

## **6. Mathematical Models of Soil Salinization and Alkalinization Processes**

### **6.1. Modelling of salt exchange between soil phases**

The change in salt concentration of the soil solutions and the solid phase is a consequence both of solute migration along the profile and the vertical redistribution of compounds due to inter-phase exchange. The mathematical approaches to the salt interaction between phases in a definite soil volume seem to be one of the main problems in the modelling of soil salinization and alkalinization. The mathematical description must be based on a basic knowledge of the physico-chemical processes in the soil and of the rules which govern them (See Chapter 5).

One of the starting points should be the conclusion formulated by GEDROITZ [1906] about the effects leading to changes in the composition of soil phases, which result in a shifting of the soil system from its initial state to a quasi equilibrium one, depending on the conditions and the related kinetic laws. With reference to the soil system GEDROITZ [1906] wrote: "... the study of the soil system should start with the investigation of the composition and concentration of the soil solution of individual soil specimens in the equilibrium state... Secondly, it is necessary to study the kinetics of soil processes, and the influence of various factors affecting it". This statement should also be a starting point in modelling the changes in the distribution of salts in the soils.

The composition of soil solutions and solid phases is influenced by abiotic and biotic factors. The extent of the effect caused by the abiotic and biotic factors and their relationship to one another depend on soil properties and the depth at which the soil layer under consideration occurs.

When modelling the changes in the salt composition of the soil system the two groups of factors mentioned above can be described separately. Afterwards, their joint influence must be analysed. A model which takes into account only the effect of abiotic factors provides an opportunity to approach a description of real situations. The less liable a given soil volume is to the effect of biological processes the more accurate this will be.

In order to model the abiogenic effects in the soil processes, let us assume the soil volume to be a physico-chemical system composed of solid, liquid and gaseous phases. In this model the liquid phase is taken as an aqueous solution containing calcium, magnesium, and sodium chlorides, sulphates and carbonates, and carbonic acid. As regards the gaseous phase of the soil the model will be concerned only with the transfer of compounds from the soil air to the solution and back. Among the compounds of the solid phase participating in salt exchange with the solution, crystalline calcite ( $\text{CaCO}_3$ ), gypsum

(CaSO<sub>4</sub>·2H<sub>2</sub>O) and the organo-mineral soil adsorbing complex (SAC) are considered. The dissolution of the compounds of SAC in the solution and the cation exchange capacities of calcium carbonate and gypsum will be neglected. A description of ion exchange equilibria in the system involves a material balance equation for each component of the system. The material balance together with the ratio of equilibrium concentrations form a model which assumes the independence of the given subsystem in the soil: apparently these factors are responsible for the fact that the behaviour of the subsystem is unaffected by other processes.

The concentrations (in kmole or kg-ion per m<sup>3</sup> of the solution) of the elements of the system in solution will be given by the symbols:

$$c_{Ca}, c_{Mg}, c_{Na}, c_{Cl}, c_{SO_4}, c_{HCO_3}, c_{CO_3}, c_{OH}, c_H, c_{H_2CO_3}, \text{ and } c_{H_2O}.$$

To express the content of the elements of the system in the solid and gaseous phases of the soil their amounts will be related to a determined soil volume containing a unit volume (one m<sup>3</sup>) of soil solution. The content of calcite and gypsum is given by the symbols  $c_{CO_3}^s$  and  $c_{SO_4}^s$  (kmole/m<sup>3</sup>), the content of adsorbed cations as  $c_{Ca}^e$ ,  $c_{Na}^e$  (kg-ion/m<sup>3</sup>), and that of carbon dioxide and water vapour in the soil air by  $c_{CO_2}^g$  and  $c_{H_2O}^g$  (kmole/m<sup>3</sup>), respectively.

In the material balance equations the following symbols are used:

— total quantities of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ions in a soil volume containing a unit volume of soil solution (m<sup>3</sup>):  $g_{Ca}$ ,  $g_{Mg}$ ,  $g_{Na}$ ,  $g_{Cl}$  and  $g_{SO_4}$  (kg-ion/m<sup>3</sup> of soil solution);

— total quantities of elements: hydrogen  $g_H$ , carbon  $g_C$ , bound oxygen  $g_O$  within the solid, liquid and gaseous phases (H<sub>2</sub>O, OH<sup>-</sup>, H<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, H<sub>2</sub>CO<sub>3</sub>, gypsum, calcite) in a soil volume containing a unit volume of solution (kg-atom/m<sup>3</sup>).

As was mentioned earlier, for the purpose of the given model the SAC compounds are examined only in terms of their cation exchange capacity and their constituents are not included in the  $g$  values.

So, a system of equations is constructed indicating the relations between unknown concentration values in equilibrium.

The amounts of compounds which are part of the various phases of the system will thus be connected with each other by the following material balance equations:

$$g_{Ca} = c_{Ca} + c_{Ca}^e + c_{CO_3}^s + c_{SO_4}^s \quad (6.1)$$

$$g_{Mg} = c_{Mg} + c_{Mg}^e \quad (6.2)$$

$$g_{Na} = c_{Na} + c_{Na}^e \quad (6.3)$$

$$g_{SO_4} = c_{SO_4} + c_{SO_4}^s \quad (6.4)$$

$$g_{Cl} = c_{Cl} \quad (6.5)$$

$$g_H = c_H + c_{OH} + 2c_{H_2CO_3} + 2c_{H_2O} + 2c_{H_2O}^g + c_{HCO_3} + 4c_{SO_4}^s \quad (6.6)$$

$$g_C = c_{CO_2}^g + c_{H_2CO_3} + c_{HCO_3} + c_{CO_3} + c_{SO_4}^s \quad (6.7)$$

$$g_O = c_{OH} + c_{H_2O} + c_{H_2O}^g + 3c_{H_2CO_3} + 3c_{CO_3} + 3c_{SO_4}^s + \\ + 2c_{CO_2}^g + 6c_{SO_4}^s + 4c_{SO_4} + 3c_{HCO_3} \quad (6.8)$$

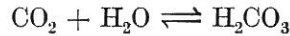
Combining the equations (6.6)–(6.8) the following equation is produced:

$$g'_H = g_H - 2(g_O - 4g_{SO_4}) + 6g_C = c_H - c_{OH} + 2c_{H_2CO_3} + 2c_{CO_2}^g + c_{HCO_3} \quad (6.9)$$

In media having neutral or alkaline reactions the CEC value of the soil adsorbing complex can be given as:

$$2(c_{Ca}^e + c_{Mg}^e) + c_{Na}^e = S \quad (6.10)$$

In connection with the description of the equilibria of salt exchange reactions in the systems, it appears that in the system under investigation, carbon dioxide of the soil air dissolves reversibly in the soil solution according to the equation:



In the equilibrium state, according to the HENRY law:

$$K'_1 = \frac{a_{H_2CO_3}}{p_{CO_2}} = \text{const.} \quad (6.11)$$

In the following, for the description of the equilibrium state, thermodynamic activities are used. At 25 °C, the value of HENRY's constant is:  $3.38 \cdot 10^{-2}$  kmole/m<sup>3</sup> atm. [ADAMS 1971]. If  $p_{CO_2}$  = partial pressure of CO<sub>2</sub> in the soil gaseous phase, then:

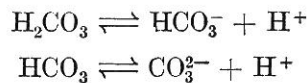
$$p_{CO_2} = 24.4 \cdot c_{CO_2}^g \frac{\theta}{\varepsilon - \theta}$$

where  $\theta$  = the volume of the interparticle solution in a unit soil volume  
 $\varepsilon$  = total porosity of the soil volume  
 24.4 = the volume of one kmole of gas under normal conditions (atm. m<sup>3</sup>/kmole)

Taking  $\theta/\varepsilon$  = constant:

$$c_{H_2CO_3} = 24.4 K'_1 c_{CO_2}^g \frac{1}{\frac{\varepsilon}{\theta} - 1} = K_1 c_{CO_2}^g \quad (6.12)$$

Carbonic acid dissociates reversibly in the solution in the following way:



The thermodynamic equilibrium constants of these processes can be described in terms of activities:

$$K_2 = \frac{a_H \cdot a_{HCO_3^-}}{a_{H_2CO_3}} \quad (6.13)$$

$$K_3 = \frac{a_{\text{H}} \cdot a_{\text{CO}_3}}{a_{\text{HCO}_3}} \quad (6.14)$$

The numerical values of the constants are available in the work of HARNED and DAVIS [1943]:  $K_2 = 4.45 \cdot 10^{-7}$ , and HARNED and SHOLES [1941]:  $K_3 = 4.69 \cdot 10^{-11}$ .

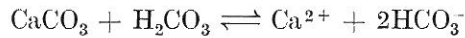
The water dissociation equilibrium in the solution can be described by the equation:



The activity product of water has a value of  $1.0 \cdot 10^{-14}$ :

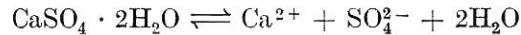
$$K_{\text{W}} = a_{\text{H}} a_{\text{OH}} \quad (6.15)$$

Calcite dissolves according to the following equation:



$$K_{\text{CaCO}_3} = \frac{a_{\text{Ca}} a_{\text{HCO}_3}^2}{a_{\text{H}_2\text{CO}_3}} \quad (6.16)$$

The value of  $K_{\text{CaCO}_3}$  is:  $4.24 \cdot 10^{-5}$  [ADAMS 1971]. The dissolution of gypsum can be given by the following equation:

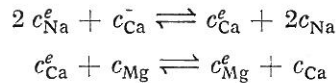


$$K_g = a_{\text{Ca}} \cdot a_{\text{SO}_4} \cdot a_{\text{H}_2\text{O}}^2 \quad (6.17)$$

where  $K_g$  is the solubility constant of gypsum, and its value is:  $K_g = 2.5 \cdot 10^{-5}$  [LATIMER 1952].

As a first approximation the water activity in the solution,  $a_{\text{H}_2\text{O}}$ , is equal to unity.

Ion exchange between salts in the solution and the adsorbing complex follows the equations:



A great variety of equations to describe exchange isotherms have been proposed by different authors [KERR 1928; VANSELOW 1932; GAPON 1934; NIKOLSKY 1941; KRISHNAMOORTHY and OVERSTREET 1950; BOLT 1967; DAVIS 1950].

The most general and thermodynamically most appropriate of these are the equations of VANSELOW, NIKOLSKY and GAPON. Their authors adopted different approaches in order to describe ion exchange mechanisms [SPOSITO and MATTIGOD 1977].

There are several approximations applying the above-mentioned equations to describe the cation exchange isotherm within a narrow salt concentration range in the aqueous phase of the system, or for other defined conditions of the cation exchange processes. The same is the case for the characterization of the sorption isotherms in soil-water systems.

