THEORY OF SORPTION CHROMATOGRAPHY

II. NUMERICAL CALCULATIONS

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SYMBOLS

f = solute concentration in mobile phase
h = solute concentration in stationary phase
c = concentration of sorbent
k_1 = rate constant for sorption
k_2 = rate constant for desorption
v = translational velocity of mobile phase
D_1, D_2 = diffusion coefficients in mobile and stationary phase respectively
V_1, V_2 = volumes per interphase area of mobile and stationary phase respectively
$f^{m_{ij}}$ = matrix element representing f
$h^{m_{ij}}$ = matrix element representing h
A_i = ith moment of the concentration distribution
μ = mean of the concentration distribution
μ_2 = variance of the concentration distribution
M = mode of the concentration distribution
τ = duration of equilibration step
γ = partition coefficient
ν = peak velocity
D = spreading coefficient
ω = velocity of concentration front in frontal analysis

$$\alpha = \frac{2D_1}{\tau v^2}$$

$$\eta = \frac{\gamma V_2}{V_1 + \gamma V_2}(1 - e^{-m\tau})$$

$$m = \frac{2D_2}{V_2}\left(\frac{\gamma}{V_1} + \frac{1}{V_2}\right)$$

INTRODUCTION

The theoretical treatment of sorption chromatography in the preceding article[1] has been supplemented by numerical calculations performed on a digital computer. As the basis of the calculations the following equations were used:

$$\frac{\partial f}{\partial t} + \frac{1}{V_1}\frac{\partial h}{\partial t} = D_1 \frac{\partial^2 f}{\partial x^2} - v\frac{\partial f}{\partial x} \tag{1}$$

$$\frac{\partial h}{\partial t} = k_1 (c - h) f - k_2 h \tag{2}$$

These equations were solved by a finite difference approximation method, leading to eqns. (40)–(42) in the Appendix. The numerical treatment of the problem followed the general outlines of the procedure in partition chromatography[2,3]. The results were obtained in the form of the matrixes $(f^m{}_{ij})$ and $(h^m{}_{ij})$ representing concentration distributions in the mobile and stationary phases respectively of the chromatographic column. The data were abstracted from the computor in the form of a few selected columns of a matrix, representing the concentration distribution at different times. The zeroth, first and second moment with respect to the origin, with the cell width as unit length, were also calculated for every column. For the jth column they are defined as follows:

$$A_0 = \sum_i f_{ij} \tag{3}$$

$$A_1 = \sum_i i\, f_{ij} \tag{4}$$

$$A_2 = \sum_i i^2 f_{ij} \tag{5}$$

with corresponding definitions for the h-matrix.

For a characterization of the concentration distributions the reduced moments, the mean μ and the variance μ_2 were used. They are defined as follows:

$$\mu = \frac{A_1}{A_0} \tag{6}$$

$$\mu_2 = \frac{A_2}{A_0} - \mu^2 \tag{7}$$

In addition the mode M, defined as the location of the maximum of the smoothed distribution curve, was also determined.

The primary results of the calculations are in the following given in terms of the parameters A_0, M, μ and μ_2.

METHOD OF CALCULATION

In the present calculations the characteristic parameters of column operation were varied in order to determine their effect on the chromatographic process.

From the form of eqns. (1) and (2) it follows that not all parameters need be varied independently. The following transformations are seen to leave the equations unchanged:

$$\left(c, \frac{a}{V_1}\right) \rightarrow \left(ac, \frac{1}{V_1}\right) \tag{8}$$

$$(c, af, k_1) \rightarrow \left(\frac{c}{a}, f, ak_1\right) \tag{9}$$

$$(at, k_1, k_2, D_1, v) \rightarrow (t, ak_1, ak_2, aD_1, av) \tag{10}$$

where a is an arbitrary constant.

Each of these transformations makes it possible to change the value of one of the parameters via corresponding changes in some other parameters. In the calculations therefore only the parameters c, D_1, k_1 and k_2 were varied, the others being kept constant and, when not otherwise stated, had the values:

$$v = 0.01 \text{ (cm sec}^{-1}\text{)} \tag{11}$$

$$V_1 = 0.004 \text{ (cm)} \tag{12}$$

$$f = 100 \tag{13}$$

$$\tau = 5 \text{ (sec)} \tag{14}$$

The value of V_1 was chosen to represent a column filling consisting of tightly packed spherical beads with a radius of approximately 0.01 cm. The value of τ may be fixed arbitrarily, but is related to the values of other variables by formula (10). (D_1, k_1 and k_2 enter the calculations in form of the combined parameters $\alpha = 2D_1/\tau v^2$, $\tau/m\ k_1$ and $\tau/m\ k_2$). The value in (14) may be used for convenience, as it provides realistic operational conditions for the column. It gives a cell width $\tau v = 0.05$ cm.

All the matrixes were of the order $n = 200$ and in all cases the value $m = 5$ was used.

The calculations were carried out with the following initial conditions:

$$f^0_{i1} = \begin{cases} 100 \text{ for } i = 1 \\ 0 \text{ for } i = 2, \ldots, 200 \end{cases} \tag{15}$$

$$f^0_{1j} = \begin{cases} 100 \text{ for } j = 1, \ldots, n \\ 0 \text{ for } j = n+1, \ldots, 200 \end{cases} \tag{16}$$

$$f^m_{0j} = \begin{cases} 100 \text{ for } j = 1, \ldots, n-1 \\ 0 \text{ for } j = n, \ldots, 199 \end{cases} \tag{17}$$

$$h^m_{i0} = 0 \text{ for } i = 1, \ldots, 200 \tag{18}$$

In the case of isolated peaks in general the value $n = 5$ was used, though for matrixes 22, 24, 25 and 26 the value of n was 2, 10, 15 and 20, respectively. In the case of frontal analysis, for matrixes 21 and 22, the value of n was 200.

