B for a resin-solute-solvent system is given by the product of two terms, the group term ϱ , a summation of the increments contributed by each additional group and the ground term Φ , a function of the sorp-

TABLE I

ILLUSTRATIVE CALCULATION OF SORPTION COEFFICIENTS B FOR n -VALERIC ACID WITH RESIN DOWEX 50W-X4

$10^3 C_0$	$10^3 C_e$	$10^3 C_r$	$10^3 B$
100	95.32	74.5	661
90	85.73	74.8	666
80	76.28	74.2	657
70	66.74	74.3	659
60	57.18	74.7	664
50	47.67	74.0	660
40	38.12	75.0	662
30	28.61	74.2	658
20	19.06	74.4	663
10	9.53	74.5	665
			Average 661.5

TABLE II

EXPERIMENTAL VALUES OF SORPTION COEFFICIENT B

Series	Acid	$10^3 B$ with Resin X equal to			$\log BX^y$ (cal.)
		4	8	12	
I	Malonic	47.1	—	—	-0.420
	Succinic	83.0	—	—	-0.180
	Glutaric	144.0	51	—	+0.060
	Adipic	251.0	87	47.8	+0.300
	Pimelic	435.0	154	83.7	+0.540
	Suberic	751.0	268	146.0	+0.780
	Azelaic	1303.0	461	250.0	+1.020
	Sebacic	2279.0	806	439.0	+1.260
II	Acetic	126.0	63	—	-0.300
	Propionic	216.0	109	73.0	-0.060
	n -Butyric	381.0	188	127.0	+0.180
	n -Valeric	661.5	326	218.0	+0.420
	n -Caproic	1137.0	570	383.0	+0.660
	n -Heptanoic	1976.0	995	666.0	+0.900
	n -Caprylic	3476.0	1729	1147.0	+1.140
III	Isobutyric	241.0	120	80.0	-0.020
	Isovaleric	412.0	209	137.0	+0.220
	Isocaproic	726.0	357	239.0	+0.460
IV	Trimethylacetic	262.0	131	87.8	+0.020
V	Phenylacetic	1051.0	524	345.0	+0.620
	3-Phenylpropionic	1802.0	907	600.0	+0.860
	4-Phenylbutyric	3161.0	1579	1045.0	+1.100
VI	Thioglycolic	134.0	66	—	-0.274
	Thiolactic	232.0	114	77.3	-0.034

tive system, provided the molecular size is not too large to be excluded from the resin phase by sieve action. Hence we have

$$B = \rho \cdot \bar{\Phi} \quad (4)$$

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

$$q = a_1^{n_1} \cdot a_2^{n_2} \cdot a_r^{n_r} \quad (5)$$

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

$$\Phi = \frac{1}{m} \cdot X^{-\gamma} \quad (6)$$

where m and γ are constants. Combining eqns. 4, 5 and 6 we have

$$B = a_1^{n_1} \cdot a_2^{n_2} \cdot a_r^{n_r} \cdot \frac{1}{m} \cdot X^{-\gamma} \quad (7)$$

Using logarithms on both sides,

$$\frac{-\Delta F}{2.303 RT} = \log B = n_1 \log a_1 + n_2 \log a_2 + n_r \log a_r - \log (mX^\gamma) \quad (8)$$

Logarithms of the experimental values of B (Table II) were plotted against the values of n_c (the number of straight-chain carbon atoms in the molecule, Table III, for each homologous series. The plots were linear and from the values of their slopes and

TABLE III
NUMERICAL VALUES OF GROUPS (EQN. 9)

Series	Acid	n_c	n_b	n_r	n_t	n_x
I	Malonic	1	0	0	0	2
	Succinic	2	0	0	0	2
	Glutaric	3	0	0	0	2
	Adipic	4	0	0	0	2
	Pimelic	5	0	0	0	2
	Suberic	6	0	0	0	2
	Azelaic	7	0	0	0	2
II	Sebacic	8	0	0	0	2
	Acetic	1	0	0	0	1
	Propionic	2	0	0	0	1
	<i>n</i> -Butyric	3	0	0	0	1
	<i>n</i> -Valeric	4	0	0	0	1
	<i>n</i> -Caproic	5	0	0	0	1
	<i>n</i> -Heptanoic	6	0	0	0	1
III	<i>n</i> -Caprylic	7	0	0	0	1
	Isobutyric	2	1	0	0	1
	Isovaleric	3	1	0	0	1
IV	Isocaproic	4	1	0	0	1
	Trimethylacetic	2	2	0	0	1
V	Phenylacetic	1	0	1	0	1
	3-Phenylpropionic	2	0	1	0	1
	4-Phenylbutyric	3	0	1	0	1
VI	Thioglycolic	1	0	0	1	1
	Thiolactic	2	0	0	1	1