The choice of a given expression to describe the ion exchange or sorption equilibrium assumes the necessity of comparing the results of modelling with

the test data. An example to illustrate this is the mathematical description of the co-transfer of the chlorides of Na and Ca in the soil core. Let us consider the following three equations for the description of ion exchange in soils:

$$K_L \frac{c_{Na}}{c_{Ca}} = \frac{s_{Na}}{s_{Ca}} \quad (6.18)$$

$$K_G \frac{c_{Na}}{\sqrt{c_{Ca}}} = \frac{s_{Na}}{s_{Ca}} \quad (6.19)$$

$$K_N \frac{c_{Na}}{\sqrt{c_{Na}}} = \frac{s_{Na}}{\sqrt{s_{Ca}}} \quad (6.20)$$

where  $s_{Na}$ ,  $s_{Ca}$  = exchangeable cations, kgeq/m<sup>3</sup> of soil.

The constants  $K_L$ ,  $K_G$  and  $K_N$  were all calculated from the same data which refer to the concentrations of the given ions in the solution and on the exchanger (Fig. 6.1a), with an almost identical degree of approximation. Varying results are obtained from computations on experimental data using a model involving only convective transfer and one of the equations (6.18)–(6.20) (see Fig. 6.1b). In fact, the differences persist even if the description of solution transfer becomes more complex. Thus the choice of an isotherm equation proves to be a component of the modelling procedure. The suitability of the description of an exchange isotherm to any particular equation, can be controlled with the mean-root-square method by determining the deviation between

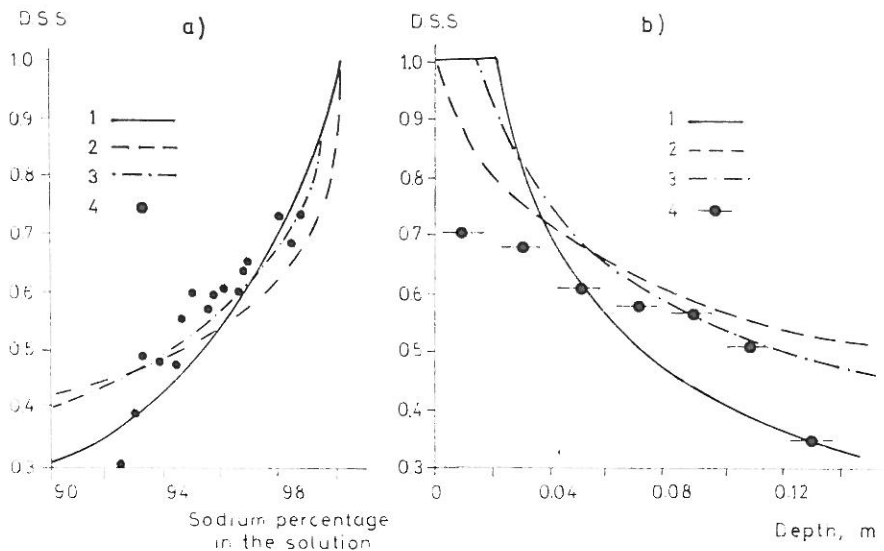


Fig. 6.1

Na—Ca ion exchange curves in the soil based on different cation exchange equations: a) equilibrium conditions, b) water migration in profile. 1. estimation for isotherm (6.18), 2. estimation for isotherm (6.19), 3. estimation for isotherm (6.20), 4. experimental data. D.S.S. = degree of sodium saturation

the measured and calculated values of the exchangeable cations. When this deviation is comparable with the standard deviation of the test data, the equation can be considered as a reasonable approximation to the description of the ion-exchange process under the given conditions. A better agreement between the calculated and test data may be achieved by including additional terms in the applied equations [CARLSON and BUCHANAN 1973]. When using any of the isotherm equations, problems arise connected with the calculation of the ion-activity coefficients in mixed salt solutions. The DEBYE and HÜCKEL equation can be applied for the calculation of ion-activity coefficients only at low ionic concentrations. In recent years, better approximations have been developed for the activities of compounds in concentrated water extracts of soils [WOOD 1975; DARAB 1977]. These approaches have made it possible to check the applicability of the VANSELOW and the NIKOLSKY equation more efficiently. The polydispersed and multi-componential character of the soil absorbing complex may cause high variability in the values of cation selectivity coefficients in the case of any of the known equations. Semi-empirical equations and some methods based on the theory of similarity and dimensions may be useful in such cases [SEDOV 1957]. The theory of dimensions primarily requires all the significant parameters describing the process (phenomenon) studied to be taken into consideration. In the case of Ca-Na exchange these are:  $\theta$ ,  $c_{Na}$ ,  $c_{Ca}$ ,  $s_{Na}$  and  $s_{Ca}$ . Where:  $\theta$  = moisture content ( $m^3$  solution/ $m^3$  soil). It is necessary to give the dimensions of all the parameters and identify those which are independent.

In the present case the dimensions are:  $[c] = kgeq/m^3$  solution,  $[s] = kgeq/m^3$  soil,  $[\theta] = m^3$  solution/ $m^3$  soil. Independent dimensions are those which cannot be obtained from each other by multiplication or division. In the present example  $[c]$  and  $[s]$  are independent, while  $[\theta]$  is dependent.

The theory of uniformities requires the use of the so-called "II-theorem" which is the following: "If a phenomenon is characterized by  $n$  parameters and  $k$  of them possess independent dimensions, it is enough to build dimensionless complexes and study the relations among  $n - k$  of them." In the present case  $n = 5$  and  $k = 2$ ; therefore the ion equilibrium isotherm should be an equation including three dimensionless complexes. For such complexes, let us take:

$$X = c_{Na}/(c_{Ca} + c_{Na}), \quad Y = s_{Na}/(s_{Ca} + s_{Na}),$$

$$E = \frac{s_{Na} + s_{Ca}}{\theta (c_{Na} + c_{Ca})}$$

As an example let us check whether or not equations (6.18) – (6.20) provide a connection between the complexes.

From (6.18), we obtain:  $K_L = \frac{1-X}{X} \cdot \frac{Y}{1-Y}$ , and from (6.19):  $K_G \sqrt{C} = \frac{Y}{1-Y} \cdot \frac{\sqrt{1-X}}{X}$ , where  $C = c_{Na} + c_{Ca}$ . If instead of  $K_G$  the dimensionless value:  $K_G^* = K_G \sqrt{\frac{\theta}{S}}$  is examined, where  $S = s_{Na} + s_{Ca}$ , the equation

$K_G^* = \sqrt{E} \frac{Y}{1-Y} \cdot \frac{\sqrt{1-X}}{X}$  does in fact connect  $X$ ,  $Y$  and  $E$ . The variability of  $K_G^*$  differs only slightly from the variability of  $K_G$  (the variation coefficients are 52% and 54% respectively). From (6.20) we deduce  $K_N \sqrt{\frac{C}{S}} = \frac{Y}{\sqrt{1-Y}} \cdot \frac{\sqrt{1-X}}{X}$ . Giving more attention to  $K_N^* = K_N \sqrt{\theta}$  than to  $K_N^*$ ,  $K_N^* = \sqrt{E} \frac{Y}{\sqrt{1-Y}} \cdot \frac{\sqrt{1-X}}{X}$  is obtained. The variabilities of  $K_N$  and  $K_N^*$  were found to be fairly similar (49% and 44%).

Thus, equation (6.18) is a relation only between  $X$  and  $Y$  but ignores the dependence on  $E$ . This may perhaps account for the higher variability of  $K_L$  (72%) and for its pronounced distribution asymmetry. Modifying (6.19) and (6.20) slightly by introducing factors with somewhat lower variability an equation giving a relation between  $X$ ,  $Y$  and  $E$  is reached. The high variability of the constants suggests the necessity of designing a better approximation. An analysis of the connected values of  $X$ ,  $Y$ ,  $E$  and  $K_N^*$  leads to the identification of the dependence of  $K_N^*$  on  $E$  and  $Y$  and gives the function  $K_N^* = \chi_N E^{0.37} Y^{0.5}$ . The isotherm equation can be expressed as follows:

$$\chi_N \left[ \left( \frac{S}{\theta C} \right)^{-0.13} \cdot C^{0.5} \right] \cdot \frac{c_{Na}}{\sqrt{c_{Ca}}} = \sqrt{\frac{s_{Na}}{s_{Ca}}}$$

The variability of the coefficient  $\chi_N$  of the isotherm is significantly lower than that of  $K_N^*$ ; the variation coefficient is 23%, and the average is: 0.251.

$K_N^*$  is a selectivity coefficient of the adsorbent for Na, since  $\frac{\partial Y}{\partial K_N^*} > 0$  at constant  $X$ . The dependence of  $K_N^*$  on  $E$ ,  $Y$  proved that soil selectivity to Na increases as the total ionic concentration of the solution decreases and it also increases with an increase in Na saturation. This is in accordance with the results published in the literature [DARAB and RÉDLY 1967]. If the isotherm equation is to be developed, attention should be paid to other factors related with ion exchange.

In our mathematical model the GAPON equation has been applied for the description of cation exchange equilibria:

$$[K_4 \cdot \frac{a_{Na}}{\sqrt{a_{Ca} + a_{Mg}}} = \frac{c_{Na}^e}{c_{Ca}^e + c_{Mg}^e}; \quad K_5 \cdot \frac{a_{Ca}}{a_{Mg}} = \frac{c_{Ca}^e}{c_{Mg}^e}] \quad (6.21)$$

The mathematical model of physico-chemical equilibrium in the soil system is based on equations (6.1)–(6.17) and (6.21).

The applicability of individual parts of the model has been verified for simple systems. For example, the uses of physico-chemical functions relating to particular soil factors were demonstrated by DARAB and FERENCZ [1969] for ion-exchange equations; by MURATOVA, PACHEPSKY and PONIZOVSKY [1977] for an interpolation applied to the description of gypsum solubility; by NAKAYAMA [1971] for the solubility equation of calcite in salt solutions. In natural soil conditions there are probably complications due to changes in

the solid-phase properties, the aggregation state of the components, porous-state geometry and solid-liquid phase interface. The suitability of each model has to be controlled by carefully conducted experiments.

In order to solve the equations (6.1) – (6.7), (6.9) – (6.17), and (6.21) of the model it is necessary to complete them with relationships for the calculation of the thermodynamic activities of the solution components. There are precise methods available for the calculation of ion activities in a wide range of soil solution concentrations and compositions [GARRELS and THOMSON 1962; WOOD 1975; DARAB et al. 1977]. Good examples for sodium ion were demonstrated in the previous Chapter. The use of the methods mentioned is possible, of course. But we realise that the model set up is only the first approximation and during the process of comparing predicted and experimental values it will become more complete and complicated in all its components. So as a first step it is assumed that:

$$\lg \gamma = -z^2 \left( \frac{0.509 \sqrt{\mu}}{1 + r \cdot \sqrt{\mu}} - b \mu \right) \quad (6.22)$$

This equation gives the dependence of  $\lg \gamma$  on the ionic strength of the solution:

$$\mu = 0.5 [4(c_{Ca} + c_{Mg} + c_{SO_4} + c_{CO_3}) + c_{Na} + c_{Cl} + c_{HCO_3} + c_H + c_{OH}].$$

In equation (6.22)  $z$  = the charge of the ion, while  $r$  and  $b$  are constants. If  $z$  is denoted as:

$$z = z(\mu) = 10^{-\frac{0.509 \sqrt{\mu}}{1 + r \cdot \sqrt{\mu}} + b \mu} \quad (6.23)$$

then, according to (6.22):

$$\gamma = z^{z^2} \quad (6.24)$$

In order to estimate an error in the calculation using equation (6.22), experimental data on the mean ion activity coefficients of the salts,  $\gamma_{\pm}$ , must be used. By definition,

$$\gamma_{\pm} = (\gamma_{+}^{n_{+}} \cdot \gamma_{-}^{n_{-}})^{\frac{1}{n_{+} + n_{-}}} \quad (6.25)$$

where  $\gamma_{+}$ ,  $n_{+}$  and  $\gamma_{-}$ ,  $n_{-}$  are individual activity coefficients and the number of dissociated cations and anions respectively. According to the demand of electroneutrality, combining the equations (6.24) and (6.25) we obtain:

$$\gamma_{\pm} = z^{z+z-}$$

From the equations (6.23) and (6.24) it follows that the values of  $\gamma_{\pm}^{\frac{1}{z+z-}}$  for different electrolytes should be identical functions of the ionic strength.

