7. The Description of Ion Transport in Soil Columns

7.1. Physical models and experiments

Characteristics of the soil sample used. — The "A" horizon (0–20 cm) of a meadow chernozem soil from Törökszentmiklós (Hungary) was used for soil column models. The main chemical and physical characteristics of the soil are given in Table 7.1.

Preparation of the soil sample for model experiments. — The soil sample was saturated with Ca^{2+} ions by repeated treatment with N $CaCl_2$ solution. After removing excess salt, the sample was dried and the 0.5–2 mm particle size fraction was used. Soil column parameters are given in Table 7.2.

Preparation of soil columns. — Plastic tubes constructed from separate 2 cm sections bound together, with the given column parameters, were uniformly packed with 68 g of soil sample and were set up vertically.

The effluent end of the columns consisted of an aluminium screw containing a filter paper resting on a perforated plexi plate and with an outlet in the centre. The flow rate of the solutions could be controlled.

Solution treatment. — The columns were initially saturated with $CaCl_2$ solutions of the same concentration as the equilibrating solution. Equilibrating NaCl solutions or $NaCl-CaCl_2$ solution mixtures were added to the top of the columns.

A 2 cm high constant head of solution was set up at the top to ensure a constant flow rate. The flow rate was controlled at a value of less than $4 \cdot 10^{-4}$ cm/sec. (making it possible for a local equilibrium to develop). In the case of the columns in the present experiment, this means $\sim$ 5 ml/hour.

During the percolation of sodium-containing salt solutions, the flow rate after the first 24 hour period gradually decreased to a fifth of that at the beginning, while at a later period of percolation it became more or less constant.

The study of dynamic equilibrium (Experiments I – VI).
Saturation (1st part of the experiment)
a) Concentration and composition of equilibrating solutions.
Soil columns were equilibrated with solutions of the concentration and composition given in Table 7.3. Every treatment was carried out in four replications. Two of them were used for the first part and two for the second part of the experiment.

Experiments were carried out at two levels of solution ionic strength, and 3 ratios between the sodium and calcium ions were set up within each level of ionic strength.

The Na^+ and Ca^{2+} concentrations in the effluent solution were continuously controlled. Break-through curves were obtained. The steady state was reach-

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Table 7.1

Chemical and physical characteristics of the soil sample used

pH (H$_2$O)	6.9	Particle density, g/cm^3	2.72
CaCO$_3$ %	1.1	Particle size distribution %:	
Salt content %	0.04	Loss after treatment with HCl	3.06
Organic matter %	3.1	1—0.25 mm	0.07
CEC (me/100 g)		0.25—0.05 mm	8.11
(measured with isotope			
dilution method)	23.25	0.05—0.01 mm	26.67
Exchangeable Na$^+$		0.01—0.005 mm	9.60
(me/100 g)	0.07	0.005—0.001 mm	14.23
ESP	0.30	<0.001 mm	38.26
Saturation percentage (SP)	64.00	Hydraulic conductivity, cm/day	1.1
		Bulk density, g/cm^3	1.16

ed with respect to Na$^+$ ion concentration, when 600—800 ml of solution had been percolated. The equilibrating time was between 200—250 hours. The columns were cut into 7 sections, each 2 cm in depth.

b) The components determined in each section of the soil columns and the methods of determination.

Soil moisture was determined using the oven drying method. The soil solution in each section was extracted and the soil was air dried. The Na$^+$ and Ca^{2+} cations in the extracts (using emission spectrometry and versenate methods) and the exchangeable cations in the soil (using Ca-45 and Na-22 isotope dilution methods) were determined for each section.

In the case of the isotope dilution method the soil suspension (with a 1 : 10 soil-water ratio) was labelled with carrier-free Ca-45 or Na-22 isotopes.

After the isotope equilibrium was reached, the solid and liquid phases were separated by centrifugation. The activity of a given isotope in the equilibrium solution was determined with solid (for Na-22) or liquid (for Ca-45) scintillation technique. The Ca^{2+} and Na$^+$ concentrations were determined by versenate titration and emission spectrometry analyses of parallel samples. The amount of exchangeable calcium and sodium was calculated using the following equation:

$$\text{Exchangeable Ca}^{2+} \text{(Na}^+\text{)} = \frac{V_a \cdot C_e \left(\dfrac{C'_a}{C'_e} - 1 \right) C_i V}{g} \times 100$$

where

V_a = volume of labelling solution
C_e = concentration of the given cation in the equilibrium solution
C'_a = activity of the labelling solution, imp/min/ml
C'_e = activity of the equilibrium solution, imp/min/ml
C_i = the concentration of the given cation in the solution which is in equilibrium with the solid phase (for a given moisture content) before labelling, me/ml
V = volume of the equilibrium solution
g = the soil weight, g

Table 7.2

Soil column parameters

General column parameters		Model soil parameters	
1. Column length (cm)	15	1. Bulk density (g/cm³)	1.1
2. Column diameter (cm)	2.2	2. Pore fraction (dimensionless)	0.56
3. Weight of model soil sample		3. Pore volume (ml)	34.00
(g)	68.0	4. CEC (me/g) (determined with isotope dilution method)	0.225

Leaching of soil columns saturated with different sodium-containing solutions (2nd part of the experiment).

a) Solutions used for leaching:

Concentration and volume of solutions are given in Table 7.3. When leaching was carried out with 100 or 200 ml of $CaCl_2$ solution 55—60 or 140, hours were necessary, respectively.

b) The components determined and the methods of determination.

The soil solution in each 2 cm section was extracted and the soil was air dried. The Na^+ and Ca^{2+} concentrations in the solution and the amount of exchangeable Na^+ and Ca^{2+} were determined in the same way as in the 1st part of the experiment.

The data measured in each section and the main parameters of the columns are given in Tables 7.4 and 7.5.