The values of the characteristic parameters for the different matrixes are listed in Table I, and the primary results of the calculations are given in Tables II and IV.

In Table II, the matrixes may be grouped together according to the following scheme. In 1, 2 and 3 the longitudinal diffusion coefficient is varied; in 4, 5, 2 and 6 the equilibrium constant is varied; in 7, 8, 9, 10, 2 and 11 the concentration of the sorbent is varied; in 12, 13, 14, 2, 15 and 16 the reaction rate is varied and in 17, 18, 2 and 19 the feed concentration is varied. Finally, the matrixes 20 and 21 represent frontal

TABLE I

VALUES OF CHARACTERISTIC PARAMETERS

Matrix No.	f	c	α	$\tau/m\,k_1$	$\tau/m\,k_2$
1	100	0.4	0	0.005	0.05
2	100	0.4	0.1	0.005	0.05
3	100	0.4	0.2	0.005	0.05
4	100	0.4	0.1	0.005	0.001
5	100	0.4	0.1	0.005	0.005
6	100	0.4	0.1	0.005	0.25
7	100	0	0.1	0.005	0.05
8	100	0.02	0.1	0.005	0.05
9	100	0.1	0.1	0.005	0.05
10	100	0.2	0.1	0.005	0.05
11	100	0.7	0.1	0.005	0.05
12	100	0.4	0.1	0.0005	0.005
13	100	0.4	0.1	0.001	0.01
14	100	0.4	0.1	0.002	0.02
15	100	0.4	0.1	0.007	0.07
16	100	0.4	0.1	0.009	0.09
17	20	0.4	0.1	0.005	0.05
18	50	0.4	0.1	0.005	0.05
19	400	0.4	0.1	0.005	0.05
20	100	0.4	0	0.0005	0.005
21	100	0.4	0.8	0.0005	0.005
22	100	0.4	0.08	0.005	0.05
23	100	0.4	0.2	0.002	0.02
24	100	0.4	0.4	0.001	0.01
25	100	0.4	0.6	0.00067	0.0067
26	100	0.4	0.8	0.0005	0.005

analysis with constant feed concentration, and there the longitudinal diffusion coefficient is varied.

RESULTS AND DISCUSSION

We will first consider isolated peaks. From the results in Table II it appears that in sorption chromatography steady state conditions are approached much more slowly than in partition chromatography. Therefore, under ordinary conditions, plots of μ and μ_2 against time yield curved lines and hence the peak velocity v and spreading coefficient D are variable quantities. However, if the sorption isotherm has a finite slope at the origin, as is the case with Langmuir isotherm, the conditions of partition chromatography are approached as a limit. We will therefore first study the asymptotic behaviour of isolated peaks.

In a column of infinite length the spreading of a peak will cause the concentration in the peak to decrease indefinitely. Thus, as f tends to zero eqn. (2) takes the asymptotic form:

$$\frac{\partial h}{\partial t} = k_1 c f - k_2 h = -k_2 \left(h - \frac{k_1 c}{k_2} f \right) \tag{19}$$

Eqns. (1) and (19) may be compared with those of partition chromatography, eqns. (1) and (2) in ref. 6. To make a direct comparison possible we delete the term for

longitudinal diffusion in the stationary phase in the latter equations and put $V_2 = 1$. Then, by identity:

$$k_2 = 2\,D_2 \tag{20}$$

and

$$\frac{k_1 c}{k_2} = \gamma \tag{21}$$

It then becomes possible to use the exact expressions for peak velocity and peak spreading, which were derived for the partition case, eqns. (36) and (39) in ref. 6. With proper values of the parameters ($V_2 = 1$ and $D_2 = 0$ in the last term in the expression for D) we get:

$$v = \frac{1}{1 + \frac{k_1 c}{k_2 V_1}} \tag{22}$$

and

$$D = \frac{D_1}{1 + \frac{k_1 c}{k_2 V_1}} + \frac{k_1 c v^2}{k_2^2 V_1 \left(1 + \frac{k_1 c}{k_2 V_1}\right)^3} = D_1 v + \frac{v^2 \nu^2 (1 - v)}{k_2} \tag{23}$$

These relations are amenable to simple physical interpretations. Thus, v is equal to the fraction of solute in the mobile phase, and is independent of the rate of the sorption reaction (k_1/k_2 is the equilibrium constant). D, on the other hand, is strongly dependent on the reaction rate. For an infinitely fast reaction the chromatographic dispersion vanishes, and the spreading is solely due to longitudinal diffusion in the mobile phase. The spreading coefficient then equals the diffusion coefficient times the fraction of solute in the mobile phase.

In order to show the deviation from asymptotic conditions for different column characteristics, v and D values were calculated for the matrixes in Table II according to eqns. (22) and (23), and from finite differences of the data in Table II, according to:

$$v = \frac{\Delta\mu}{\Delta t}, \quad D = {}^1/_2 \frac{\Delta\mu_2}{\Delta t} \tag{24}$$

The results for the mobile phase are listed in Table III. They are expressed in local units (τ and $\nu\tau$ as units of time and length respectively) and refer to the mid-points of the respective intervals.