The values of  $\gamma_{\pm}^{\frac{1}{z+z-}}$  calculated from the data on activity coefficients of some salts [VOZNESENSKAYA and MIKULIN 1968] are shown in Figure 6.2. Even though the functions for the salts studied do not fit each other, the calculated values never deviate from those determined from experimental data,  $\gamma_{\pm}^{\frac{1}{|z_{+}+z_{-}|}}$ , by more than  $\pm 10$  percent. The calculation was



carried out by the same function of  $\alpha$  with  $r = 1.075$ ,  $b = 0.0536$  and using equation (6.24). Within such an error it can be assumed that equations (6.23) and (6.24) determine the individual ion activity coefficients. The difference between the numeric values of molar and molal concentrations never exceeds 2–3 percent, up to 2 mole/l concentration for the salts studied. When com-

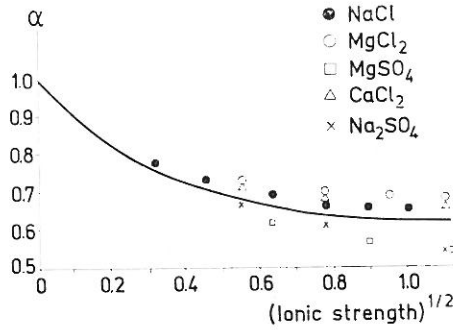


Fig. 6.2

Coefficients of ion activity of electrolytes in soils.  $\alpha = \gamma_{\pm}^{\frac{1}{|z_{+} z_{-}|}}$ ,  $\gamma_{\pm}$  = activity coefficient of salt,  $z_{+}$  and  $z_{-}$  = valences of positive and negative ions

puting the thermodynamic activities of the components of the system, the molar, and not the molal concentrations were used in all the equations.

For the simplification the model variables are renamed as follows:

$$\begin{array}{llll}
 u_1 = c_{Ca}; & u_5 = c_{Mg}; & u_9 = c_{SO_4}; & u_{13} = c_{H_2CO_3}; \\
 u_2 = c_{Mg}; & u_6 = c_{Na}; & u_{10} = c_{Cl}; & u_{14} = c_H; \\
 u_3 = c_{Na}; & u_7 = c_{SO_4}^s; & u_{11} = c_{HCO_3}; & u_{15} = c_{CO_2}^g; \\
 u_4 = c_{Ca}^s; & u_8 = c_{CO_3}^s; & u_{12} = c_{CO_2}; & u_{16} = c_{OH}.
 \end{array} \quad (6.26)$$

Because of the validity of (6.1)–(6.17), and (6.21)–(6.25), the equilibrium concentration values achieved during the interaction of soil phases will be expressed by the following system of equations:

$$f_{Cl} = u_{10} \quad (6.27)$$

$$f_{Mg} = u_2 + u_5 \quad (6.28)$$

$$f_{Na} = u_3 + u_6 \quad (6.29)$$

$$\frac{K_4 u_3}{\alpha^{|z_{+} z_{-}|} (u_1 + u_2)} = \frac{u_6}{(u_4 + u_5)}; \quad K_5 \cdot \frac{u_1}{u_2} = \frac{u_4}{u_5}; \quad (6.30)$$

$$2(u_4 + u_5) + u_6 = S \quad (6.31)$$

$$f_{SO_4} = u_7 + u_9 \quad (6.32)$$

$$u_9 = \begin{cases} \frac{K_g}{\alpha^8 \cdot u_1} & \text{if } u_7 > 0 \\ f_{SO_4} & \text{if } u_7 = 0 \end{cases} \quad (6.33)$$

$$u_1 = g_{Ca} - u_4 - u_7 - u_8 \quad (6.34)$$

$$\mu = 0.5 [4(u_1 + u_2 + u_9 + u_{12}) + u_3 + u_{10} + u_{11} + u_{14} + u_{16}] \quad (6.35)$$

$$\alpha = I^{-0.509} \sqrt{\bar{\mu}} / (1 + 1.075 \sqrt{\bar{\mu}}) + 0.0536\mu \quad (6.36)$$

$$u_{13} = K_1 u_{15} \quad (6.37)$$

$$\frac{K_3}{\alpha^4} = \frac{u_{14} u_{12}}{u_{11}} \quad (6.38)$$

$$\frac{K_2}{\alpha^2} = \frac{u_{14} u_{11}}{u_{13}} \quad (6.39)$$

$$u_{13} = \begin{cases} \frac{u_{11}^2 u_1}{K_{CaCO_3}} \cdot \alpha^6 & \text{if } u_8 > 0 \\ g_c - u_{11} - u_{12} - u_{15} & \text{if } u_8 = 0 \end{cases} \quad (6.40)$$

$$g_c = u_8 + u_{11} + u_{12} + u_{13} + u_{15} \quad (6.41)$$

$$\frac{K_w}{\alpha^2} = u_{14} u_{16} \quad (6.42)$$

$$g'_H = u_{11} + 2u_{13} + u_{14} - u_{16} + 2u_{15} \quad (6.43)$$

In view of the accepted methods for the calculation of activity coefficients, the equation system (6.27)–(6.43) can be divided into two subsystems. With a known calcium concentration in solution  $u_1$  and known ionic strength  $\mu$ , the values of  $u_2$ ,  $u_3$ ,  $u_4$ ,  $u_5$  and  $u_6$  can be obtained from (6.28)–(6.31) and the values of  $u_7$  and  $u_9$  from (6.32)–(6.33), i.e. the composition of exchangeable cations can be computed together with the content of  $Na^+$ ,  $Mg^{2+}$  and  $SO_4^{2-}$  in the solution. It is also possible, for the same values of  $u_1$  and  $\mu$ , to obtain  $u_{11}$ ,  $u_{12}$ ,  $u_{13}$ ,  $u_{14}$ ,  $u_{15}$ ,  $u_{16}$  and  $u_8$  from equations (6.37)–(6.43), i.e. the distribution of carbonates and hydrogen between the soil phases.

The construction of this equation system makes it possible to compute the  $u_1$  and  $\mu$  values using non-linear programming methods to carry out a search for the values of  $u_1$ ,  $\mu$  whereby the right-hand side of equations (6.34) and (6.35), which were computed after the system of equations (6.27)–(6.33) and (6.36)–(6.43) had been solved, differ little or nothing from the adopted values:  $u_1$ ,  $\mu$ .

Among the parameters of the model described above, the constants of dissolution and dissociation:  $K'_1$ ,  $K_2$ ,  $K_3$ ,  $K_{CaCO_3}$  and  $K_g$  are taken from the literature:

– equilibrium constants for liquid phase, gaseous phase and soil adsorbing complex interactions, i.e.  $K_1$ ,  $K_4$ ,  $K_5$ , respectively, are to be calculated from experimental data;

– values of  $g$  are to be determined from standard soil analyses.

The following components of the model must be analytically determined:

– concentrations of Na, Mg, Ca, Cl,  $SO_4$  and  $HCO_3$  ions in the soil solution;

- pH of the soil solution;
- exchangeable cations and CEC value;
- gypsum and  $\text{CaCO}_3$  content in the soil;
- soil bulk density, moisture content and porosity;
- $\text{CO}_2$  content in the gaseous phase of the soil.

With these data the dependence of the salt solution densities on the ionic strength may be calculated using the following equation:  $\rho = 1.000 + 0.032 \mu$  and it is possible to calculate successively:  $g_{\text{Ca}}$ ,  $g_{\text{Mg}}$ ,  $g_{\text{Na}}$ ,  $g_{\text{SO}_4}$ ,  $g_{\text{Cl}}$  and  $S$  from equations (6.1)—(6.5) and (6.10),  $c_{\text{H}_2\text{CO}_3}$  from equation (6.13),  $c_{\text{CO}_2}^g$  and  $K_1$  from (6.12),  $c_{\text{CO}_2}$  from (6.14) and  $c_{\text{OH}}$  from (6.15), then  $g_{\text{C}}$ ,  $g'_{\text{H}}$  and, finally,  $K_4$  and  $K_5$  from (6.21).

In the following some examples are given of how the model can be used for the description of salinization and alkalization. The computation deals with the change in the salt composition of the phases in a soil volume due to the percolation of leaching or ground waters. The well-known method which was used by MINASHINA [1972], FILEP [1972a], PACHEPSKY and POPOVA [1972] for routine land-improvement computations is applied for the early stages of the leaching of saline soils. The method is based on a special conception of the plate model theory. The soil column is considered to be subdivided into a number of layers. For every layer the percolating soil solution substitutes some proportion of the equilibrium soil solution and a new equilibrium of salt exchange and dissolution is reached. So the continuous process of percolating is replaced by a series of discrete steps along the soil column. The soil solution volume to be substituted at each step by the percolating solution is defined by the authors as the difference between the total moisture capacity and the field moisture capacity. Obviously, the model described above may be suitable for such calculations. Indeed, each step represents a change in easily definable values such as the difference between the concentrations in the equilibrium and percolating solutions multiplied by a factor "F", which means a ratio of the effluent and the existing solution volume of the column layer. The constants in the model never change from one step to another and the new steady-state condition can easily be calculated.

We shall now consider the description of changes in the salt composition of soil phases during salinization of a chernozem sample with a solution having a total salt concentration of 5.27 g/l and a salt composition characteristic of the ground waters in long term irrigated areas [MORGUN 1976].

The basic data are given in Table 6.1 and the results of the calculation are represented in Figure 6.3. The abscissa represents the quantity of the solution percolated through the soil sample. The total soil moisture capacity has been taken as the unit for the quantity of percolating solution, as is recommended by PANIN [1968]. On the vertical axis the concentrations of the components in the soil system are given.

It is clear from the figure that first the chloride and bicarbonate concentrations increase gradually as the degree of salinization in the soil system increases, but then remain at a constant level.