The concentration of Na^+ and Ca^{2+} and the amount of exchangeable Na^+ and Ca^{2+} are given in me/ml and me/g respectively. For plotting the ion exchange isotherm, the relative value of Na^+ concentration in the liquid phase $\left(X = \dfrac{Na^+}{Na^+ + Ca^{2+}}\right)$, and that of exchangeable Na^+ in the solid phase

$$\left(Y = \frac{\text{Exchangeable } Na^+}{\text{Exchangeable } Na^+ + \text{Exchangeable } Ca^{2+}}\right) \text{ were used.}$$

Study of non-equilibrium systems (Experiments VII—XII).

Saturation (1st part of the experiment)

a) Concentration and composition of the solutions. The ionic strength and volume of the NaCl solutions used is given in Table 7.6.

For the percolation of 100 ml of solution 25 hours, for that of 200 ml 55 hours, and for that of 300 ml 82 hours were necessary. The flow rate was about 1 cm/hour. During the experiment a continuous decrease was observed (down to 0.4 cm/hour).

After the predetermined amount of exchanging solution had been added to the column, the flow was terminated and the columns were cut into 7 sections, each 2 cm in depth.

b) The components determined in each section of the soil columns and the methods used.

Table 7.3

Experiment for the study of dynamic equilibrium
Percolating solution parameters in the 1st and 2nd part of the experiment

Experiment No	Parallel samples of columns	1st part of the experiment (saturation)				2nd part of the experiment (leaching)	
		Ionic strength	Na$^+$	Ca^{2+}	Na : Ca ratio	CaCl$_2$ solutions used for leaching	
			concentration				
			mole/l			concentration me/ml	volume ml
		of equilibrating solution					
I	1 2	$1.21 \cdot 10^{-1}$	$1.04 \cdot 10^{-1}$		NaCl solution	Cut into sections and analysed after saturation	
	3 4					$1.09 \cdot 10^{-2}$	100 200
II	1 2	$1.18 \cdot 10^{-1}$	$8.26 \cdot 10^{-2}$	$9.3 \cdot 10^{-3}$	9.14 ($\sim$10)	Cut into sections and analysed after saturation	
	3 4					$1.09 \cdot 10^{-2}$	100 200
III	1 2	$1.14 \cdot 10^{-1}$	$9.13 \cdot 10^{-2}$	$2.1 \cdot 10^{-3}$	43.50 ($\sim$50)	Cut into sections and analysed after saturation	
	3 4					$1.09 \cdot 10^{-2}$	100 200
IV	1 2	$9.50 \cdot 10^{-3}$	$9.50 \cdot 10^{-3}$	$9.50 \cdot 10^{-3}$	NaCl solution	Cut into sections and analysed after saturation	
	3 4					$1.00 \cdot 10^{-2}$	100 200
V	1 2	$9.39 \cdot 10^{-3}$	$8.42 \cdot 10^{-3}$	$9.2 \cdot 10^{-4}$	9.33 ($\sim$10)	Cut into sections and analysed after saturation	
	3 4					$9.85 \cdot 10^{-3}$	100 200
VI	1 2	$1.07 \cdot 10^{-2}$	$9.65 \cdot 10^{-3}$	$1.9 \cdot 10^{-4}$	51.6 ($\sim$50)	Cut into sections and analysed after saturation	
	3 4					$1.00 \cdot 10^{-2}$	100 200

The moisture content was determined using the oven drying method. The soil solution was extracted and the soil was air dried. The Ca^{2+} and Na^+ concentration in the solution and the amount of exchangeable Na^+ and Ca^{2+} was determined in the above-mentioned way using the same methods.

The concentration values (me/ml), the exchangeable cation values (me/g) and the main parameters of the columns are given in Table 7.6.

Table 7.4

Analytical data of experiments in equilibrium systems (Nos I—VI)
Part 1. Saturation. (Average values)

Experiment No	Ionic strength of equilibrating NaCl solution mole/l	Ratio of Na : Ca ions in the equilibrating solution	Equilibration time, hours	Mean flow rate at the	
				start	end
				of the experiment, cm/h	
I	$1.21 \cdot 10^{-1}$	—	200	1.05	0.20
II	$1.18 \cdot 10^{-1}$	10	192	1.05	0.20
III	$1.14 \cdot 10^{-1}$	50	196	1.05	0.20
IV	$9.5 \ \cdot 10^{-3}$	—	236	1.44	0.36
V	$9.39 \cdot 10^{-3}$	10	—	1.44	0.36
VI	$1.07 \cdot 10^{-2}$	50	236	1.44	1.36

Experiment No and depth of column cm	Moisture, weight %	Concentration of cations in the solution me/ml $\cdot 10^3$		Exchangeable cations me/g $\cdot 10^2$	
		Na^+	Ca^{2+}	Na^+	Ca^{2+}
I					
0—2	49.31	139.50	2.20	14.40	5.90
2—4	44.50	127.52	3.15	12.95	5.95
4—6	36.20	126.54	4.20	11.80	7.50
6—8	42.01	113.00	5.60	11.25	8.15
8—10	39.60	112.50	6.35	10.45	7.90
10—12	42.31	101.00	7.80	10.40	9.75
12—14	48.40	129.52	10.45	6.90	13.30
II					
0—2	36.55	92.50	8.85	12.95	10.10
2—4	33.95	83.07	9.45	10.80	10.25
4—6	36.33	86.52	11.00	10.35	11.35
6—8	38.18	92.05	11.30	79.50	13.40
8—10	37.72	96.00	12.65	8.30	15.60
10—12	39.05	91.02	14.60	8.70	13.40
12—14	47.61	109.00	14.55	8.30	13.65
III					
0—2	48.76	113.00	4.32	12.25	9.50
2—4	46.11	119.00	4.06	12.80	7.40
4—6	44.50	119.04	4.00	12.60	6.85
6—8	44.15	115.05	5.81	13.20	8.10
8—10	43.17	93.03	5.52	12.45	7.40
10—12	49.76	117.00	6.53	9.95	6.20
12—14	57.35	128.04	5.50	7.90	9.15
IV					
0—2	48.70	10.60	1.02	4.62	15.50
2—4	49.60	10.75	1.08	4.25	15.95
4—6	48.80	9.75	1.27	3.68	16.50
6—8	51.50	10.10	1.22	3.43	16.75
8—10	52.60	9.35	1.38	3.10	15.95
10—12	56.30	9.55	0.97	2.70	16.15
12—14	55.40	10.20	1.01	2.27	16.55