The data in Table III show that v generally is rather close to its asymptotic value, whereas for D pronounced deviations occur. The deviations are small if the initial concentration is low, as in matrixes 17 and 18. Also, in the case of large D values the asymptotic conditions are rapidly approached. Then the peak spreads out rapidly and its concentration falls to a level where asymptotic conditions prevail. This is the case in matrixes 12, 13 and 14 where the reaction rate is low and hence D is large. In cases when the concentration in a peak remains high, usually pronounced deviations from asymptotic conditions occur. This happens when the column is overloaded, matrix 19, and also when the reaction rate is high, matrixes 15 and 16.

TABLE II

PRIMARY RESULTS OF THE CALCULATIONS

For each matrix the rows, reading from top to bottom, give the values of A_0, M, μ and μ_2.

Matrix No.	*Column No.*								
	Mobile phase					*Stationary phase*			
	10	*50*	*100*	*150*	*200*	*10*	*50*	*100*	*200*
1	126.111	68.588	61.152	58.091	56.317	1.4956	1.7257	1.7554	1.7747
	4.8	12.60	19.81	26.45	32.65	4.6	12.54	19.75	32.61
	4.0224	10.600	17.034	22.989	28.708	3.6475	10.286	16.714	28.380
	1.6984	9.7520	18.301	26.474	34.470	2.3889	11.446	20.652	37.722
2	123.498	67.282	60.086	57.133	55.424	1.4952	1.7110	1.7397	1.7583
	4.7	12.36	19.54	25.98	32.18	4.5	12.25	19.50	32.12
	3.9773	10.508	16.892	22.806	28.491	3.6522	10.227	16.602	28.190
	1.6973	9.6061	18.594	26.995	35.218	2.4484	11.579	21.003	38.552
3	120.103	65.994	59.038	56.192	54.547	1.4980	1.6963	1.7239	1.7418
	4.6	12.07	19.17	25.63	31.74	4.4	11.98	19.10	31.70
	3.9362	10.420	16.755	22.630	28.280	3.6648	10.171	16.492	28.005
	1.7265	9.9579	18.932	27.578	36.053	2.5214	11.728	21.397	39.451
4	9.6332	2.4568	2.0591	1.8304	1.6769	1.9613	1.9882	1.9879	1.9866
	4.9	4.1	4.5	4.6	4.8	2.6	3.3	3.7	4.5
	4.4815	3.6217	3.8065	3.9852	4.1539	3.0292	3.2932	3.5202	3.8943
	1.2111	1.9654	2.3040	2.5824	2.8276	2.2075	2.7091	3.0882	3.6873
5	31.436	13.033	10.493	9.4131	8.7810	1.8723	1.9368	1.9427	1.9465
	4.6	5.71	7.14	8.47	9.55	3.5	5.50	6.87	9.34
	3.7826	4.8012	5.9842	6.9985	7.9256	3.1137	4.5336	5.7071	7.6316
	1.6851	3.5698	5.1717	6.5948	7.9360	2.2635	4.5542	6.4001	9.5094
6	238.848	192.418	183.839	180.226	178.117	1.0265	1.2103	1.2446	1.2675
	5.2	23.51	43.43	62.54	81.22	5.2	23.52	43.42	81.22
	4.8280	21.532	40.470	58.845	76.939	4.7332	21.362	40.294	76.759
	2.0536	15.664	32.885	50.054	67.224	2.7010	17.416	35.405	70.835

8	459.080	428.881	406.426	392.063	382.909	0.14402	0.26448	3.5430	4.1836
	7.5	46.64	93.42	137.79	180.03	7.4	46.39	92.69	178.05
	7.7654	43.972	86.474	129.942	166.145	6.5889	39.852	81.307	160.879
	2.6059	27.424	94.473	183.724	282.373	7.2454	59.010	146.728	359.992
9	341.762	212.619	188.169	178.755	173.412	0.61478	1.1295	1.2273	1.2864
	6.8	33.58	56.14	70.56	95.88	6.7	32.84	55.49	95.19
	6.6890	28.259	48.312	66.822	84.607	5.6525	26.360	46.496	82.818
	2.3631	45.099	99.778	152.654	204.608	5.5739	56.221	115.985	227.796
10	239.843	124.792	110.917	105.362	102.145	1.0246	1.4808	1.5362	1.5714
	6.1	21.75	35.00	47.12	56.58	6.0	21.50	34.76	58.29
	5.6326	18.219	30.010	40.928	51.406	4.7835	17.374	29.184	50.569
	2.1894	24.483	48.157	70.817	93.000	4.0784	29.070	54.653	102.094
11	66.190	38.656	34.757	33.170	32.255	1.7337	1.8266	1.8411	1.8510
	2.8	7.13	11.22	14.94	18.54	2.7	7.13	11.22	18.54
	2.6526	6.4143	10.106	13.538	16.884	2.6119	6.3409	10.017	16.742
	0.9285	4.5136	8.5170	12.4024	16.3148	1.4144	5.3026	9.6288	17.801
12	148.374	54.145	51.625	50.428	49.706	1.3986	1.7681	1.7750	1.7813
	6.3	10.28	15.59	20.87	26.08	5.6	11.78	15.202	22.60
	6.8402	12.942	18.205	23.425	28.490	3.9451	9.8471	15.202	25.428
	7.3502	47.812	80.931	113.328	145.359	5.2846	41.351	75.968	142.318
13	105.427	58.387	54.346	52.599	51.567	1.5722	1.7489	1.7629	1.7737
	6.0	10.02	16.03	21.74	26.84	1.8	8.2	14.47	25.81
	5.4799	10.559	16.238	21.644	26.910	3.6630	9.2225	14.903	25.563
	3.6926	22.351	40.353	57.866	75.124	4.0726	22.681	41.689	77.903
14	104.221	63.012	57.398	55.035	53.653	1.5757	1.7287	1.7504	1.7654
	5.0	10.94	17.59	23.70	29.59	3.6	10.33	17.00	29.06
	4.3586	10.108	16.159	21.836	27.327	3.5571	9.5346	15.578	26.735
	2.6085	11.405	24.394	35.308	46.041	3.0368	14.664	26.745	49.516
15	127.997	67.781	60.344	57.317	55.571	1.4765	1.7090	1.7386	1.7577
	4.7	12.60	19.78	26.35	32.57	4.5	12.58	19.76	32.56
	3.9732	10.627	17.047	22.982	28.683	3.6854	10.359	16.768	28.395
	1.5896	9.6680	18.326	26.632	34.756	2.3866	11.435	20.760	38.107