At the beginning of the percolation of the saturating solution, the sodium concentration is close to zero, due partly to the exchange of magnesium and partly to calcium-sodium ion exchange reactions. As soon as the soil adsorption complex becomes saturated, mainly with sodium, the concentration of the sodium ion abruptly increases.

Table 6.1

## Initial data for modelling salinization and desalinization processes

Process	Initial composition of soil solution in the samples me/l						
	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>
Salinization	0.00	2.85	2.39	1.84	6.37	1.09	0.03
Desalinization	0.00	8.00	14.20	134.70	38.00	50.50	68.40

Process	Exchangeable cations me/100 g			SO <sub>4</sub> gypsum	CO <sub>3</sub> carbonate	Total moisture capacity
	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	%		
Salinization	15.00	3.00	1.00	0	2.5	45
Desalinization	3.45	7.25	2.30	5	2.5	40

Process	Composition of percolating solution, me/l						
	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>
Salinization	0.00	5.71	53.96	20.60	10.28	18.36	51.63
Desalinization	0.32	1.52	1.20	1.44	1.66	1.80	1.08

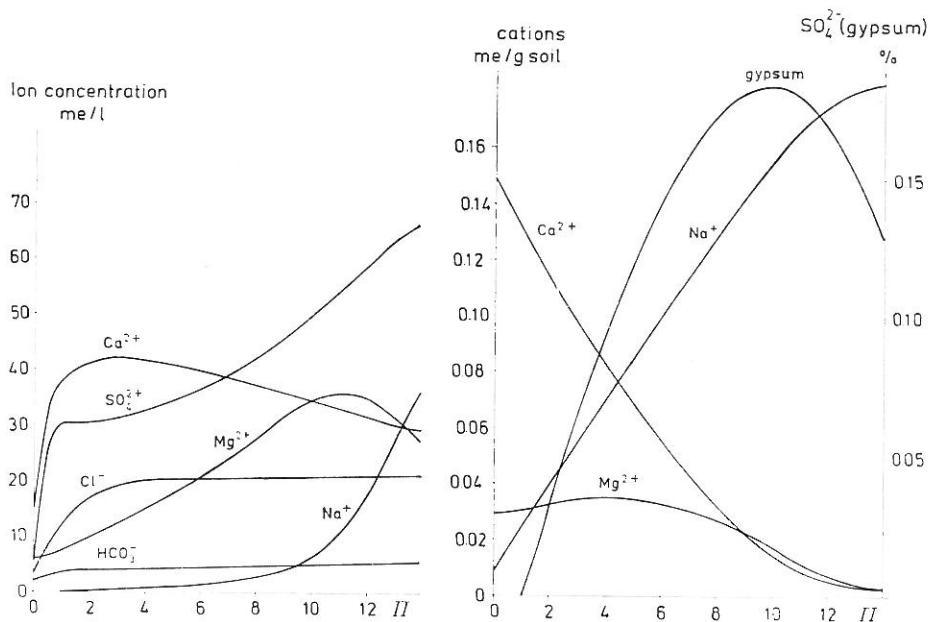


Fig. 6.3

Results of calculations of the salinization of the soil layer, influenced by the transport of mineralized water. *II* = ratio of the amount of leaching water to the field moisture capacity

The calcium concentration changes in an opposite manner and reaches its maximum value right at the beginning of the treatment. Its concentration corresponds in all probability to the solubility of gypsum under the existing matrix effect of other components in the solution.

After the saturation of the solution with calcium, the latter precipitates in the form of gypsum. The concentration of the calcium in the solution gradually decreases, in spite of the influx of calcium with the percolating solution and the sodium-calcium exchange process.

The variation in sulphate ion content is similar to the change in the calcium concentration at the beginning of the process. After the solution is saturated with gypsum, the sulphate content still increases and then the rate of the increase declines.

The value of the magnesium concentration reaches the maximum within the studied range. This effect may be explained mainly by sodium-magnesium ion exchange, and the movement of the solution.

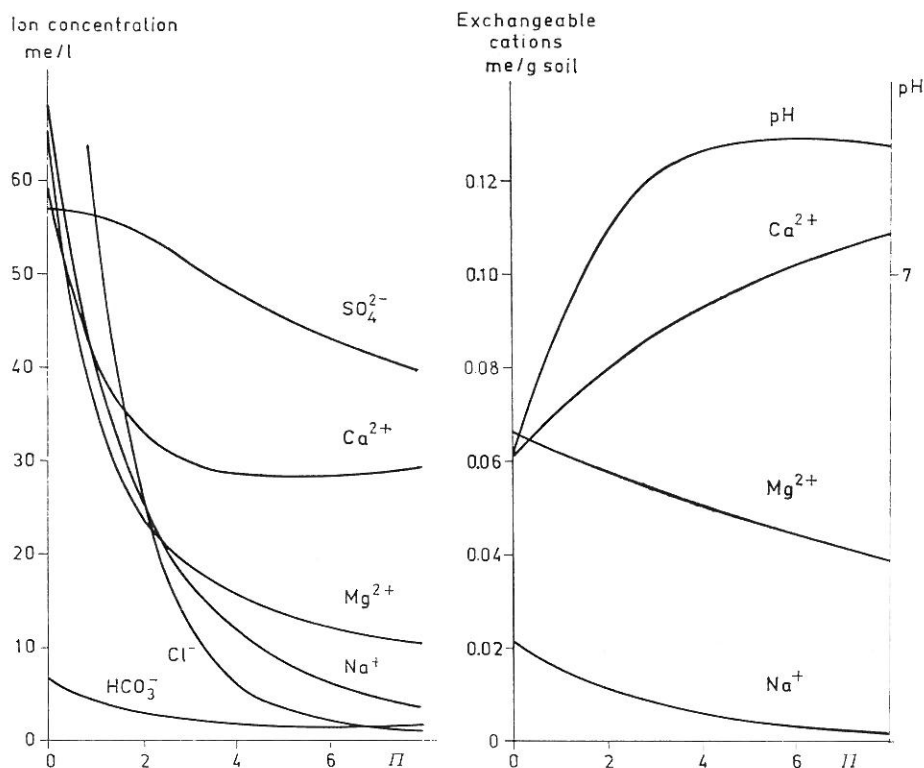


Fig. 6.4

Calculated ion concentration of leaching water in sulphate-chloride-containing saline soil. II = the same as in Fig. 6.3.

The pH of the soil solution during the sample salinization stabilizes quickly at the pH value of the salinizing solution.

The other group of calculations is made on the changes in the salt composition of the soil phases during the desalinization of a meadow saline area (solonchak) with a slightly mineralized solution (0.29 g/l), the composition of which approximates to that of the irrigation waters used in the steppe region. The original data regarding the soil composition are given in Table 6.1, and the results of the calculation are shown in Figure 6.4.

It is clear from the figure that the concentrations of all the components in the system in the interparticle solution gradually decrease, as they are leached with a weakly mineralized solution. The calcium ion concentrations, and perhaps also those of sulphate, change due to the change in gypsum solubility as the composition of the salt solution changes. The concentrations of other ions drop to the level of their concentrations in the leaching solutions.

The solubility of gypsum is influenced by the "desalting" effect of sulphate ions.

When gypsum dissolves, the equilibrium between calcium, magnesium and sodium ions shifts in favour of  $\text{Ca}^{2+}$  ion adsorption.

The leaching solution has a higher pH than the initial soil solution of the sample; this can be proved by the ratio of  $\text{CO}_3$  and  $\text{HCO}_3$  concentrations in these solutions, and is due to the fact that the pH of the soil solution rises during the leaching process to a value of about 7.3.

Thus, the model constructed offers a way of describing basic modifications in the equilibrium salt content of the soil during the percolation of solutions. In the same way the process of salinization can be studied when salts accumulate in the sample as the salt concentrations increase due to the change in the soil moisture content.

The real process of salt exchange between soil phases, from the initial to the equilibrium state, can be described in a model which simulates the kinetics of soil processes. A knowledge of the parameters of the system in the initial and equilibrium states is necessary if a proper kinetic model is to be constructed. For this purpose a good understanding is needed of the relationships between each of the parameters playing a role in the exchange between the phases. Of the processes mentioned above, ion-exchange is the quickest one,  $\text{CO}_2$  dissolution is somewhat slower, and the dissolution of gypsum and carbonates proceeds at the lowest rate. There are few data in the literature relating to the kinetics of the exchange processes even in the case of very simple systems and the explanations of the experimental data published by different authors are contradictory.

The application of some approximate kinetic functions is one way in which salt interaction models of soils can be put to practical use. The example given below describes a model often used to study the kinetics of ion exchange or the sorption process.

A fairly convenient equation which connects the rate constants of the processes with the parameters of the system is as follows [BOWER et al. 1957]:

$$\frac{\partial s_j}{\partial t} = k_e \varphi (s_j^0 - s_j) \quad (6.44)$$

where  $j$  is the number of migrants;  $\varphi$  is a function indicating the availability of the exchanger surface to the ions of the solution,  $\varphi(0) = 0$ ;  $k_e$  is the rate constant of the exchange process and  $s_j^0$  is the equilibrium concentration of the adsorbed components.

Similar calculations have been carried out quite often with the following approximations [LAPIDUS and AMUDSON 1952; LINDSTROM and BOERSMA 1971]:

$$k_e = \text{const. } \varphi(s^0 - s) = s^0 - s \quad (6.45)$$

ODDSON et al. [1970] criticized this method of calculation in the case of sorption. They pointed out that  $k_e$  was never constant but decreased as the system approached the equilibrium state. A similar approach was given by DARAB [1974] for ion-exchange. The author proved that the ion exchange process consists of partial processes with rate constants of different magnitude. Until now neither the function  $k_e$  nor  $\varphi$  has been defined in a sufficiently broad range of the parameters of the system for any one of the migrants.

In the study of the movement of the solution at a fairly low velocity of percolation the time required for reaching an exchange or sorption equilibrium  $\tau_e \ll L/Q$  ( $L$  = the depth to which the solution infiltrates,  $Q$  = the volume of solution percolated through a unit cross section per unit of time). In these circumstances, the hypothesis of instant ion exchange (or sorption) may be adopted:

$$s_j = s_j^0 \quad \text{and} \quad \frac{\partial s_j}{\partial t} = \sum_{i=1}^N \frac{\partial s_j^0}{\partial c_i} \frac{\partial c_i}{\partial t} \quad (6.46)$$

where  $c_i$  ( $i = 1, 2, \dots, N$ ) is the concentration of migrants in the solution, and  $N$  is their quantity. A calculation method is proposed for the case when a part of the migrant is adsorbed instantly and the adsorption of the remainder proceeds more slowly. Then:

$$\frac{\partial s_j}{\partial t} = \sum_{i=1}^N \frac{\partial s_j^0}{\partial c_i} \frac{\partial c_i}{\partial t} + k_e \varphi(\bar{s}_j^0 - s_j) \quad (6.47)$$

In general  $\bar{s}_j^0$  differs from  $s_j^0$  [CAMERON and KLUTE 1977]. An appropriate model seems to be the equivalent of a model with instant sorption, which takes into account the mass-exchange in the moving solution and that of the dead-end pores.