Table 7.4 continued

Experiment No and depth of column cm	Moisture, weight %	Concentration of cations in the solution me/ml · 10³		Exchangeable cations me/g · 10²	
		Na⁺	Ca²⁺	Na⁺	Ca²⁺
V					
0—2	49.60	9.15	1.92	3.00	14.50
2—4	50.30	8.80	1.92	2.42	14.60
4—6	50.60	9.60	1.97	2.30	15.00
6—8	48.70	9.15	1.87	1.40	15.55
8—10	49.60	8.80	1.72	1.40	15.15
10—12	51.20	8.80	1.90	1.30	16.50
12—14	50.60	8.95	1.97	1.30	16.00
VI					
0—2	48.6	10.05	1.93	3.53	14.15
2—4	51.2	10.70	1.83	3.15	16.10
4—6	51.3	10.40	1.93	3.20	16.90
6—8	54.2	9.00	1.73	2.60	16.70
8—10	56.3	8.85	1.22	2.55	17.80
10—12	51.6	8.25	1.17	1.80	17.75
12—14	52.4	9.80	1.38	2.25	18.00

Simplifications of the physical model:

1. Equilibrium between the ions in the solution and those adsorbed on the surface in each column section.

2. The flow rate of the exchanging solutions was the same during the above-mentioned periods (i.e. the first 24 hours and the later period of the experiment).

3. The CEC and the moisture content of the soil was the same within the column.

Experimental results. — The vertical distribution of Na^+ and Ca^{2+} ion concentrations in the solution and that of exchangeable Na^+ and Ca^{2+} in columns equilibrated with solutions containing $NaCl-CaCl_2$ at ionic concentrations of 1.10^{-1} and $1 \cdot 10^{-2}$ mole/l is demonstrated in Table 7.4 (1st part of experiment).

The Na^+ and Ca^{2+} concentrations in the solution are uniformly distributed (within the error of analyses) along the soil column. The distribution is similar to that of the moisture.

The distribution pattern of exchangeable sodium can be characterized by a chromatographic curve, the shape of which corresponds to the unfavourable isotherm of the $Na^+ - Ca^{2+}$ exchange. A sharp maximum in exchangeable sodium content can be found in the top layers of the column which are in direct contact with the solution. In the lower parts of the column, the ratio between the exchangeable Na^+ and the sodium content of the solution is shifted in favour of the latter.

The degree of sodium saturation increases with the ionic strength of the equilibrating solution. In the case of equilibration with a $1 \cdot 10^{-1}$ mole/l solution, the maximum sodium saturation in the top layer of the column is 60%, in the case of equilibration with a $1 \cdot 10^{-2}$ mole/l solution it amounts to 20%.

At the same level of solution ionic strength, the degree of sodium saturation increases with the Na : Ca ratio in the solution.

Table 7.5

Analytical data of experiments in equilibrium systems (Nos I—VI)
Part. 2. Leaching

Experiment No	Concentration of equilibrating CaCl₂ solution me/ml	Mean flow rate cm/hr	Percolation time for	
			100 ml (sample No 3)	200 ml (sample No 4)
			solution, hours	
I	$1.09 \cdot 10^{-2}$	0.44	52	135
II	$1.09 \cdot 10^{-2}$	0.41	58	140
III	$1.09 \cdot 10^{-2}$	0.40	—	129
IV	$1.00 \cdot 10^{-2}$	0.38	64	145
V	$0.99 \cdot 10^{-2}$	0.40	65	138
VI	$1.00 \cdot 10^{-2}$	0.46	62	136

Experiment No and depth of column cm	Sample No 3						Sample No 4					
	Moisture weight %	Concentration of cation in the solution me/ml · 10³		Exchangeable cations me/g · 10²			Moisture weight %	Concentration of cation in the solution me/ml · 10³		Exchangeable cations me/g · 10²		
		Na⁺	Ca²⁺	Na⁺	Ca²⁺			Na⁺	Ca²⁺	Na⁺	Ca²⁺	
I												
0—2	61.95	47.5	2.4	5.3	7.4		67.39	36.1	6.2	3.2	14.6	
2—4	62.46	59.0	2.0	8.4	7.4		71.83	42.0	3.4	3.2	16.2	
4—6	58.40	57.1	2.0	9.5	6.9		61.14	51.4	3.6	9.4	10.6	
6—8	53.40	62.0	2.0	10.6	7.6		61.07	56.0	4.0	10.5	10.1	
8—10	47.20	75.0	3.6	11.8	7.2		59.59	78.2	4.5	10.7	8.9	
10—12	44.46	80.4	4.6	12.8	8.1		63.03	80.1	4.8	10.8	9.6	
12—14	46.41	121.1	8.5	12.9	8.9		70.53	85.1	6.1	10.2	9.8	
II												
0—2	21.90	25.1	6.0	3.7	14.7		37.19	35.2	9.0	2.8	15.2	
2—4	22.95	30.0	6.0	4.3	10.2		36.72	25.0	9.0	2.9	16.1	
4—6	23.20	40.0	6.0	5.5	8.9		37.42	52.0	6.0	4.4	9.2	
6—8	25.10	35.3	5.0	6.5	10.6		41.17	22.0	6.0	6.5	10.1	
8—10	25.50	47.0	6.0	6.3	11.3		43.09	22.0	6.0	6.0	10.6	
10—12	23.50	33.3	6.0	7.3	14.3		48.41	21.2	6.0	6.5	12.1	
12—14	27.90	33.1	6.0	6.3	14.6		58.16	21.0	7.0	5.8	12.2	
III												
0—2							57.80	68.1	14.1	3.2	17.8	
2—4							69.37	71.0	8.2	6.2	11.2	
4—6							59.47	70.4	9.1	10.5	8.9	
6—8							55.10	91.3	7.6	10.7	8.8	
8—10							53.45	106.0	4.1	13.7	9.6	
10—12							53.75	111.0	4.2	8.3	8.5	
12—14							71.00	111.1	4.2	10.9	9.8	
IV												
0—2	52.65	3.3	4.1	0.68	18.7		48.16	1.9	7.8	0.18	21.5	
2—4	54.42	4.2	4.1	0.52	17.6		52.50	3.3	6.1	0.29	21.7	
4—6	58.16	4.9	4.1	0.71	17.0		61.42	3.1	5.4	0.43	22.5	
6—8	62.05	6.9	2.5	1.31	16.7		50.61	3.1	4.1	0.62	19.8	
8—10	58.42	9.3	1.2	1.93	16.3		48.90	2.6	5.2	0.89	20.5	
10—12	55.16	9.5	4.1	2.32	15.9		49.51	4.5	3.1	1.38	20.7	
12—14	52.70	9.1	8.3	4.95	16.3		48.16	8.8	1.6	2.73	18.7	