(continued on p. 46)

TABLE II (*continued*)

Matrix No.	*Column No.*								
	Mobile phase					*Stationary phase*			
	10	*50*	*100*	*150*	*200*	*10*	*50*	*100*	*200*
16	129.716	67.868	60.371	57.331	55.581	1.4693	1.7087	1.7385	1.7577
	4.7	12.65	19.85	26.46	32.63	4.5	12.64	19.84	32.63
	3.9775	10.670	17.095	23.032	28.735	3.6988	10.401	16.816	28.446
	1.5544	9.6618	18.334	26.645	34.767	2.3597	11.444	20.779	38.142
17	59.979	50.061	48.469	47.804	47.415	1.7729	1.7804	1.7861	1.7903
	1.8	6.24	11.39	16.37	21.29	1.7	6.21	11.36	21.26
	2.0412	6.3548	11.326	16.188	20.998	2.065	6.343	11.307	20.974
	0.8577	4.8799	9.8704	14.842	19.802	0.9468	5.1401	10.250	20.349
18	81.953	57.285	53.381	51.756	50.810	1.6695	1.7512	1.7665	1.7768
	2.8	8.60	14.08	20.17	25.63	2.7	8.55	14.54	25.59
	2.7495	7.9634	13.531	18.839	24.020	2.7135	7.8897	13.446	23.926
	1.1320	6.1853	12.177	18.068	23.901	1.4214	6.9305	13.235	25.392
19	318.544	107.617	84.652	76.372	71.761	0.7083	1.5496	1.6414	1.6930
	7.0	29.2	41.3	51.1	60.3	7.0	29.4	41.5	60.5
	6.6133	21.789	31.219	39.316	46.792	5.3824	19.744	29.339	44.953
	1.8307	43.651	78.864	109.377	137.944	5.5842	54.906	93.526	157.288
20	556.007	2597.37	5214.34	7833.34	10452.4	1.77597	9.61053	19.1426	38.1905
21	560.996	2579.01	5193.57	7812.39	10431.4	1.88860	9.82940	19.3712	38.4197

However, it should be noted that the use of finite differences in the calculations involves an approximation which becomes less satisfactory at high reaction rates (see Appendix). The deviations in the latter case are therefore exaggerated.

TABLE III

VALUES OF RELATIVE PEAK VELOCITIES AND SPREADING COEFFICIENTS

For each matrix ν is given in the first row and D in the second.

Matrix No.	*Time (in units of τ)*				
	30	*75*	*125*	*175*	∞
1	0.1644	0.1287	0.1191	0.1144	0.09091
	0.1006	0.0855	0.0817	0.0799	0.03005
2	0.1633	0.1277	0.1183	0.1137	0.09091
	0.0909	0.0899	0.0840	0.0822	0.03460
3	0.1621	0.1267	0.1175	0.1130	0.09091
	0.1029	0.0897	0.0865	0.0848	0.04114
4		0.003695	0.003576	0.003373	0.001996
		0.00339	0.00278	0.00245	0.000895
5	0.02546	0.02366	0.02029	0.01854	0.009901
	0.01884	0.01752	0.01423	0.01342	0.004378
6	0.4176	0.3788	0.3675	0.3619	0.3333
	0.1701	0.1722	0.1717	0.1717	0.07592
7	1.0000	1.0000	1.0000		1.0000
	0.05000	0.05000	0.04999		0.05000
8	0.9052	0.8500	0.8093	0.7841	0.6667
	0.3102	0.6705	0.8925	0.9865	0.6260
9	0.5393	0.4010	0.3702	0.3557	0.2857
	0.5342	0.5468	0.5288	0.5201	0.2476
10	0.3147	0.2360	0.2182	0.2096	0.1667
	0.2787	0.2367	0.2266	0.2218	0.1009
11	0.09405	0.07384	0.06863	0.06613	0.05405
	0.04481	0.04033	0.03915	0.03882	0.01376
12	0.1526	0.1064	0.1032	0.1013	0.09091
	0.5058	0.3312	0.3240	0.3203	0.3051
13	0.1270	0.1136	0.1081	0.1053	0.09091
	0.2332	0.1800	0.1751	0.1726	0.1548
14	0.1437	0.1210	0.1135	0.1098	0.09091
	0.1100	0.1299	0.1091	0.1073	0.07968
15	0.1664	0.1284	0.1187	0.1140	0.09091
	0.0808	0.0866	0.0831	0.0813	0.02600
16	0.1673	0.1285	0.1188	0.1140	0.09091
	0.1013	0.0867	0.0831	0.0812	0.02124
17	0.1078	0.0994	0.0973	0.0962	0.09091
	0.0503	0.0499	0.0497	0.0496	0.03460
18	0.1303	0.1114	0.1062	0.1036	0.09091
	0.0632	0.0599	0.0589	0.0583	0.03460
19	0.3764	0.1886	0.1619	0.1495	0.09091
	0.5228	0.3521	0.3051	0.2857	0.03460