What has been said above suggests that a mathematical description of ion exchange and sorption should include a definition of the functions  $s_j^0(c_1, c_2, \dots, c_N)$ ,  $\varphi(z)$ ,  $k_e(s_1, s_2, \dots, s_M, c_1, c_2, \dots, c_M)$  with  $j = 1, 2, \dots, M$ , where  $M$  is the quantity of migrants capable of remaining in the solid phase. The function  $s_j^0$  for the case of a mono-ionic system may be expressed directly from the equations of the sorption equilibrium isotherm, and for ion exchange and multi-ionic sorption, from an equation system which consists of exchange equilibrium isotherm equations and assumes the constancy of the CEC value:  $\sum s_j = S$ .

For the exchange Na ( $i, j = 1$ ) - Ca ( $i, j = 2$ ), for example, the functions involved,  $s_1^0(c_1, c_2)$ , can be obtained from isotherm equations (6.18) - (6.20) by the elimination of  $s_2^0 = S - s_1^0$ .

## 6.2. Synthetic models of solute migration in soils

The ion and salt distribution in the soil is the result of several processes. If this system of interrelated and interacting processes is to be described mathematically, knowledge about only some of the processes, data relating to them, is not sufficient.

Therefore mathematical models in soil science always include several main processes, which determine the phenomenon under consideration. However, very often one cannot say *a priori*, what processes should be a sufficient approximation of the whole system of processes. Then the description of the phenomenon may be approached by creating a sequence of models. At each stage

1. the processes assumed to be the main ones are selected,
2. mathematical models which are in accordance with the experimental conditions, are selected to describe them,
3. constants are determined in the models constructed,
4. a synthetic model (SM) is constructed from the models of the separate processes [ANOKHIN 1974],
5. the system of SM equations is solved.

If there is satisfactory agreement between the measured and calculated values this means that the selected processes really are the determining ones and the modelling may be considered to be complete. If this agreement is not reached, then the next stage of modelling starts, with a return to point 1, and the inclusion of more processes, etc. The same phenomenon may be described by several different SMs as it depends on how the processes under consideration are selected [PACHEPSKAYA et al. 1976].

Below, one-dimensional flow will be considered. The vertical coordinate is the direction identical with the direction of macroscopic filtration in the solutions. It is assumed that all the relations of the models can be defined by the mean values of the parameters given in terms of profile cross-section, which depend only on coordinate  $x$  and time  $t$ . The parameter distribution in the profile cross-section area will be ignored. When the variability of the parameters in the cross-section area is not too high, the one-dimensional hypothesis works quite well.

The starting point to construct the SM of salt migration in the soil may be a differential equation — an expression of the law of material balance in the liquid phase of the soil:

$$\frac{\partial m}{\partial t} = - \frac{\partial J}{\partial x} + I \quad (6.48)$$

where:  $m^l$  is the mass of migrant in the solution per unit soil volume,  $J$  is the flow of the mass of migrant per unit of time per unit of cross-section area perpendicular to the  $x$ -axis, and  $I$  is the mass of migrant entering into the interparticle solution of a unit of soil volume per unit of time. Synthetic models set up on the basis of (6.48) are the subject of mathematical chromatography.

The equation (6.48) is derived from the analysis of the material balance of the migrant in the cylindrical volume of soil of a finite thickness  $\Delta x$  during time period  $\Delta t$ . The upper cross-sectional area of this cylinder is situated across the  $x$ -axis at the point  $x$ , and the lower one at the point  $x + \Delta x$ , the vertical axis of the cylinder corresponds to  $x$ , and the area of the column surface is  $\omega$ .



The mass of migrant in the solution is equal to  $M^l(x, x + \Delta x, t) = \omega \int_x^{x+\Delta x} m^l(\xi, t) d\xi$ . Assuming that  $m^l$  varies continuously between  $x$  and  $x + \Delta x$ , it is possible to substitute the integral by the product of the length of the integration interval  $\Delta x$  and the value of the subintegral function  $m^l(\xi, t)$  at a certain point  $\xi_*$  between  $x$  and  $x + \Delta x$ , i.e.  $\int_x^{x+\Delta x} m^l(\xi, t) d\xi = \Delta x m^l(\xi_*, t)$ ,  $\xi_* = x + \sigma_1 \Delta x$ ,  $0 \leq \sigma_1 \leq 1$ . Then  $M^l(x, x + \Delta x, t) = \omega \Delta x m^l(x + \sigma_1 \Delta x, t)$  and analogously  $M^l(x, x + \Delta x, t + \Delta t) = \omega \Delta x m^l(x + \sigma_2 \Delta x, t + \Delta t)$ . During the same period of time  $\Delta t$ , a mass of migrant equal to  $\omega \int_t^{t+\Delta t} J(x, \tau) d\tau = \omega \Delta t J(x, t + \sigma_3 \Delta t)$  has entered the cylinder through the  $x$ -section, and  $\omega J(x + \Delta x, t + \sigma_4 \Delta t)$  has left the cylinder through the  $x + \Delta x$  section. And finally, a mass of migrant equal to  $\omega \int_x^{x+\Delta x} d\xi \int_t^{t+\Delta t} d\tau I(\xi, \tau) = \omega \Delta t \Delta x I(x + \sigma_5 \Delta x, t + \sigma_6 \Delta t)$  has entered the volume under consideration. All values of  $\sigma_p$  ( $p = 2, 3, \dots, 6$ ), like those of  $\sigma_1$ , are between 0 and 1. The balance of the mass for the cylindrical volume is:

$$\begin{aligned} M^l(x, x + \Delta x, t + \Delta t) - M^l(x, x + \Delta x, t) &= \omega \Delta x [m^l(x + \sigma_2 \Delta x, t + \Delta t) - \\ &- m^l(x + \sigma_1 \Delta x, t)] = \omega \Delta t [J(x, t + \sigma_3 \Delta t) - J(x + \Delta x, t + \sigma_4 \Delta t)] + \\ &+ \omega \Delta t \Delta x I(x + \sigma_5 \Delta x, t + \sigma_6 \Delta t). \end{aligned}$$

Let us divide both parts of the equation by  $\omega \Delta t \Delta x$ :

$$\begin{aligned} &\frac{m^l(x + \sigma_2 \Delta x, t + \Delta t) - m^l(x + \sigma_1 \Delta x, t)}{\Delta t} = \\ &= - \frac{J(x, t + \sigma_3 \Delta t) - J(x + \Delta x, t + \sigma_4 \Delta t)}{\Delta x} + I(x + \sigma_5 \Delta x, t + \sigma_6 \Delta t) \end{aligned}$$

when  $\Delta t$  and  $\Delta x$  approach zero, equation (6.48) will be obtained.

If the movement of  $N$  migrants is studied the use of  $N$  equations of type (6.48) gives:

$$\frac{\partial m_j^l}{\partial t} = - \frac{\partial J_j}{\partial x} + I_j \quad (j = 1, 2, \dots, N) \quad (6.49)$$

where index  $j$  refers to the  $j$ th migrant. The equation system (6.49) is not complete and should be supported with a function which makes it possible to calculate  $J_j, I_j$ .

The values of  $I_j$  are determined by the salt exchange between the liquid and other soil phases, which can be determined using the model described in the previous section. The equations to identify  $J_j$  have to describe transport processes in the soil interparticle solution. Under isothermal and electro-neutral conditions, these latter include: a) transport by convection, b) molecular diffusion in the direction of flow, c) hydrodynamic dispersion in the soil, d) mass-exchange between the moving solution and that in the micropores in

soil micro-aggregates and e) MOROZOV-type gravitation movements [MOROZOV 1956] due to solution density differences at various levels in the soil profile. This process plays a role in soils with coarse structures (gravitation instability).

In addition, solution transport is influenced by the effects of heterogeneity in the structure of the soils: uneven packing of the soil column, the presence of macro-cracks and wall effect under the experimental conditions. In the following neither the uneven structure of soil column, nor the gravitation instability due to density variations in different parts of the profile are taken



Fig. 6.5

Soil structure with the arrangement of aggregates. 1. pore volume zone filled with mobile water, 2. micropores within macroaggregates

into account during the study of solution movement [SOKOLENKO et al. 1976]. The soils differ from any other porous media in the heterogeneous pore size distribution of the aggregates (Fig. 6.5). As a result, an essential part of the interparticle space inside the macro-aggregates (stagnant zone) becomes saturated with solutions which are limited in their movement. In the case of a high velocity of percolation, differences may arise in the concentrations of migrant in the so-called transfer and stagnant zones. In this case, the use of a mean concentration relating to the entire interparticle space can be misleading with regard to the quantity of adsorbed migrant. This is the case, for example, with non-linear sorption isotherms.

Assuming, for example, that there are sodium and calcium ions in the percolating solution, the ion exchange equilibrium can be given by the isotherm:

$$K_G \frac{\hat{c}_{Na}}{\sqrt{\hat{c}_{Ca}}} = \frac{\hat{s}_{Na}}{\hat{s}_{Ca}}, \quad K_G \frac{\bar{c}_{Na}}{\sqrt{\bar{c}_{Ca}}} = \frac{\bar{s}_{Na}}{\bar{s}_{Ca}} \text{ with } K_G = 0.7$$

(value typical for chernozem).  $\bar{c}_{Na} + \bar{c}_{Ca} = \hat{c}_{Na} + \hat{c}_{Ca} = 0.1 \text{ kgeq/m}^3$ ,  $\bar{s}_{Na} + \bar{s}_{Ca} = \hat{s}_{Na} + \hat{s}_{Ca} = 0.22 \text{ kgeq/m}^3$ . The values for the transfer zone are  $\hat{c}$ ,  $\hat{s}$  and those for the stagnant zone,  $\bar{c}$ ,  $\bar{s}$ ;  $c_{Na}$ ,  $c_{Ca}$  are the concentrations in the solution in  $\text{kgeq/m}^3$ , and  $s_{Na}$ ,  $s_{Ca}$  are the respective contents of exchangeable ions in  $\text{kgeq/m}^3$ .

Let us assume that the equivalent fraction of Na for the stagnant zone is  $\bar{X} = \frac{\bar{c}_{Na}}{\bar{c}_{Na} + \bar{c}_{Ca}} = 0.9$  and that for the transfer zone  $\hat{X} = \frac{\hat{c}_{Na}}{\hat{c}_{Na} + \hat{c}_{Ca}} = 0.98$ .

Assuming that the relation between the adsorption capacities of the two zones  $\bar{s}/\hat{s}$  is equal to 2, we obtain  $\hat{s}_{\text{Na}} = 0.044$ ;  $\bar{s}_{\text{Na}} = 0.056$ ,  $s_{\text{Na}} = \hat{s}_{\text{Na}} + \bar{s}_{\text{Na}} = 0.100$  mgeq/cm<sup>3</sup>.