intercepts, the logarithm of the group constants and the numerical values of $\log m$ and γ (Table IV) were computed. Using the values thus obtained, we may write

$$\frac{-\Delta F}{2.303 RT} = \log B = 0.24 n_c + 0.04 n_b + 0.92 n_r + 0.026 n_t - 0.12 n_x - 0.42 - \log X^\gamma \quad (9)$$

Rearranging eqn. 9, we get

$$\log BX^\gamma = 0.24 n_c + 0.04 n_b + 0.92 n_r + 0.026 n_t - 0.12 n_x - 0.42 \quad (10)$$

In the above equations, n_b is the number of branched-chain carbon atoms, n_r the number of terminal benzene rings, n_t the number of α -mercapto groups, n_x denotes the number of terminal carboxylic groups (Table III), T the absolute temperature and R the gas constant, ΔF is the change in free energy due to sorption, which should be due to the change in intra- and intermolecular interactions. According to eqns. 8 and 9, this free-energy change may be expressed as a summation of the contribution of the constituent groups and the ground term of the sorptive system⁴⁹. The last column of Table II gives the values of $\log BX^\gamma$ calculated according to eqn. 10.

TABLE IV
VALUES OF CONSTANTS (EQNS. 8 AND 13)

Series	$\log m$	γ	α_1	α_2	α_3
I	0.42	1.5	0.19	1.6	0.06
II	0.42	1.0	0.25	1.0	0.12
III	0.42	1.0	0.31	1.0	0.12
IV	0.42	1.0	0.43	1.0	—
V	0.42	1.0	0.50	1.0	0.18
VI	0.42	1.0	0.39	1.0	—

It is evident from the B values (Table II) that sorption increases with increase in chain length in each homologous series. This may be attributed to the decrease in the solubility of the solute in the solvent and the increase in the dispersion forces (which accounts for a major part of the total attractive forces in the case of organic compounds, particularly hydrocarbons) between the resin matrix and the solute molecules. Furthermore, there is an indication that the branched-chain acid shows a lower sorption than its straight-chain isomer. The substitution of an $-\text{SH}$ group on an α -carbon atom increases the value of the sorption coefficient B by a small amount only. The sorption of dicarboxylic acid is lower than that of the corresponding monocarboxylic acid. The contribution of the terminal benzene ring is approximately equal to that of a straight chain of four carbon atoms.

Column elution study

The sorption coefficient should be related to the peak elution volume, the width of the elution curve, the number of theoretical plates and the resolution¹⁶. In this study, a series of runs were carried out with twenty-four aliphatic carboxylic

acids on the column of resin X4 in hydrogen form to study the effect of load, feed volume, concentration and column length in aqueous medium⁴³. The elution curves were fairly symmetrical under suitable conditions and could be described as Gaussian curves. However, the elution curves tend to become somewhat asymmetrical and/or may exhibit tailing⁴⁹ when the column is overloaded. The thioacids studied, thioglycolic and thiolactic, exhibit tailing on both sides of elution curve even at relatively small load. Hence, the σ_θ values of these two acids are not considered in Table V. Volumes are expressed in ml and column capacities in mequiv.