Peak asymmetry

The form of the concentration peaks was found to be rather similar in all cases studied. From the data in Table II it appears that generally $\mu < M$. Thus, the peaks exhibit negative skewness (according to Pearson's measure $S = (\mu - M)/\sqrt{\mu_2}$). This behaviour can be explained as an effect of the nonlinear sorption isotherm, which has the tendency to compress the leading boundary of a peak. This effect is reduced when asymptotic conditions are approached. It is realized from eqns. (22) and (23) that in the limit of partition chromatography the operational conditions are symmetric, as the equations are invariant under the reversal of the velocity of the mobile phase. Under these conditions an originally symmetric peak will remain symmetric. Some typical peaks are reproduced in Figs. 1, 2 and 3. In Fig. 1 the peaks both in the mobile and stationary phases are shown, whereas in Figs. 2 and 3 the variation of shape with time is shown.

Convergence of the numerical solutions

In order to investigate the dependence of the numerical solutions on the size of the finite differences, some calculations were carried out in which the number of cells for a given length of column was varied. Thus, in the matrixes 22, 23, 24, 25 and 26, the initial peak is confined to 2, 5, 10, 15 and 20 cells, respectively, and the operational conditions of the corresponding chromatographic columns are identical if τ is assigned the values 10, 4, 2, $^4/_3$ and 1 sec, respectively. The results for the mobile phase are listed in Table IV in the form of $\tau\mu$ and $\tau^2\mu_2$ values for two columns of each matrix,

TABLE IV

CONVERGENCE OF THE NUMERICAL SOLUTIONS

Matrix No.	τ (*sec*)	*Column No.*	$\tau\mu$	$\tau^2\mu_2$	v	D
22	10	10	28.336	126.952	0.1333	0.5867
		20	41.665	244.283		
23	4	25	26.834	115.947	0.1347	0.4923
		50	40.308	214.411		
24	2	50	26.633	116.946	0.1346	0.4893
		100	40.092	214.814		
25	$^4/_3$	75	26.595	117.672	0.1345	0.4913
		150	40.041	215.939		
26	1	100	26.583	118.116	0.1344	0.4929
		200	40.020	216.689		

representing the situations at the same time instances. It also contains v and D values, calculated from the differences between the two sets of values according to eqn. (24). Finally, in Fig. 4 the concentration distributions for a peak, resulting from some of these matrixes, are compared. It may be concluded that the convergence of the numerical solutions is quite satisfactory.

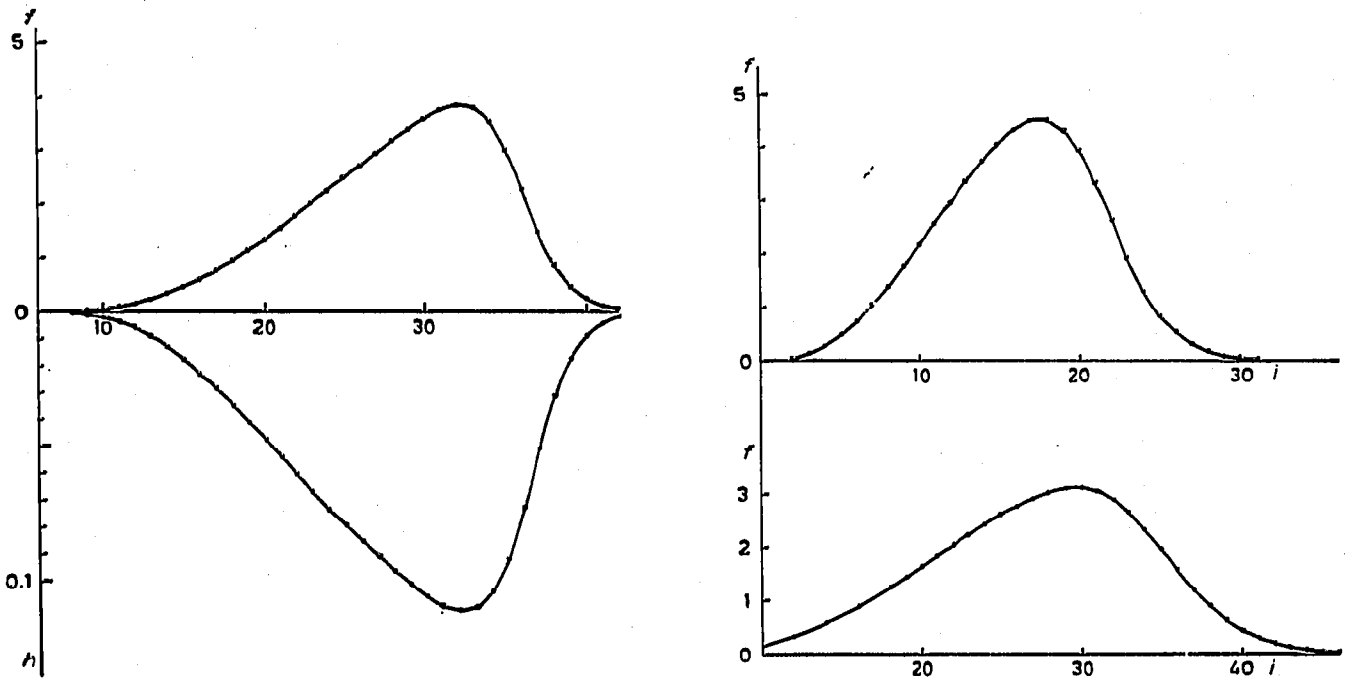

Fig. 1. Concentration distribution in the mobile and stationary phases. Column j = 200 of matrix No. 2.