Table 7.5 continued

Experiment No and depth of column cm	Sample No 3					Sample No 4				
	Moisture weight %	Concentration of cation in the solution me/ml · 10³		Exchangeable cations me/g · 10²		Moisture weight %	Concentration of cation in the solution me/ml · 10³		Exchangeable cations me/g · 10²	
		Na+	Ca²+	Na+	Ca²+		Na+	Ca²+	Na+	Ca²+
V										
0—2	46.51	2.6	5.1	0.25	21.6	44.65	2.2	6.2	0.10	22.1
2—4	48.92	2.9	4.8	0.23	24.2	45.56	2.6	5.8	0.12	22.3
4—6	53.65	3.5	5.2	0.23	24.8	49.55	3.5	5.8	0.23	23.4
6—8	41.52	3.8	4.7	0.29	22.5	53.61	3.8	3.6	0.22	22.1
8—10	38.76	3.8	5.2	0.34	17.7	58.45	3.8	3.9	0.31	19.5
10—12	42.50	6.1	3.6	0.59	18.9	49.61	3.8	5.4	0.24	21.8
12—14	46.40	7.8	2.1	0.96	19.3	46.50	3.9	5.9	0.31	19.9
VI										
0—2	53.16	2.4	5.8	0.28	19.5	51.65	1.6	8.3	0.20	24.1
2—4	52.65	3.5	5.1	0.32	19.5	52.65	1.3	7.1	0.30	23.4
4—6	60.70	3.6	4.2	0.31	21.0	48.76	3.4	5.2	0.18	23.8
6—8	54.65	5.5	2.1	0.67	20.6	49.52	4.8	3.5	0.35	23.7
8—10	53.52	5.9	2.9	0.90	19.2	53.45	5.1	5.2	0.25	19.5
10—12	58.40	7.9	1.1	1.47	19.8	55.16	5.4	4.7	0.35	23.4
12—14	52.16	9.1	0.8	2.70	17.5	52.10	6.1	4.1	0.51	23.1

Regardless of the concentration of the equilibrating $NaCl - CaCl_2$ solutions, Na^+ could not be removed from the soil column by treating with distilled water. The water did not penetrate into the $2-3$ cm top layers. This shows, in accordance with our earlier work [RÉDLY and SZABOLCS 1974], that an increase in sodium saturation in the upper layers of the column is accompanied by certain changes in the colloid properties of the soil. After percolating the columns with different volumes of $CaCl_2$ solutions, the maximum of exchangeable Na^+ becomes less clearly defined and moves to the deeper layers (Table 7.5, second part of the experiments). This can also be clearly seen when the concentration of the leaching $CaCl_2$ solution is lower than that of the equilibrating solution, or if the volume of leaching solution is about twice the total moisture capacity (Table 7.5, sample No. 3).

The corresponding data measured in non-equilibrium systems with the same parameters (Table 7.6) represent the gradual development of the above-mentioned distribution pattern of sodium and calcium ions both in the solution and in exchangeable form.

The mathematical model of the approximative description of the flow phenomena and ion exchange processes taking place under the conditions of the demonstrated experimental system and the problems and possibilities of describing mass transport processes in such systems are presented in Chapter 7.2.

Table 7.6

Analytical data of experiments in non-equilibrium systems (Nos. VII—XII)
Part 1. Saturation

Experiment No.	Percolating NaCl solution		Duration of the experiment hours	Volume of percolating NaCl solution ml	Mean flow rate at the	
	Ionic strength	Na+ concentration			start	end
	mole/l				of the experiment cm/h	
VII	$1.17 \cdot 10^{-1}$	$9.21 \cdot 10^{-2}$	26	100	1.14	0.406
VIII			58	200	0.985	0.35
IX			84	300	1.15	0.38
X	$1.20 \cdot 10^{-2}$	$9.85 \cdot 10^{-3}$	24	100	1.17	0.42
XI			52	200	1.14	0.39
XII			80	300	1.15	0.36