Defining the value  $S_{\text{Na}}$  directly from the formula for the equation of the isotherm, the formula is used for the entire interparticle space. The concentration value of Na is taken as the weighted mean for the whole interparticle space; the ratio of the contributions to porosity of the stagnant ( $\bar{\epsilon}$ ) and transfer ( $\hat{\epsilon}$ ) zones will also be taken to equal 2. In this case,  $s_{\text{Na}} = 0.108$ . The difference between the real and calculated values is 8 percent, and may be still higher if  $\bar{s}/\hat{s} > \bar{\epsilon}/\hat{\epsilon}$  and if the value of the total concentration  $c_{\text{Na}} + c_{\text{Ca}}$  is low. Conditions like this are to be avoided. In the following a separate treatment of the migrant concentrations in the stagnant and transfer zones and that of the concentrations of exchangeable cations will be carried out.

The mathematical models of the transport processes in the soil were obtained by the more precise application of the laws concerning the physical, chemical and hydrodynamic processes in porous media. For instance, convective transport is described by the convective mass flow of migrant  $J_c$  through a unit of the cross-section area, in the direction of the  $x$ -axis per unit of time:

$$J_c = Q\hat{c} \quad (6.50)$$

where  $Q$  is the volume of solution flowing through a unit of the section area per unit of time.

Molecular diffusion in the transfer zone changes to a macroscopic mass flow of migrant in the direction of the  $x$ -axis. The expression for the  $J_d$  value of this flow per unit of time through a unit of cross-section area is identical to the equation of FICK's law:

$$J_d = -\hat{\epsilon} D_d \frac{\partial \hat{c}}{\partial x} \quad (6.51)$$

where  $D_d = \beta D_\mu$  and  $D_\mu$  are the values of coefficients of molecular diffusion of a migrant in the soil and the solution respectively, and  $\beta$  is the coefficient of tortuosity, which is often taken to be equal to 2/3 [ROSE and PASSIOURA 1971].

The hydrodynamic dispersion obviously means the actual difference between the rates of certain parts of the moving solution, which are under the influence of solid walls, limiting the flow region. The presence of the zone of intraporous convection and its great influence on the porous media increases the effect of hydrodynamic dispersion.

The effect of hydrodynamic dispersion is similar to that of diffusion.

Consequently, the model for the description of mass flow is similar to that for diffusion flow [BEAR, ZASLAVSKY and IRMAY 1968].

$$J_h = -\hat{\epsilon} D_h \frac{\partial \hat{c}}{\partial x} \quad (6.52)$$

The experimental data prove that dispersion  $D_h$  depends on a dimensionless parameter  $\eta = \frac{Ud}{D_\mu}$ :  $D_h = f_h(\eta)$  in porous media regardless of the aggregate structure. Where:  $U = \frac{Q}{\epsilon}$  the average velocity in porous space,  $d$  = the average aggregate diameter.

To express the above relations, several functions of  $f_h(\eta)$  were formulated theoretically and proved experimentally:  $f_h = A\eta$ ,  $A = \text{const.}$  [NIKOLAEVSKY 1959; CHURAEV et al. 1967; PASSIOURA 1971];  $f_h = 0.65 \sqrt{\eta}/(1.0 + 7.0 \sqrt{\eta})$  [HIBY 1962];  $f_h = B \sqrt{\eta}$ ,  $B = \text{const.}$  [FRIED and CAMBARNOUS 1971].

For samples with different textures  $d_k$  ( $k = 1, 2, \dots, n$ ), the  $d$  value necessary for the calculations can be found using the equation

$$d = \sqrt{\sum_{k=1}^n d_k^2 p_k}$$

where:  $p_k$  = is the relative content of particles with average diameter  $d_k$  [ROSE and PASSIOURA 1971].

The  $D_h$  value is usually determined according to the relation between the filtrate composition and the volume of the effluent (break-through curve) obtained by leaching with a solution of non-sorbing migrant. The experimental break-through curve corresponded approximately with the SM, which included only the convective, diffusive and dispersive transport zones and ignored the presence of the stagnant zone. The value of  $D_h$  however, was found to be 10–1000 times more than that determined from the  $f_h(\eta)$  function when  $a$  corresponded to the diameter of the macroaggregates [RAGIMOV 1973; ABDURAGIMOV 1973; BARON 1972]. Without taking into consideration the polydispersity of the soil, agreement between the data cannot be achieved by modelling the soil, or other porous media. Regarding the migration of compounds in soils, the mass exchange between the stagnant and transfer zones plays an important role. Three models were developed for the description of the above-mentioned phenomena.

PASSIOURA [1971] derived a model with an implicit description of the mass exchange between the transfer and stagnant zones (Model 1). The whole porous space is considered as a transfer zone, and the limitation in the flow of migrant compounds due to the existence of micropores is simulated by the introduction of a fictive flow determined by the gradient of concentration, similarly to the diffusion flow:

$$J_s = -\varepsilon D_s \frac{\partial c}{\partial x} \quad (6.53)$$

where  $D_s$  is a "structural diffusion coefficient". According to the results of ROSE and PASSIOURA [1971]:  $\frac{D_s}{D_\mu} = \frac{D_\mu}{\bar{D}\beta_f} \cdot \eta^2$  where  $\bar{D}\beta_f$  is a coefficient with a value of 0.1, and  $\bar{D}$  is the diffusion coefficient in micropores ( $\bar{D} \sim 0.1 - 0.01 D_\mu$ ).  $D_s$  may exceed the value of  $D_h$  10–1000 times.

An implicit description by Model 1 is convenient because a separate analysis of the concentration values in the stagnant zone is not necessary. The solutions of SM equations for non-sorbing migrants were obtained by standard methods [BRENNER 1962] and fairly simple methods have been elaborated to determine the combination of parameters  $D = \varepsilon D_a + \varepsilon D_h + \bar{\varepsilon} D_s$ , required for calculations with the SM [ROSE and PASSIOURA 1971; BRIGHAM et al. 1961; HASHIMOTO et al. 1964]. Good agreement was obtained

between the calculated and measured vertical distribution of a non-sorbing migrant in the profile.

This approach can be applied for a sorbing migrant with a linear isotherm of sorption (e.g. pesticides). If two ions migrate, and ion exchange occurs, the applicability of an implicit model is limited by the type of exchange isotherm [LAI and JURINAK 1972].

The second way of modelling the mass exchange between transfer and stagnant zones (Model 2) is based on the determination of the  $I_s$  value, which is the rate of the transport of a migrant mass from the stagnant zone to the transfer one, within a unit of soil volume in a unit of time [BARON 1972; BARON and PLANIN 1974; SCOPP and WARRICK 1974].

The diffusion transport within micropores can be expressed as follows:

a) a  $y$ -coordinate is introduced, perpendicular to the direction of the main flow,

b)  $y = 0$  is the coordinate of the border between the micropores (dead-end pores) and the transfer zone,

c) the pores of the stagnant zone are considered to be similar to each other and to have the length  $R$ ; at  $y = R$ , there is no mass transfer through the bottom of the pore and the condition is  $\frac{\partial \bar{c}}{\partial y} = 0$ ,

d) between the boundaries,  $0 \leq y \leq R$ , the equation  $\frac{\partial \bar{c}}{\partial t} = \frac{\bar{D} \partial^2 \bar{c}}{\partial y^2}$  obtains.

The  $I_s$  value is determined either as a diffusive flow from the stagnant to the transfer zone:  $I_s = \bar{\omega} \bar{D} \left. \frac{\partial \bar{c}}{\partial y} \right|_{y=0}$ , or as a flow due to the transfer of

compounds on the border between the micropores and the transfer zone, proportional to the difference between the corresponding concentrations:  $I_s = \bar{\omega} k (\bar{c} - c|_{y=0})$  where  $\bar{\omega}$  = area of the dead-end pores and micropore sections which serve for the mass transport and exchange between the zones in a unit of volume,  $\bar{D}$  = diffusion coefficient in the micropores,  $k$  = a constant characterizing the rate of concentration equilibration.

The SM constructed on the basis of Model 2, including the determination of the ion concentrations in both zones, satisfactorily describes solute migration [SCOPP and WARRICK 1974]. In order to give the concentrations, the determination of three ( $\bar{\omega}$ ,  $\bar{D}$ ,  $R$ ) or even four ( $\bar{\omega}$ ,  $\bar{D}$ ,  $R$ ,  $k$ ) parameters is necessary.

The third approach (Model 3) has been described in the works of PHILIP [1968], MIRONENKO and PACHEPSKY [1976] and others. In this case, mass exchange between the zones is again modelled by the  $I_s$  value. The details of ion migration in micropores however are not taken into account. The average concentration of migrants in the micropores is taken, and it is assumed that the velocity of mass exchange is proportional to the difference between the average concentrations in the two zones:  $I_s = k_s (\bar{c} - c)$ . The two unknown parameters are:  $k_s$  and  $\varepsilon$ . It is impossible at present to select *a priori* one of the three above-mentioned approaches. Therefore, the choice of the model for the description of mass transfer between the two zones, on the basis of experimental data relating to non-sorbing migrants, is also included in the above-mentioned successive approximation of modelling.

The analysis and comparison of solutions to the SM equation system for each of the models 1–3, are possible with the methods given in the next section. The analysis needs time-consuming computation. Here an analysis is made of the properties of the solutions, deduced by the application of model 3 to the description of leaching in a thin soil layer when the solution of SM equations allows a direct analysis. For a thin soil layer the mass conservation equation takes the form:

$$L \frac{d\bar{m}}{dt} = Q(\bar{c} - \hat{c}) \quad (6.54)$$

where  $L$  is the thickness of the layer. The vertical changes in the concentration of migrants in the layer should be ignored, the processes of diffusion and dispersion have no importance.  $\bar{c}$  is a known concentration of the influent; the effluent concentration concurs with the mean concentration in the transfer part of the whole layer  $\hat{c}$ . In this case: the mathematical description of the leaching in a thin layer of soil initially saturated with the solution of the non-sorbing migrant is studied. Taking Model 3 for the description of the mass exchange between the stagnant and the transfer zones, the system of SM equations will consist of two ordinary differential equations:

$$L \left( \hat{\varepsilon} \frac{d\hat{c}}{dt} + \bar{\varepsilon} \frac{d\bar{c}}{dt} \right) = -Q\hat{c} + Q\bar{c};$$

$$\bar{\varepsilon} \frac{d\bar{c}}{dt} = k_s(\hat{c} - \bar{c}); \quad \hat{c}(0) = \bar{c}(0) = c_0. \quad (6.55)$$

After determining the dimensionless variables  $V = \frac{Qt}{\varepsilon L}$ ,  $\zeta = \frac{k_s L}{Q}$ , and  $\nu = \frac{\bar{\varepsilon}}{\hat{\varepsilon}}$  it can be obtained from (6.55) that:

$$\frac{1}{1+\nu} \cdot \frac{d\hat{c}}{dV} = -\hat{c} + \bar{c} - \frac{\nu}{1+\nu} \cdot \frac{d\bar{c}}{dV}; \quad \frac{\nu}{1+\nu} \cdot \frac{d\bar{c}}{dV} = \zeta(\hat{c} - \bar{c}) \quad (6.56)$$