TABLE V

CALCULATED VALUES OF CHROMATOGRAPHIC QUANTITIES FOR COLUMN ELUTION RUNS WITH RESIN DOWEX 50W-X4

Series	Acid	$10^3 V_\theta$	$10^3 \sigma_\theta$	N_θ
I	Malonic	266.2	266.0	1.001
	Succinic	322.5	322.1	1.003
	Glutaric	420.8	419.6	1.006
	Adipic	592.8	589.0	1.013
	Pimelic	894.6	883.3	1.026
	Suberic	1429.0	1395.0	1.049
	Azelaic	2385.0	2283.0	1.092
	Sebacic	4139.0	3828.0	1.169
II	Acetic	377.2	375.3	1.010
	Propionic	473.4	467.7	1.024
	<i>n</i> -Butyric	645.6	628.4	1.055
	<i>n</i> -Valeric	959.4	907.5	1.118
	<i>n</i> -Caproic	1548.0	1392.0	1.237
	<i>n</i> -Heptanoic	2709.0	2236.0	1.468
	<i>n</i> -Caprylic	5128.0	3700.0	1.921
III	Isobutyric	555.5	548.7	1.025
	Isovaleric	745.7	725.0	1.058
	Isocaproic	1093.0	1031.0	1.125
IV	Trimethylacetic	691.8	691.8	1.000
V	Phenylacetic	1737.0	1542.0	1.269
	3-Phenylpropionic	2900.0	2310.0	1.576
	4-Phenylbutaric	5430.0	3647.0	2.217
VI	Thioglycolic	524.0	—	—
	Thiolactic	622.0	—	—

The peak elution volume. The peak elution volume (V_m) denotes the volume of the eluent from the start of the elution run to the midpoint of the peak. Taking the interstitial volume as $0.4 V_b$, it may be expressed as

$$V_m = V_d + 0.4 V_b + \bar{V}_m \quad (11)$$

where V_d is the disc volume, V_b is the bed volume and

$$\bar{V}_m = 0.4 V_f + C \cdot V_\theta \quad (12)$$

where V_f is the feed volume, C is the total exchange capacity of the resin in the column and V_θ may be expressed as

$$V_\theta = \alpha_1 + \alpha_2 B + \alpha_3 B^2 \quad (13)$$

where α_1 , α_2 and α_3 are constants (Table IV). For each homologous series, the values of α_1 , α_2 and α_3 were calculated from the experimental values of V_m for the members of corresponding series.

The peak width. Two parameters may be used to describe the peak width of an elution curve: σ , half of the width measured at the ordinate (C_m/\sqrt{e}) and β , the width measured at the ordinate (C_m/e), where C_m is the peak height of the elution curve and e is the base of natural logarithm. For a Gaussian curve,

$$B = 2\sqrt{2} \cdot \sigma \quad (14)$$

In general, the width of an elution curve should depend on the sorption coefficient of the solute and the column parameters such as resin particle size, area of cross-section, bed length, flow-rate, feed volume and temperature. By considering one variable at a time holding other parameters constant, its effect on the width of an elution curve can be studied. In this study, the effect of sorption coefficient, column length, feed volume and load on σ and β was studied keeping other parameters constant. Under this condition σ may be given by

$$\sigma = V_f/6 + \sqrt{C} \cdot \sigma_\theta \quad (15)$$

and σ_θ may be expressed as

$$\sigma_\theta = f_1\alpha_1 + f_2\alpha_2B \quad (16)$$

where f_1 and f_2 are constants determined by the particle size of the resin. For the experimental results obtained in this study we may assume $f_1 = f_2 = 1$. Eqns. 15 and 16 give the variation of σ with sorption coefficient and column parameters.

The peak height. The peak height, C_m , is the concentration at the peak elution volume. This depends upon the amount of the solute loaded, W , which refers to the area under the elution curve, and the width of the elution curve. For a Gaussian curve,

$$C_m = \frac{W}{\sqrt{2\pi} \cdot \sigma} \quad (17)$$

The number of theoretical plates. The number of theoretical plates, N , or the plate height, H , is an indirect measure of the width of an elution curve and hence the column performance. It is given by

$$N = \left(\frac{\bar{V}_m}{\sigma} \right)^2 \quad (18)$$

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

$$N_\theta = \left(\frac{V_\theta}{\sigma_\theta} \right)^2 \quad (19)$$

TABLE VI

SOME ILLUSTRATIVE EXAMPLES OF SEPARATION OF MIXTURES OF CARBOXYLIC ACIDS

Resin: Dowex 50W-X4 (100-200 mesh); $V_f = 10$ ml.