Fig. 2. Concentration distribution in the mobile phase. Columns j = 100 and j = 200 of matrix No. 14.

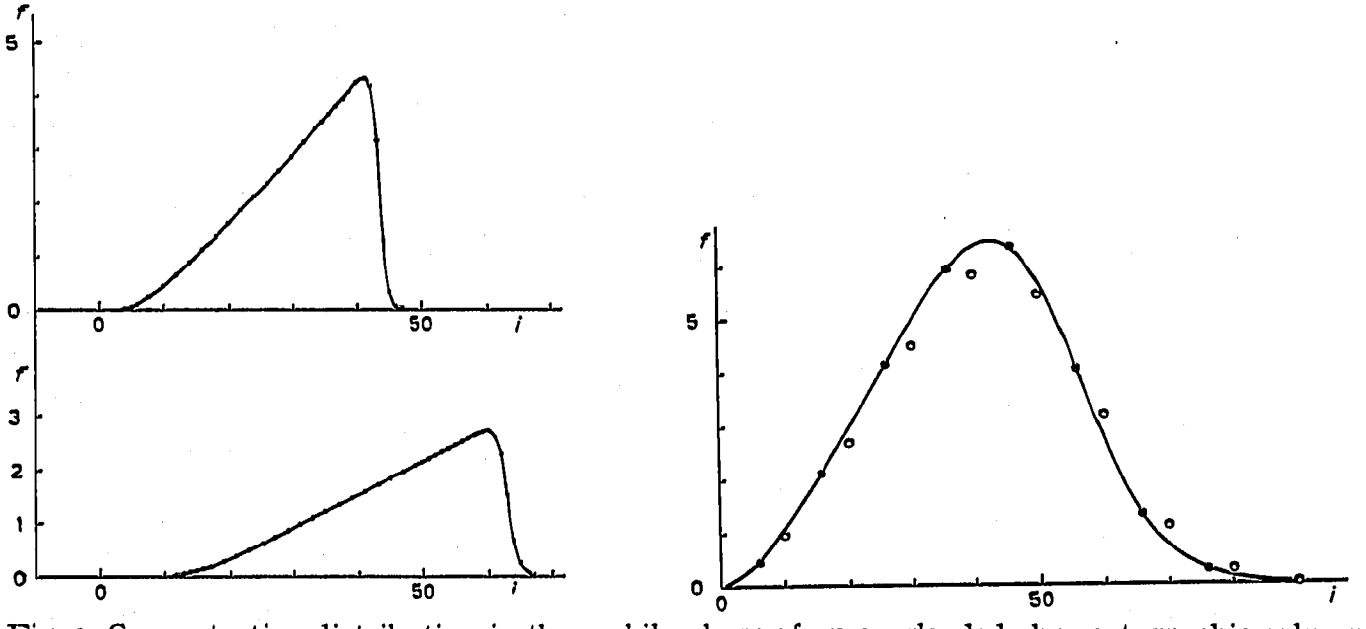

Fig. 3. Concentration distribution in the mobile phase of an overloaded chromatographic column Columns j = 100 and j = 200 of matrix No. 19.

Fig. 4. Concentration distributions in the mobile phase resulting from calculations with finite differences of varying size. The curve represents column j = 200 of matrix 26, filled circles column j = 100 of matrix 24 and unfilled circles column j = 20 of matrix 22.

Frontal analysis

We will next consider a column fed with a solution of constant concentration. This case is amenable to a straightforward analytical treatment and has been studied by earlier investigators[4,5]. We will indicate here a more direct approach where longitudinal diffusion is also taken into account. We start with eqns. (1) and (2) and investigate their solution for a stationary boundary. The existence of such a boundary is guaranteed by the nonlinearity of the sorption isotherm, which makes the movement of different points of the boundary a function of concentration.

Denoting the velocity of the stationary boundary by ω, we may determine it directly from the mass balance equation:

$$vtV_1 f_0 = \omega t V_1 f_0 + \omega t h_\infty \tag{25}$$

where f_0 and h_∞ refer to feed concentration and equilibrium concentration of f and h, respectively. From (25) and (2) (with $\partial h/\partial t = 0$) we get:

$$\frac{\omega}{v} = \frac{f_0}{f_0 + \frac{h_\infty}{V_1}} = \frac{1}{1 + \frac{1}{V_1}\frac{c}{f_0 + \frac{k_2}{k_1}}} \tag{26}$$

We will next switch to a new coordinate system, which follows the movement of the boundary. Thus we make the transformation:

$$\xi = x - \omega t \tag{27}$$

Eqns. (1) and (2) take the form:

$$\frac{\partial f}{\partial t} = D_1 \frac{\partial^2 f}{\partial \xi^2} - (v - \omega)\frac{\partial f}{\partial \xi} - \frac{1}{V_1}\left(\frac{\partial h}{\partial t} - \omega \frac{\partial h}{\partial \xi}\right) \tag{28}$$

$$\frac{\partial h}{\partial t} - \omega \frac{\partial h}{\partial \xi} = k_1 f(c - h) - k_2 h \tag{29}$$