From the physical point of view, variable  $V$  represents the ratio between the total volume of flowing water and the total water capacity of the soil. The solution is obtained as a function of the amount of filtrate. Analysing the solution of (6.56) for the case when exchange between the zones occurs more slowly than filtration, i.e.  $\frac{L}{Q} \ll \frac{1}{k_s}$  or  $\zeta \ll 1$ , then it is evident that:

$$\frac{\hat{c} - \bar{c}}{c_0 - \bar{c}} \approx \zeta e^{-\frac{\zeta}{\nu}(1+\nu)V} + (1 - \zeta)e^{-(1-\zeta)(1+\nu)V} \quad (6.57)$$

The equation demonstrates that the coefficient preceding  $V$  in the first term is small (as  $\zeta$  is small), and the coefficient before the first exponential

function is also small. In the second term the coefficients  $1 - \zeta$  preceding  $V$  and the exponential function are close to 1. The exchange  $\hat{c}$  according to (6.57) will occur in the following way. The rapid decrease of the difference  $\hat{c} - \bar{c}$  occurs at the initial stages of the leaching due to the rapid decrease of the second term in the equation (6.57). The first term changes slowly as the coefficient before the exponent  $V$  is small. Its contribution at the initial stage will not be perceptible, because the exponential function is multiplied by a small coefficient. In the later stages of leaching the second term has no importance and the main contribution to  $\frac{\hat{c} - \bar{c}}{c_0 - \bar{c}}$  will be given by the first component, which is small as before, but its value diminishes more slowly than that of the second term. The general picture of the changes in  $\frac{\hat{c} - \bar{c}}{c_0 - \bar{c}}$  and the influence of values  $\zeta$  and  $\nu$  on the character of the curves are illustrated by Figure 6.6a. They show that the process of leaching is clearly divided into two stages: a rapid decrease in the quantity of migrant effluent in the early period and a slow process at the later stages.

Regarding the experimental data, there are a lot of publications containing the results of soil leaching. Let us now consider the results of leaching

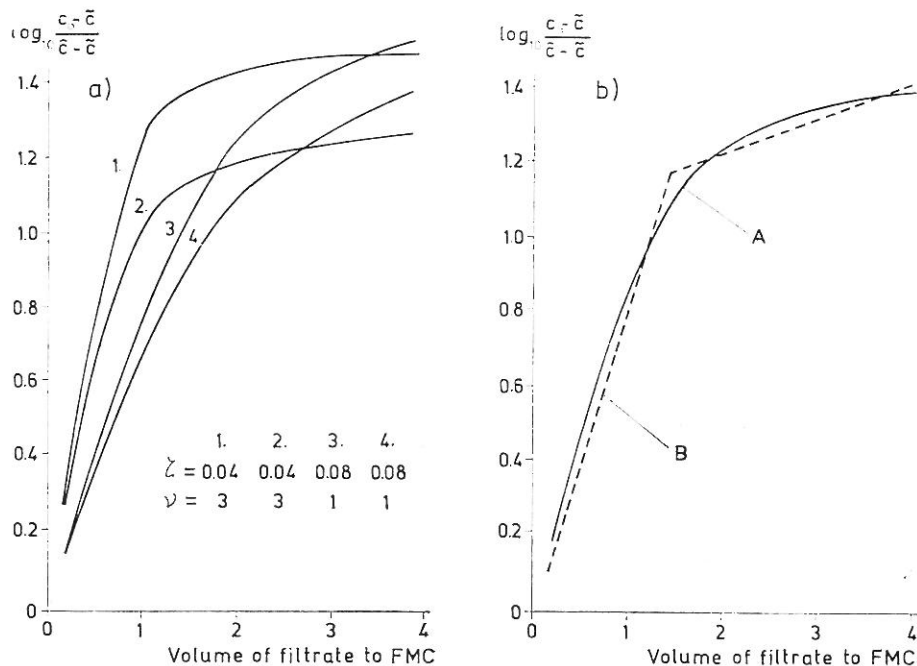


Fig. 6.6

Break-through curves for a thin soil layer calculated according to Model 3. a) influence of dimensionless parameters, b) comparison of calculated (A) and measured (B) break-through curves

in short columns ( $L = 6$  cm) filled with disturbed samples of chernozem soil with a particle size diameter of 0.25–1 mm [FILEP and KUN 1975]. The authors' main conclusions are that two stages of leaching with different rate constants can be distinguished. The slope of leaching curves reflects different stages, with rate constants differing by an order of magnitude. Leaching is not a simple process; it can be subdivided into two part processes: one with a high rate constant, that is, a period of rapid leaching, and a period of slow leaching, with a lower rate constant. These conclusions correspond to those obtained by analysing the solution of SM equations for a thin layer of soil. The hypothesis established by the authors concerning the mechanisms of salt exchange may be of some interest. FILEP and KUN [1975] wrote that in order to characterize this phenomenon one has to take into consideration the role of forms of moisture having different mobility. The precipitation and irrigation water quite rapidly mixes with the mobile part of the soil solution and the infiltrating water leaches only a part of the water-soluble salts. This process, as has been proved in their work, takes place quite rapidly under favourable conditions. The leaching of salts dissolved in the immobile moisture by the mass transfer to the mobile zone has a lower concentration of migrant due to the high velocity of the first part process. The mass transfer between the two zones (i.e. migration of salts and ions to a mobile phase) occurs mainly by diffusion. When another portion of water is added, these salts begin to leach and the whole process repeats itself. The mass transfer between the immobile moisture and the mobile soil solution is a slow process, so this part of the process is characterized by a small rate constant. This explanation agrees with the conclusion derived from the explicit model which includes the properties related to the structure of the interparticle space in the soil.

Based on the above-mentioned results it is possible to evaluate the model parameters.

In Figure 6.6b the relationships between  $\lg(\hat{c} - \bar{c})$  and  $\Pi$  measured experimentally and the estimated values from equation (6.57), where  $\zeta = 0.06$  and  $\nu = 2$ , are demonstrated. The agreement is satisfactory and points to the applicability of Model 3 for the description of the above-mentioned and other experiments of this character.

An example is now provided of SM construction for  $N$  migrants moving in the porous space of a moisture-saturated soil and sorbed on the solid phase of the soil (or subject to ion exchange). The mass of the  $j$ th migrant in the liquid phase of the soil is:  $m_j^l = \hat{e}\hat{c}_j + \bar{\varepsilon}\bar{c}_j$ . If  $\bar{s}_j$ ,  $\hat{s}_j$  are the concentrations of the migrant in the solid phase per unit soil volume in the stagnant and transfer zones, then  $I_j$ , the velocity of liquid-to-solid phase exchange, is equal to

$$\left( \frac{\partial s_j}{\partial t} + \frac{\partial \bar{s}_j}{\partial t} \right).$$

The migrant flow is summarized from the flows characterized by equations (6.50) – (6.52):

$$J_j = (J_c)_j + (J_a)_j + (J_n)_j = Q\hat{e}_j - \hat{\varepsilon}D_\mu \left[ \beta + f_n \left( \frac{Qd}{\varepsilon D_\mu} \right) \right] \frac{\partial c_j}{\partial x}.$$

It is obtained from (6.48) that:



$$\frac{\partial(\hat{\epsilon}\hat{c}_j)}{\partial t} + \frac{\partial(\bar{\epsilon}\bar{c}_j)}{\partial t} + \frac{\partial\hat{s}_j}{\partial t} + \frac{\partial\bar{s}_j}{\partial t} = \frac{\partial(Q\hat{c}_j)}{\partial x} + \frac{\partial}{\partial x} \left\{ \hat{\epsilon}D_\mu \left[ \beta + f_h \left( \frac{\partial d}{D_\mu \hat{\epsilon}} \right) \right] \frac{\partial\hat{c}_j}{\partial x} \right\} \quad (6.58)$$

The process of mass exchange between the zones is described with Model 3:

$$\frac{\partial(\bar{\epsilon}\bar{c}_j)}{\partial t} = k_s(\hat{c}_j - \bar{c}_j) - \frac{\partial\bar{s}_j}{\partial t} \quad (6.59)$$

The kinetic equation of the ion exchange or sorption can be given according to (6.44):

$$\begin{aligned} \frac{\partial\hat{s}_j}{\partial t} &= k_e \varphi[\hat{s}_j^0(\hat{c}_1, \hat{c}_2, \dots, \hat{c}_N) - \hat{s}_j] \\ \frac{\partial\bar{s}_j}{\partial t} &= k_e \varphi[\bar{s}_j^0(\bar{c}_1, \bar{c}_2, \dots, \bar{c}_N) - \bar{s}_j] \end{aligned} \quad (6.60)$$

Besides the four unknown functions  $\hat{c}_j$ ,  $\bar{c}_j$ ,  $\hat{s}_j$ ,  $\bar{s}_j$ , depending on  $x$  and  $t$  there are other functions and parameters in (6.58)–(6.60), namely:

$$\hat{\epsilon}, \bar{\epsilon}, Q, \beta, D_\mu, f_h, d, k_s, k_e, \varphi \text{ and } s_j^0 \quad (6.61)$$

Values or mathematical models should be found for these, so that the system of equations (6.58)–(6.60) will become a closed one. The SM includes this system of equations with definite parameters (6.61), and also the dependence of  $\hat{c}_j$ ,  $\bar{c}_j$ ,  $\hat{s}_j$ ,  $\bar{s}_j$  on  $x$  at the initial moment and on the boundary conditions in the region of migration. Similarly one can construct a SM for other variants of the determining process and models for them, as discussed above. It should be noted that the boundary conditions for the region of migration are usually the cross-sections  $x = 0$  and  $x = L$ , if the region of migration is assumed to reach the total length  $L$ . Under this boundary condition a determination is made either of the  $I_j$  value [by substituting a combination of (6.50)–(6.53) into (6.48)], or the value of concentration  $\hat{c}_j$ , or the condition of free outflow:  $\frac{\partial\hat{c}_j}{\partial x} = 0$ .

When leaching takes place in the total length of the column and the vertical axis has the symbol  $x$  ( $x = 0$  at the top), the concentration of the percolating solution  $\bar{c}$  is equal to the concentration of the influent; for  $x = L$ , the effluent moves freely, so the boundary condition at the surface for equations (6.58)–(6.60) can be given in the following form:

$$J|_{x=0} = \left\{ Q\hat{c} - \hat{\epsilon}D_\mu \left[ \beta + f_h \left( \frac{Qd}{\hat{\epsilon}D_\mu} \right) \frac{\partial\hat{c}}{\partial x} \right] \right\}_{x=0} = Q\bar{c}.$$

At the bottom of the column  $\frac{\partial\hat{c}}{\partial x}|_{x=L} = 0$ .  $L = \infty$  is often taken; but this assumption must be proved during further modelling,

A remark should be made on the construction of SMs with the extension of the number of determining processes. If, besides the above-mentioned processes, new ones are included, that influence the geometry of the interparticle space and the rate of filtration (hydration, peptization of soil colloids, etc.) by affecting the concentration of the migrant, the equation (6.48) may be used, as before, as the basis for SM. The models of the transfer and salt exchange between liquid and other phases of the soil should be completed with the conservation law of soil moisture mass:

$$\frac{\partial(\hat{\varepsilon} + \bar{\varepsilon})}{\partial t} = \frac{\partial Q}{\partial x} + I_W$$

where  $I_W$  is the rate of increase of moisture in a unit of soil volume not connected with solution transport. If the root activities of the plants or the activities of microorganisms are included, the models describing the effect of such processes have to be added to the relationships for  $I$  in (6.48). For the investigation of migration in gas and solid phases, equation (6.48) is insufficient; here the mass conservation law of the migrant in these phases should be used in a form similar to (6.48) [PACHEPSKY et al. 1976].