Series	Acid mixture	C_{min}	L (cm)
I	Malonic + glutaric	293.2	105.9
	Pimelic + azelaic	53.2	19.2
	Glutaric + pimelic	38.1	13.8
	Succinic + adipic	168.0	60.7
	Adipic + pimelic	276.7	100.0
	Adipic + suberic	72.7	26.3
	Adipic + malonic	115.0	41.6
II	Acetic + <i>n</i> -butyric	192.3	69.5
	Acetic + <i>n</i> -valeric	74.2	26.8
	Propionic + <i>n</i> -caproic	43.5	15.7
	Propionic + <i>n</i> -valeric	109.4	39.5
	<i>n</i> -Butyric + <i>n</i> -valeric	277.0	100.0
	<i>n</i> -Valeric + <i>n</i> -caproic	169.5	61.2
	<i>n</i> -Caproic + <i>n</i> -heptanoic	104.4	37.7
III	<i>n</i> -Heptanoic + <i>n</i> -caprylic	62.2	22.5
	Isobutyric + isocaproic	112.0	40.5
	Isovaleric + isocaproic	284.8	102.9
V	Phenylacetic + 3-phenylpropionic	115.3	41.7
	4-Phenylbutyric + 3-phenylpropionic	57.6	20.8

TABLE VII

ILLUSTRATIVE CALCULATION (FIGS. 1-3)

Resin: Dowex 50W-X4 (100-200 mesh). $V_d = 6.5$ ml, $V_b = 139.4$ ml, $V_f = 10.0$ ml, $L = 57.8$ cm, $V_s = 10.0$ ml, $C = 160.0$ mequiv.

	<i>n</i> -Valeric		<i>n</i> -Caproic		<i>n</i> -Valeric + <i>n</i> -Caproic	
	Exp.	Calc.	Exp.	Calc.	Exp.	
B (ml/mequiv.)	0.661	0.657	1.137	1.142	0.661	1.137
W (mmol)	1.103	—	0.712	—	0.552	0.356
V_m (ml)	221.0	220.8	318.0	315.0	223.0	317.0
\bar{V}_m (ml)	158.8	158.5	255.8	252.8	160.8	254.8
σ (ml)	13.00	13.15	18.00	19.28	13.00	18.00
β (ml)	37.00	37.19	50.00	54.53	37.00	50.00
C_m (mmol/l)	33.02	33.47	15.80	14.73	16.51	7.900
N_θ	1.180	1.118	1.461	1.237	1.180	1.461
C_{min} (mequiv.)						
exp.	—	—	—	—	156.86	
calc.	—	—	—	—	169.60	
R_n						
exp.	—	—	—	—	1.0110	
calc.	—	—	—	—	0.9680	

Eqns. 18 and 19 give the variation of N with sorption coefficient. From eqns. 13, 16 and 19 the values of V_θ , σ_θ and N_θ were calculated and are given in Table V. During this study several series of runs, varying one parameter at a time, were actually carried out to test the validity of the above equations and the results were quite satisfactory.

The resolution (separation study). The extent of separation of the two components is conveniently expressed in terms of resolution, (R_n):

$$R_n = \frac{\Delta V_m}{n(\sigma_1 + \sigma_2)} = \frac{V_{m2} - V_{m1}}{n(\sigma_1 + \sigma_2)} \tag{20}$$

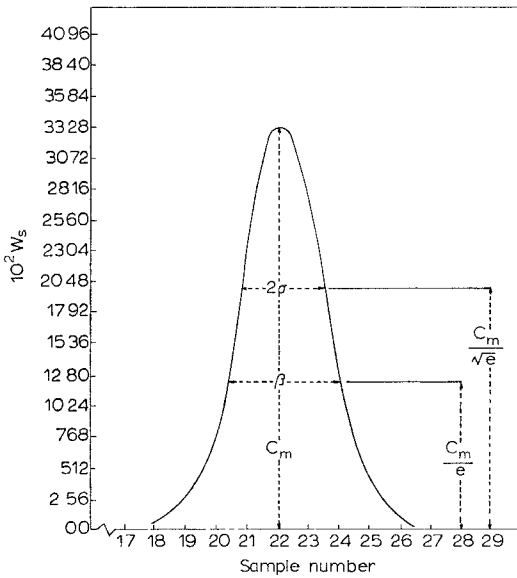


Fig. 1. Elution run for *n*-valeric acid.