Depth of column cm	Concentration of cations in the solution me/ml · 10³		Exchangeable cations me/g · 10²		Concentration of cations in the solution me/ml · 10³		Exchangeable cations me/g · 10²	
	Na+	Ca²⁺	Na+	Ca²⁺	Na+	Ca²⁺	Na+	Ca²⁺
	Experiment No. VII				Experiment No. VIII			
0—2	109.1	8.2	5.9	18.9	115.0	7.5	6.6	15.4
2—4	100.4	15.1	3.1	17.9	90.4	11.7	4.6	24.7
4—6	93.0	26.0	1.9	27.5	109.5	17.7	2.3	17.9
6—8	84.0	34.0	3.3	24.3	99.1	22.7	2.6	16.5
8—10	48.2	39.0	2.6	24.6	87.0	17.2	2.9	16.8
10—12	26.5	37.0	3.1	22.7	109.5	20.0	1.9	18.2
12—14	25.0	39.0	1.0	27.9	115.0	20.9	1.6	21.8
	Experiment No. IX				Experiment No. X			
0—2	107.6	3.0	13.4	17.5	11.3	10.6	1.0	23.6
2—4	76.0	1.1	11.2	19.1	12.1	12.2	2.0	35.1
4—6	93.2	8.0	11.0	15.0	8.6	9.0	0.7	22.4
6—8	93.1	9.0	7.1	11.1	7.2	9.1	0.7	18.3
8—10	97.0	10.0	7.0	12.1	6.3	10.6	0.4	23.0
10—12	83.0	12.0	7.0	12.3	6.1	11.1	0.3	23.0
12—14	103.2	17.0	4.5	15.1	3.2	11.0	0.2	25.2
	Experiment No. XI				Experiment No. XII			
0—2	14.1	5.1	5.0	26.2	23.4	0.5	18.2	13.5
2—4	10.5	4.0	3.0	31.0	24.1	1.0	16.0	16.2
4—6	12.3	5.0	2.0	25.6	14.0	2.0	14.3	20.1
6—8	10.1	4.3	2.0	26.2	9.6	3.0	12.2	21.4
8—10	10.0	4.1	1.7	23.7	11.3	4.0	14.0	20.3
10—12	7.6	4.2	1.8	21.0	10.5	3.0	12.1	22.2
12—14	9.0	7.0	1.2	21.1	10.2	5.0	11.0	28.3

7.2. Mathematical description and calculations

The mathematical modelling procedure applied to the experiments in the previous section is given in Chapter 6. The method used for synthetic model sequence generation consists of a successive approximation. The calculated

results are compared with the experimental data of Chapter 7.1. The processes taken into consideration are the transport processes discussed in Chapter 6.2 and ion exchange. The number of processes included in the SM (synthetic model) is to be expanded successively by comparing the calculated and experimental data, following every step of the iterations. When proper agreement is achieved between the computed and measured values it means that all the main processes have been included.

Of course, it may well occur that with the introduction of all the processes of ion transport and exchange mentioned above, no fair agreement will exist between theoretical and experimental data. In this case, either some of the models of the processes are unsuitable and should be checked again, or it is necessary to introduce processes of a different nature and include models of the latter in the SM.

The first variation takes into account convective transport and instantaneous ion exchange. Using equations (6.49), (6.45) and (6.50) the system of SM equations (6.67) – (6.70) discussed previously in Chapter 6.3 is constructed. Among the parameters given in (6.61) only ε, S and s_1^0 are to be determined. The respective values of ε and S of each of the layers $0-2$ cm, $2-4$ cm, etc. are known from the experiments. It is further assumed, however, that ε and S do not depend on the vertical axis but are taken to be the mean values for all experiments of Chapter 7.1: $\varepsilon = 0.45$; $S = 0.22$ kg-eq/m³ of soil. The assumption seems to be valid because:

— the variability of S and ε values is relatively small (Fig. 7.1),

— if S and ε are selected from the data of each particular layer, the mean value would involve a lower error than the deviation between two parallel determinations in the same layer,

— calculations for SM are carried out for layers less than 2 cm thick,

— vertical changes in ε and S values may also occur within a 2 cm layer because layers of less than 2 cm were not analysed.
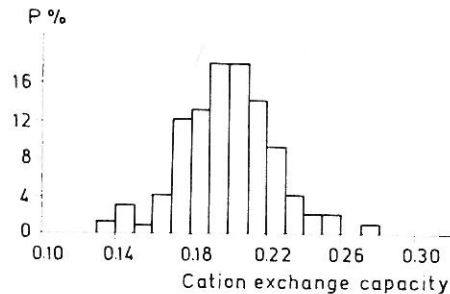

Fig. 7.1

Histogram of the distribution of CEC values in each 2 cm layer of soil columns

Values for $Q(t)$ of 0.05 m/day on the first day, and of 0.01 m/day on succeeding days were taken.

The solution of the system of SM equations given by equation (6.65) for the experimental conditions is illustrated in Figure 7.2. Qualitative agreement between the calculated and experimental values exists for each layer, except in the top section of the column. The estimated curves correspond to

higher values than those constructed from the experimental data. Such deviations do not mean that the isotherm is unsuitable, but that all the processes have not yet been included in the SM. The GAPON ion exchange isotherm is applied for further computation.