For a stationary boundary we have:

$$\frac{\partial f}{\partial t} = \frac{\partial h}{\partial t} = 0 \tag{30}$$

Hence:

$$D_1 \frac{\mathrm{d}^2 f}{\mathrm{d}\xi^2} - (v - \omega)\frac{\mathrm{d}f}{\mathrm{d}\xi} + \frac{\omega}{V_1}\frac{\mathrm{d}h}{\mathrm{d}\xi} = 0 \tag{31}$$

$$\omega \frac{\mathrm{d}h}{\mathrm{d}\xi} + k_1 f(c - h) - k_2 h = 0 \tag{32}$$

A first integration of (31) gives:

$$D_1 \frac{\mathrm{d}f}{\mathrm{d}\xi} - (v - \omega) f + \frac{\omega}{V_1} h = K \tag{33}$$

For an originally empty column we have:

$$f = h = \frac{df}{d\xi} = 0 \tag{34}$$

hence:

$$K = 0$$

Thus, in this case the stationary boundary is determined by the following equations:

$$D_1 \frac{df}{d\xi} - (v - \omega) f + \frac{\omega}{V_1} h = 0 \tag{35}$$

$$\omega \frac{dh}{d\xi} + k_1 f (c - h) - k_2 h = 0 \tag{36}$$

These equations may be solved directly for $D_1 = 0$. Then according to (35):

$$f = \frac{\omega}{V_1 (v - \omega)} \cdot h \tag{37}$$

With (37) and (26), the integration of (36) yields:

$$\frac{f}{f_0} = \frac{1}{1 + e^{\frac{k_1 f_0}{\omega} \xi}} \tag{38}$$

The case $D_1 \neq 0$ is more troublesome. However, owing to the small value of D_1, the solution for $D_1 = 0$ is a good first order approximation. It is therefore possible to solve the full equations by iteration, inserting the approximate solution into the non-linear term in eqn. (36). The resulting linear equations may then be solved by standard methods.

In Table II numerical solutions are given for the case $\alpha = 0$ and $\alpha = 0.8$. Choosing $\tau = 1$ sec. this gives $D_1 = 0$ and $D_1 = 4 \cdot 10^{-5}$ cm^2 sec^{-1} respectively. In Table II only the values of A_0 are given. They determine the first moment μ of the boundary. We have:

$$\mu f_1 = \sum_{i=1}^{\infty} i(f_i - f_{i+1}) = \sum_{i=1}^{\infty} i f_i - \sum_{i=1}^{\infty} (i+1) f_{i+1} + \sum_{i=1}^{\infty} f_{i+1} = \sum_{i=1}^{\infty} f_i = A_0 \tag{39}$$

Here f_1 is the constant concentration in the plateau region. In the mobile phase we have $f_1 = 100$, hence $\mu = A_0/100$. From the data in Table II we see that the velocity of a stationary boundary is constant. It has exactly the value predicted by eqn. (26). In Fig. 5, the boundaries for the two cases are shown in detail. We see that in the case of non-vanishing longitudinal diffusion the boundary is not symmetrical. The effect of diffusion is seen to be rather small, however, and the translational velocity of the boundary remains unaffected.

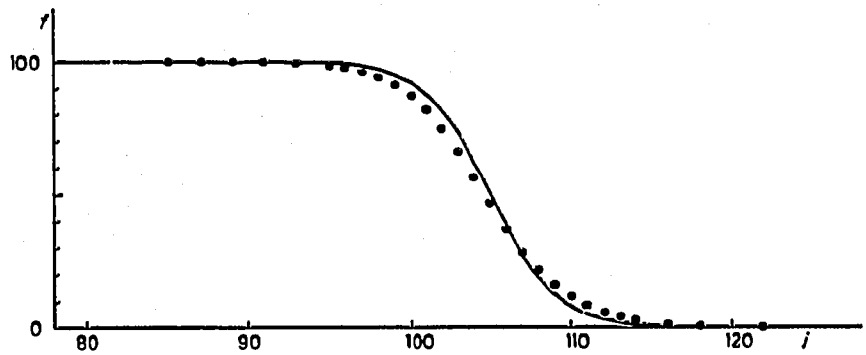

Fig. 5. Concentration profiles in frontal analysis. Columns $j = 200$ of matrixes Nos. 20 (line) and 21 (filled circles).

APPENDIX

Some aspects concerning the errors involved in the application of the finite difference method to chromatography are now considered. First, for the sake of generality, the recursion formulae in partition and sorption chromatography are reformulated on a common basis, and then take the form:

$$f^0_{ij} = f_{ij} + {}^1/_2 \alpha \, (f_{i-1,\,j} - 2 f_{ij} + f_{i+1,\,j}) \tag{40}$$

$$f_{i+1,\,j+1} = f^0_{ij} - \beta \delta_{ij} \tag{41}$$

$$h_{i,\,j+1} = h_{ij} + \delta_{ij} \tag{42}$$

Here the term δ_{ij} represents the exchange of solute between the mobile and stationary phases in a cell, and is thus determined by the kinetics of the chromatographic process. The parameter β has the values V_2/V_1 and $1/V_1$ for partition and sorption chromatography respectively. In the case of partition chromatography we get according to eqns. (23), (24) in ref. 2:

$$\beta \delta_{ij} = \eta \left(f^0_{ij} - \frac{1}{\gamma} h_{ij} \right) \tag{43}$$

(here h_{ij} is the solute concentration in the stationary phase, but is designated γg_{ij} in ref. 2).