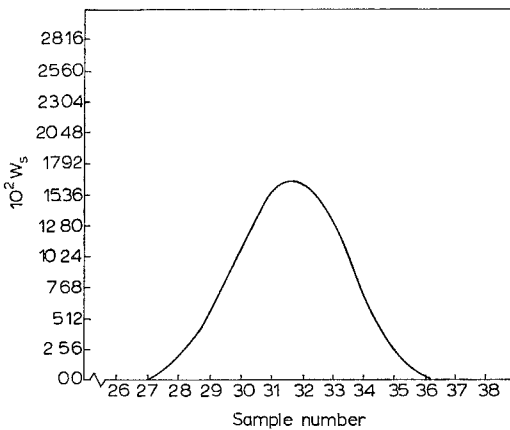


Fig. 2. Elution run for *n*-caproic acid.

where ΔV_m is the gap between the centers of the peaks of neighbouring elution curves and n is an integer greater than zero. The magnitude of n indicates the degree of separation and it depends on the type of problem and chromatography. The generally accepted criterion of minimum resolution in liquid-solid chromatography is to select the value $n = 3$ and this means that after having divided the effluent (V_e) into a fraction at a point $V_e = V_{m_1} + 3\sigma_1$, at least 99.86% of each of the components is in its appropriate fraction and the impurity amounts to at most 0.14% of the peak of the contiguous components. Combining eqns. 11, 15 and 20, we get

$$R_n = \frac{C(V_{\theta_2} - V_{\theta_1})}{3 \sqrt{C(\sigma_{\theta_1} + \sigma_{\theta_2}) + V_f}} \quad (21)$$

Thus, the extent of separation could be predicted for a given pair of components having the sorption coefficients B_1 and B_2 . $R_n = 1$ indicates a satisfactory separation. Setting $R_n = 1$ in eqn. 21 we have

$$1 = \frac{C_{\min}(V_{\theta_2} - V_{\theta_1})}{3 \sqrt{C_{\min}(\sigma_{\theta_1} + \sigma_{\theta_2}) + V_f}} \quad (22)$$

From eqn. 22, C_{\min} can be calculated for the separation of a pair of components. If $R_n < 1$, it means overlap of bands, still if the peaks are distinguishable, the run should be useful for qualitative work. The separation can be improved by increasing the column length if the cross-section of the column is kept constant decreasing the feed volume and/or decreasing the particle size of exchangers depending on the practical limits of pressure drop, solubility of components in the solvent and their detectability in the effluent samples. The elution runs with a number of mixtures were carried out and the elution of each component was practically unaffected by the presence of the other. Fig. 3 gives an illustrative separation run. The values of R_n calculated using

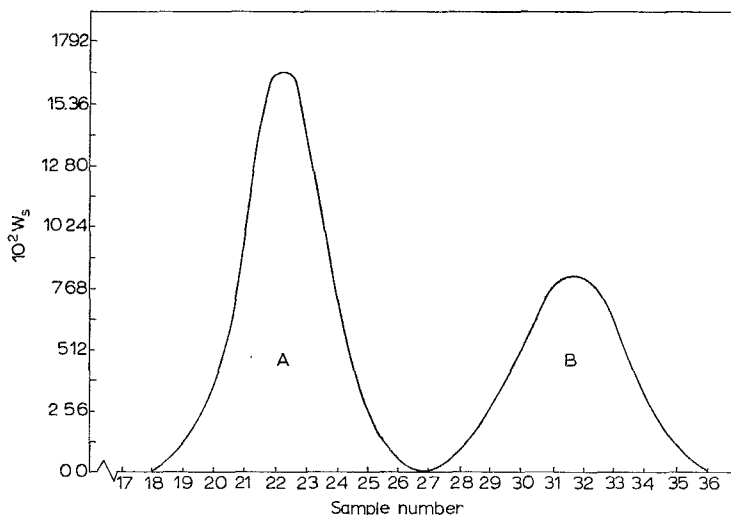


Fig. 3. Separation run for *n*-valeric acid (A) and *n*-caproic acid (B).

eqn. 21 were in agreement with those obtained from the experimental values according to eqn. 20. A number of mixtures were experimentally tried and the agreement between the experimental and calculated values of C_{\min} was fair. In Table VI are given the values of C_{\min} (calculated from the values of V_{θ} and σ_{θ} from Table V) and corresponding bed length L for the separation runs of some of the mixtures carried out. Table VII gives illustrative calculations for column elution of n -valeric acid (Fig. 1), n -caproic acid (Fig. 2) and a mixture of n -valeric and n -caproic acids (Fig. 3).

The present study has thrown some light on the structure and sorption relationship and provides a technique of interest for qualitative as well as quantitative analysis of mixtures of the aliphatic carboxylic acids studied using suitable column parameters and experimental conditions.

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