As the SM used still does not produce acceptable agreement between the experimental and calculated data, the number of processes must be expanded. First, processes which can be estimated in advance to have an effect on the studied phenomenon, such as molecular diffusion and hydrodynamic dispersion (see Chapter 6.3), together with processes which lead gradually to an ion exchange equilibrium between the soil particles and the solution, are included in the SM. The coefficient of molecular diffusion has the value $D_d = \beta D_\mu$ where $\beta = 0.67$ and $D_\mu = 1.73 \cdot 10^{-4}$ m²/day for chloride [ROSE and PASSIOURA 1971; GAMAYUNOV 1973]. $f_h(\eta) = \eta$ is taken for the calculation of $D_h = f_h(\eta) \cdot D_d$ where $\eta = \dfrac{Qa}{\hat{\varepsilon} D_\mu}$. It is assumed that the value of a is equal to 0.1 cm, which corresponds to the average diameter of the macroaggregates in the experiments and is the same as that introduced by ROSE and PASSIOURA [1971] for well-structured soil (the bulk density of soil in columns corresponds to a well-structured ploughing horizon). In this case, the BRENNER number in
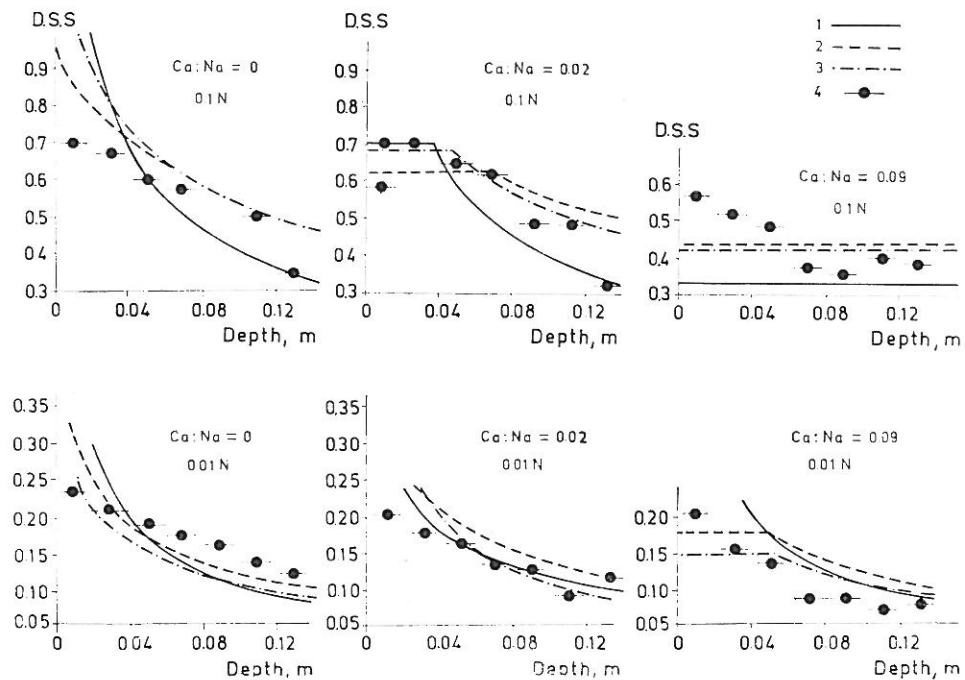
Fig. 7.2

Pattern of sodium saturation along the soil column calculated by a SM including only convective transport and instantaneous ion exchange, 1. calculated with (6.18), 2. calculated with (6.19), 3. calculated with (6.20) isotherms, 4. measured values. D.S.S. = degree of sodium saturation

the experiments is approximately $10-25$. With these values of the BRENNER number (see Fig. 6.9) it can be assumed that the contribution of the two processes mentioned above will be relatively small.

Equation (6.45) is applied to describe the kinetics of ion exchange. Other derivations for the kinetics of ion exchange are given in the literature [DARAB 1974]. When this method of calculation is introduced specific experimental data are necessary. The present system does not need this type of detailed analysis. As was proved by DARAB [1974], three part processes of ion exchange exist with characteristic rate constants of 10^{-2}, 10^{-3} and 10^{-4} sec^{-1}. The different rates of ion exchange in the soil-solution system are connected not only with processes related to the solid phase of the soil, but also with the rate of exchange of compounds between solutions with different mobilities. This part process is greatly affected by the fact that diffusion on the surface of the exchanger is the slowest of the processes leading to equilibrium. In this case, it can be assumed that it does not take more than one day to reach equilibrium in ion exchange. Consequently, the parameter $\zeta = \dfrac{\varepsilon L k_e}{Q}$ has an approximate value in the range of $10-10^2$. In accordance with Figure 6.10, using these values of ζ, a slight influence of the kinetics of ion exchange on the whole process can be expected. To take this into account it is enough to use a rate constant of exchange with the value $k_e = 1 \text{ day}^{-1}$.

A SM including the above-mentioned processes can be described with the system of equations below:

$$\varepsilon \frac{\partial C}{\partial t} = \varepsilon D_\mu \left[\beta + \frac{Qa}{\varepsilon D_\mu}\right] \frac{\partial^2 C}{\partial x^2} - Q \frac{\partial C}{\partial x}$$

$$\varepsilon \frac{\partial c_1}{\partial t} = \varepsilon D_\mu \left[\beta + \frac{Qa}{\varepsilon D_\mu}\right] \frac{\partial^2 c_1}{\partial x^2} - Q \frac{\partial c_1}{\partial x} - \frac{\partial s_1}{\partial t}$$

$$\frac{\partial s_1}{\partial t} = k_e(s_1^0 - s_1)$$

$$C\big|_{x=0} = \tilde{C} \qquad\qquad c_1\big|_{x=0} = \tilde{c}_1$$

The parameters of the SM are determined. The numerical solution with the RASNA programme (Appendix 3) leads to the results given in Figure 7.3. The figure reflects that the processes additionally included contribute only slightly to the migration of compounds in soil columns.

The change caused by the inclusion of the above processes in the SM is not sufficient to bring about agreement between the calculated and measured data.

Consequently, the mass exchange between the stagnant and transfer parts of the solute in the interparticle space has to be taken into account. Model 3, which is suitable for the description of experiments of this sort (see 6.2), is used, and (6.81)−(6.87) is obtained as a system of SM equations. Additional parameters $\hat{\varepsilon}$, k_s and $\hat{s}/\bar{s}$ should be determined by introducing the new processes mentioned above. It is assumed that $\hat{s}/\bar{s} = \hat{\varepsilon}/\bar{\varepsilon}$, and that values of

$\hat{\varepsilon}$ and k_s chosen to fit one of the treatments are then applicable for the calculations throughout the whole experiment. The choice of the mentioned values is accomplished iteratively as all the SM equations are being solved. It has been obtained that $\hat{\varepsilon} = 0.21$, $k_s = 1.25$ day^{-1}. The distributions of exchangeable sodium in the soil column calculated with the RASNA programme (App. 3) are compared with the measured values (Fig. 7.4). It is clear that the introduction of mass exchange between the two phases of the interparticle space considerably improves the agreement between the experimental and computed values.