In sorption chromatography with Langmuir kinetics we get according to eqns. (12)–(16) in ref. 1

$$\delta_{ij} = \delta^1_{ij} + \delta^2_{ij} + \ldots + \delta^m_{ij} \tag{44}$$

with

$$\delta^k_{ij} = \frac{\tau}{m} [k_1 f^{k-1}_{ij} \, (c - h^{k-1}_{ij}) - k_2 h^{k-1}_{ij}] \qquad k = 1, 2, \ldots, m \tag{45}$$

(here, by comparison to ref. 1, the indices have been changed for convenience).

The object is now to establish the variation with time in the first and second moments of a concentration distribution and compare the results with exact formulae. Such formulae are available in partition chromatography and the treatment will therefore be restricted to this case only, the results also being valid asymptotically

for sorption chromatography. We will consider isolated peaks and, in the formulae below, let all summation limits refer to points on both sides of the peak, in regions of zero concentration. For the second moment at time $j + 1$ we then get:

$$A_{2,\,j+1} = \sum_i i^2 f_{i,j+1} = \sum_i (i+1)^2 f_{i+1,\,j+1} = (1-\eta) \sum_i (i+1)^2 f^0_{ij} + \\ + \eta/\gamma \sum_i (i+1)^2 h_{ij} \quad (46)$$

To evaluate the first term on the right hand side we substitute for f^0_{ij} from eqn. (40) and use the identities:

$$(i+1)^2 = i^2 + 2i + 1$$

$$(i+1)^2 = (i-1)^2 + 4(i-1) + 4$$

Then:

$$A_{2,\,j+1} = (1-\eta)(A_{2\,j} + 2A_{1j} + A_{0j} + \alpha A_{0j}) + \eta/\gamma \sum_i (i+1)^2 h_{ij} \quad (47)$$

Using the same procedure we get for the first moment:

$$A_{1,\,j+1} = (1-\eta)(A_{1\,j} + A_{0j}) + \eta/\gamma \sum_i (i+1) h_{ij} \quad (48)$$

In general these expressions are dependent on the original concentration distributions (f_{i0}, h_{i0}) and hence become exceedingly complicated for high values of j. However, when the reaction rate is so high that equilibrium between the two phases in a cell is established in an equilibration step, this dependence disappears and the equations take simple forms. We may use eqns. (21)–(24) in ref. 2 and, as then: $m = \infty$ in the expressions for η and ξ, we get $\eta = \xi$, which implies:

$$f_{i+1,\,j} = \frac{1}{\gamma} h_{ij} \quad (49)$$

Also, as the concentration in a phase is now constant, we use normalized distributions and put:

$$A_{0j} = 1 \quad (50)$$

Inserting the last two equations into (47) and (48) we get:

$$A_{2,\,j+1} = A_{2\,j} + (1-\eta)(2A_{1\,j} + 1 + \alpha) \quad (51)$$

$$A_{1,\,j+1} = A_{1\,j} + 1 - \eta \quad (52)$$

For the variance we get:

$$\mu_{2,\,j+1} = A_{2,\,j+1} - A^2_{1,\,j+1} = \mu_{2\,j} + \alpha(1-\eta) + \eta(1-\eta) \quad (53)$$

We are now in the position to write down expressions for the peak velocity v and spreading coefficient D. In local units they take the form:

$$v = A_{1,\,j+1} - A_{1\,j} = 1 - \eta \tag{54}$$

$$D = {}^1/_2\,(\mu_{2,\,j+1} - \mu_{2\,j}) = {}^1/_2\,\alpha(1-\eta) + {}^1/_2\,\eta(1-\eta) \tag{55}$$

Substituting the values of α and η and comparing the formulae with eqns. (36) and (39) in ref. 6 we find that no error is involved in the expression for v, and that in the expression for D the term representing longitudinal diffusion is exact, while the chromatographic dispersion is subject to the error ${}^1/_2\,\eta\,(1-\eta)$.

This is strictly valid for an infinitely fast equilibration reaction and it is therefore of interest to consider the error at lower reaction rates. Although a general theoretical analysis of this problem is impracticable, some information may be obtained from the numerical data in this paper and in ref. 3. Thus, it appears that for steady state conditions the error in v always is very small and that the error in D generally decreases with decreasing reaction rate. This indicates that ${}^1/_2\,\eta\,(1-\eta)$ represents the upper limit of the error of the chromatographic dispersion. Further the fact that no error is involved in the longitudinal diffusion is of great interest. If pure diffusion is considered, this implied that the finite difference method (Schmidt's formula, *cf.* ref. 7) leads to macroscopically correct results (with respect to μ_2, *cf.* ref. 8). This result may be generalized and, with the help of the formula in ref. 8, it may be shown that the result is correct even when the diffusion coefficient is a linear function of concentration.

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SUMMARY

The operation of a chromatographic column with a sorption reaction following Langmuir kinetics has been simulated by numerical calculations on a digital computer. The operational conditions of the column are varied within wide limits and the results are related to theoretical considerations. It is shown that in sorption chromatography the conditions of partition chromatography are asymptotically approached and the process may then be described by the exact analytical formulae of linear partition chromatography. The errors in the finite difference method are discussed and evaluated for some special cases.

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