For the correct prediction of experimental data in the column model, the mass exchange between the stagnant and transfer zones must be taken
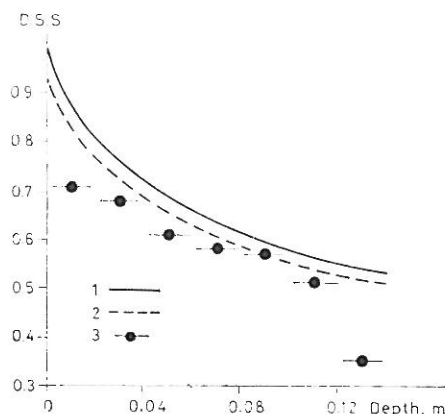
Fig. 7.3

Effect of the introduction of molecular diffusion, hydrodynamic dispersion and the kinetics of ion exchange into the SM. 1. SM with convective transport and instantaneous ion exchange, 2. SM after the introduction of additional processes, 3. measured values. D.S.S. = Y = degree of sodium saturation on the solid phase of the soil

into consideration. Further SM improvement may be attained by developing the transport and ion exchange models. In particular, when a break observed if Y varies from 0.35 to 0.45 may be related to a local jump in the $\frac{dY}{dX}$ derivative and the sodium selectivity coefficient Na at $X = 0.9$. Regardless of this, an improvement in the SM may be achieved by an extension of the processes included, that is, by considering the effect of salt composition on the geometry of the interparticle space, and the rate and volume of mass exchange between the stagnant and transfer zones. It is known [DARAB and FERENCZ 1969] that a high sodium saturation percentage in the soil is associated with a number of processes (soil colloid peptization, swelling, hydration, deflocculation, etc.) which cause a total change in the structure and water permeability of the soil.

A simple example shows how modelling depends on these processes. Considering convective transport and instantaneous ion and mass exchange between the two zones and assuming that:

(i) the ratio of the transfer zone volume to the pore volume depends on the degree of sodium saturation, i.e. $\hat{\varepsilon} = \hat{\varepsilon}(\hat{Y})$; with an increase in the exchangeable sodium, the transfer zone shrinks, and part of its pore volume is appropriated by the stagnant zone.

(ii) with a further increase in the sodium content the "expropriated" pores do not exchange with the moving solute.

It is assumed, as above, that the ratio between the sorption capacities of the two zones is equal to that between the corresponding pore volumes. If the total concentration C is constant, the mass conservation equation is as follows:

$$C\left[\frac{\partial(\hat{\varepsilon}\,\hat{X})}{\partial t} + E\,\frac{\partial(\hat{\varepsilon}\,\hat{Y})}{\partial t}\right] + \frac{\partial(\bar{m}_{Na})}{\partial t} = -C\,\frac{\partial(Q\hat{X})}{\partial x}$$

where $E = S/\varepsilon C$ and the variable $\bar{m}_{Na}$ is the total sodium content in the stagnant zone, which, owing to the assumption made, satisfies the following equation:

$$\frac{\partial \bar{m}}{\partial t} = C\,\frac{\partial \hat{\varepsilon}}{\partial t}\,(\hat{X} + E\hat{Y})$$

The SM equation has the following form:

$$\frac{\partial m}{\partial t} = C\hat{\varepsilon}\left(\frac{\partial \hat{X}}{\partial t} + E\,\frac{\partial \hat{Y}}{\partial t}\right) = -C\,\frac{\partial(Q\,\hat{X})}{\partial x} \tag{7.1}$$

which is analogous to (6.67). With the conditions (6.70) and $X = \hat{X}$, this equation has a solution formally corresponding to (6.65). However, if it is to be applied, the relationship between $\hat{\varepsilon}$ and $\hat{Y}$ has to be known. To determine this, a corollary of (7.1) is applied:

$$m(x,t) = C\int_0^t \hat{\varepsilon}\left(\frac{\partial \hat{X}}{\partial t} + E\,\frac{\partial \hat{Y}}{\partial t}\right)dt = \int_0^{\hat{x}}\hat{\varepsilon}(\hat{X})\left(1 + E\,\frac{d\hat{Y}}{d\hat{X}}\right)d\hat{X}$$

i.e. m depends only on $\hat{X}$ (or $\hat{Y}$), which is actually present in the transfer zone. In other words, it depends on $\xi = \dfrac{x}{q}$. The relationship between m and ξ may also be found from experimental data (with the value of q corresponding to the end point of the experiment, $0 \leq x \leq 0.14$). Let us assume that $m_t(\xi)$ represents the experimental function. It follows from (6.65) that:

$$m(\xi) = C\int_0^{\hat{x}}\hat{\varepsilon}\left(1 + E\,\frac{d\hat{Y}}{d\hat{X}}\right)d\hat{X} = \int_0^{\hat{x}}\frac{d\hat{X}}{\xi}$$

From the last equation function $\xi(\hat{X})$, corresponding to the experimental data, may be found, if $m(\xi)$ is replaced with $m_t(\xi)$. When compared with (6.65) it gives $\hat{\varepsilon}(Y)$. From the experiments discussed in Chapter 7.1, the linear function is satisfactory:

$$\hat{\varepsilon} = \varepsilon(1 - 0.55\hat{Y}) \tag{7.2}$$

The data calculated using (6.65) with regard to $\hat{\varepsilon}(\hat{Y})$ are presented in Figure 7.5. It can be seen that the exactness in the approximation of the experimental and calculated data is comparable if the model (6.81 – 6.87) is applied (Fig. 7.4). The two systems of SM equations discussed here include two limiting cases of mass exchange between zones, namely:

(6.81 – 6.87) — The independence of the pore volume of the zones from the composition of the exchangeable cations, and a constant rate of mass exchange between the two zones.

(7.1, 7.2, 6.70) — The simple zone volume depends on the degree of sodium saturation. The initially infinite mass exchange rate is reduced to zero in subsequent moments.

In practice some intermediate situation seems to take place. The ratio of the volumes of the two interparticle space zones is determined by the cation composition in the stagnant zone and in the transfer zone. It is also affected by the whole process of cation replacements; the mass exchange rate between the zones is higher in the first than in the subsequent moments, as certain pores adsorb sodium in a non-mobile form. The agreement between the experimental and theoretical values in both cases proves the possibility of an adequate description of the sodium saturation in the soil column by estimating the zone volume ratio and the average mass exchange rate. The lack of agreement
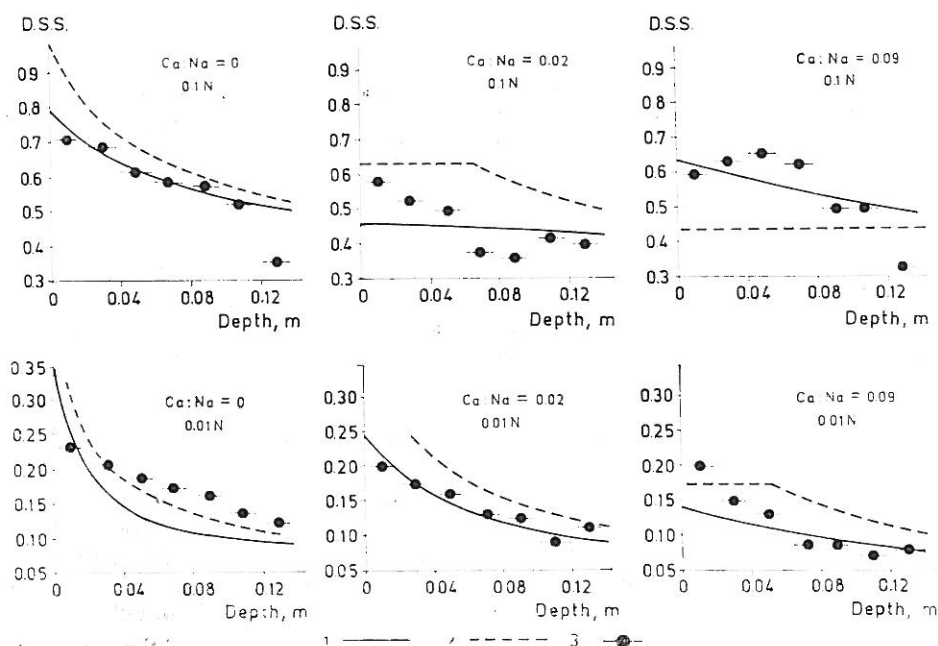

Fig. 7.4

Results of modelling when mass exchange between the stagnant and transfer zones of the interparticle space is introduced into the SM. 1. including mass exchange between the zones, 2. SM including only convective transport and instantaneous ion exchange, 3. measured values. D.S.S. = Y = degree of sodium saturation on the solid phase of the soil

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between the calculated and experimental data on replacing the sodium by calcium ions (Fig. 7.6) in the soil column, indicates that irreversible changes in interparticle space geometry can play a definite role and that further improvement in the model is necessary. Naturally, a new mass of experimental data is needed to determine whether the influence of the new processes to be included can be characterized by constants or if they are functions of the solute composition.
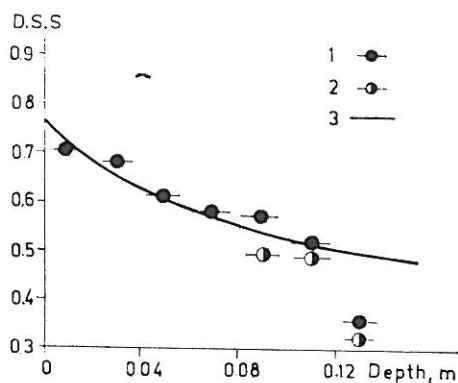

Fig. 7.5

Results of modelling when the dependence of the volumes of the stagnant and transfer zones on the degree of Na saturation is taken into account. An experiment with 0.1 N solution. 1. C_{Ca}: $C_{Na} = 0$, 2. C_{Ca} : $C_{Na} = 0.02$, 3. calculated data.
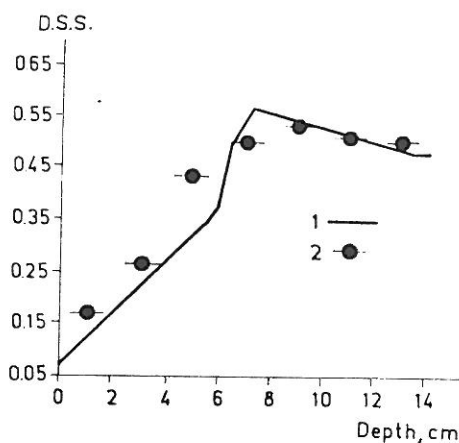
Fig. 7.6

Results of modelling the Ca—Na exchange phase of the experiments. 1. calculated, 2. measured values D. S. S. = degree of sodium saturation of the solid phase of the soil.

The contents of this chapter show that the modelling of solute migration in the soil by the methods of mathematical chromatography represents an iterative process of consecutive improvement of SMs. It is based on the concepts held by soil science on the limiting processes of migration and the interaction of these processes. The mathematical modelling of solute migration is closely related to physical modelling, since it is based on physical models and describes certain processes and phenomena of the migration as a whole; mathematical modelling, in turn, influences physical modelling. It helps in the planning of experiments to obtain information on the effect of certain processes. Both the methods for solving mathematical chromatography problems, and the methods for the physical modelling of solute migration in soils, are fairly well developed and are constantly improving. Consequently, the method of modelling can be characterized as an effective tool for the study of solute migration in soils.