### 6.3. The solution of the equation system for synthetic models of water migration

Two cases are possible in the analysis of the system of SM equations: either general equations containing the analytical solution can be obtained, or, if this proves impossible, the results can be obtained by numerical solution. Analytical solutions have a special importance not only in connection with the possibility of a direct use of the corresponding synthetic models, but as a control basis for algorithms of numerical methods to solve more complicated systems of SM equations. Therefore, to start with, an analysis is made of several synthetic models for the leaching of a homogeneous layer of soil, initially saturated uniformly with migrant solutions. For these models analytical solutions can be found. The  $x$ -coordinate is directed downwards in the column and  $x = 0$  is the upper section of the sample, where an influent with a constant concentration is supplied.

The solution of the SM has been studied in detail for cases when the stagnant zone can be ignored, of the transport processes only convection is taken into consideration and the sorption reaction is instantaneous. According to (6.48), (6.50) and (6.45):

$$\varepsilon \frac{\partial c}{\partial t} = Q \frac{\partial c}{\partial x} - \frac{\partial s^0}{\partial c} \cdot \frac{\partial c}{\partial t} \quad (6.62)$$

$$\text{and} \quad c(x, 0) = c_0, \quad c(0, t) = \bar{c}, \quad c_0 > \bar{c} \quad (6.63)$$

It is not necessary to give the boundary condition at the lower section of the layer due to the properties of equation (6.62). This means that the outflow of migrant from the region of filtration has no influence on its migration in this region. By determining the coordinate  $q = \int_0^t Q dt$  as the volume of the

solution percolated through a unit of the section area of the layer, it is found from (6.62) that:

$$\left(1 + \frac{1}{\varepsilon} \cdot \frac{ds^0}{dc}\right) \frac{\partial c}{\partial q} + \frac{\partial c}{\partial(\varepsilon x)} = 0 \quad (6.64)$$

A general property of the solutions of equations (6.63) and (6.64) is that the value  $c$  according to (6.64) depends on  $q$  and  $x$ . As a matter of fact,  $c$  depends on the combination of  $q$  and  $x$ . This combination is  $\xi = \frac{\varepsilon x}{q}$  and so  $c$  is the function only of a single variable. Therefore,  $c = \text{constant}$  if  $\xi = \text{constant}$ , that is: for different pairs of the values  $q$  and  $x$ ,  $c$  will be the same if  $\frac{\varepsilon x}{q}$  is the same. It means that in the plane of the variables  $q$  and  $x$ ,  $c$  will

be constant along the straight lines  $\frac{x}{q} = \text{const.}$

The solution for (6.63) and (6.64) is determined in the region  $0 \leq \xi \leq 1$ ,  $\xi = 1$  by the equation of movement of the replacement front. In fact  $\xi = 1$  or  $q = \varepsilon x$  corresponds to those sections of the sample which have been reached by the leaching solution; the volume of the influent solution is equal to the volume saturating the porous space. Sections where  $\xi < 1$  have already been percolated by the influent.

The type of solution (6.64), (6.63) depends on the sign of the second derivative  $d^2s/dc^2$ , under the condition  $\tilde{c} < c < c_0$ . If  $d^2s^0/dc^2 >$  for fixed  $q$ , the value  $c$  changes continuously from  $c_0$  to  $\tilde{c}$  as  $x$  decreases from  $q/\varepsilon$  to 0.

The solution is expressed by the equations:

$$\begin{aligned} c &= \tilde{c} & \text{for} & & 0 \leq \xi \leq \tilde{\xi} \\ \xi &= \xi(c) & \text{for} & & \tilde{\xi} \leq \xi \leq \xi_0 \\ c &= c_0 & \text{for} & & \xi_0 \leq \xi \leq 1 \end{aligned} \quad (6.65)$$

$$\xi(c) = \left(1 + \frac{1}{\varepsilon} \cdot \frac{ds^0}{dc}\right)^{-1}, \quad \xi_0 = \xi(c_0), \quad \tilde{\xi} = \xi(\tilde{c})$$

If  $d^2s/dc^2 < 0$  when  $\tilde{c} < c < c_0$ , then the solution has a quite different character. When  $x$  changes from  $x = \frac{q}{\varepsilon}$  to  $x = 0$  at the beginning  $c$  has the constant value:  $c_0$ , then it instantly changes to  $c = \tilde{c}$  and remains at this value till  $x = \xi = 0$ .

The equations for the solution are:

$$\begin{aligned} c &= \tilde{c} & \text{for} & & 0 \leq \xi \leq \xi_* \\ c &= c_0 & \text{for} & & \xi_* \leq \xi \leq 1 \end{aligned} \quad (6.66)$$

$$\xi_* = \left(1 + \frac{1}{\varepsilon} \cdot \frac{s^0(\tilde{c}) - s^0(c_0)}{\tilde{c} - c_0}\right)^{-1}$$

In more complicated cases, when  $d^2s/dc^2$  changes sign in the interval  $c_0 \leq c \leq \tilde{c}$ , the solution consists of several continuous intervals separated by sharp discontinuities [KUZNETSOV 1967].

The relationships between  $c$  and  $\xi$  can be used in two ways. If  $q$  is fixed at the value  $q_s$  then  $c(\xi) = c\left(x \frac{\varepsilon}{q_s}\right)$  and we get the distribution of concentrations in the layer at the moment when  $q_s$  cm of the solution has percolated. If  $x$  is fixed at  $x = x_s$ ; then  $c(\xi) = c\left(\frac{1}{q} \cdot \varepsilon x_s\right)$  and we have the value  $c$  in a section of the sample as a function of time (or the effluent amount).

The solution above can also be used if the movement of two migrants is included and their distribution between the solid and liquid phases.

It is assumed that the chlorides of Na ( $j = 1$ ) and Ca ( $j = 2$ ) are migrating, and the basic processes, as above, are convective transport and instantaneous ion exchange.

The equations of the SM are:

$$\varepsilon \frac{\partial c_1}{\partial t} = -Q \frac{\partial c_1}{\partial x} - \frac{\partial s_1}{\partial t} \quad (6.67)$$

$$\varepsilon \frac{\partial c_2}{\partial t} = -Q \frac{\partial c_2}{\partial x} - \frac{\partial s_2}{\partial t} \quad (6.68)$$

$$c_1(x, 0) = c_{01}; \quad c_1(0, t) = \tilde{c}_1 \quad (6.69)$$

$$c_2(x, 0) = c_{02}; \quad c_2(0, t) = \tilde{c}_2 \quad (6.70)$$

The concentrations  $s_j$ ,  $c_j$  ( $j = 1, 2$ ) are given in kgeq/m<sup>3</sup>. Summarizing (6.67) and (6.68):

$$\frac{\partial(c_1 + c_2)}{\partial t} = -Q \frac{\partial(c_1 + c_2)}{\partial x} - \frac{\partial(s_1 + s_2)}{\partial t}$$

Supposing that the cation exchange capacity  $S = s_1 + s_2$  does not depend on time, and denoting  $c_1 + c_2 = C$ , it can be derived that:

$$\varepsilon \frac{\partial C}{\partial t} = -Q \frac{\partial C}{\partial x} \quad \text{or} \quad \varepsilon \frac{\partial C}{\partial q} = -\frac{\partial C}{\partial x} \quad (6.71)$$

This equation expresses the physical fact that the sum of the charges of the cations in the volume of the solution does not change during its migration in the layer of the soil. The solution of (6.71) is  $C = C(q - \varepsilon x)$ , i.e. at the point  $q_*$ ,  $x_*$  the value of  $C$  is the same as at  $x = 0$ ,  $q = q_* - \varepsilon x_*$ . Since the value of  $\tilde{C} = \tilde{c}_1 + \tilde{c}_2$  is constant at the section  $x = 0$ ,  $C$  is constant for the conditions:  $0 \leq \xi \leq 1$ . Consequently, for the conditions  $0 \leq \xi \leq 1$ ,  $s_1^0$  may be considered as a function of  $c_1$  only. This is because  $s_1^0$ , which depends on  $c_1$ ,  $c_2$ , may in any case be considered as a function of  $c_1$ ,  $C = c_1 + c_2$ , and  $c$  is constant for  $0 \leq \xi \leq 1$ . So in the equation (6.67)  $\frac{\partial s_1}{\partial t}$  may be replaced by  $\frac{ds_1^0}{dc_1} \cdot \frac{\partial c_1}{\partial t}$ . Then

$$\varepsilon \frac{\partial c_1}{\partial t} = -Q \frac{\partial c_1}{\partial x} - \frac{ds_1^0}{dc_1} \cdot \frac{\partial c_1}{\partial t}$$

$$\text{or} \quad \left(1 + \frac{1}{\varepsilon} \cdot \frac{ds_1^0}{dc_1}\right) \frac{\partial c_1}{\partial q} + \frac{\partial c_1}{\partial(\varepsilon x)} = 0 \quad (6.72)$$

It is clear that (6.72) and (6.69) agree with (6.64) and (6.65) up to index "1". Therefore the solution of (6.65) or (6.66), depending on the sign of  $d^2s_1^0/dc_1^2$ , is suitable for describing the migration. In chernozems  $d^2s_1^0/dc_1^2 > 0$  and if Ca is replaced by Na, i.e.  $\tilde{c}_1/\tilde{c}_2 > c_{01}/c_{02}$ , the continuous solution (6.65) is suitable but when Na is replaced by Ca, the solution with sharp discontinuities (6.66) is better. A comparison of the solutions of the system of equations (6.67)–(6.70) with experimental data was carried out for the "linear" isotherm (6.18) in various works [FILEP 1972a; RÉDLY and SZABOLCS 1974] and for the GAPON isotherm in chapter 7.2 of this book.

Based on the composition of the solutions (6.63), (6.64) one can construct a description of a more complicated phenomenon with a change in the composition of the influent solution, when at the beginning Ca is replaced by Na, and then at a certain moment  $q = q'$  the replacement of Na by Ca starts.  $c_1(0, t) = \tilde{c}'_1$ ,  $c_2(0, t) = \tilde{c}'_2$  and  $\tilde{c}'_1/\tilde{c}'_2 < \tilde{c}_1/\tilde{c}_2$ . The structure of the solutions may be analysed in the  $q - x$  plane (Fig. 6.7).

Solution (6.65) is illustrated by Figure 6.7a. According to (6.65) it is possible to give equations of the straight lines separating the regions with different properties of solution. For line OA  $\xi = 1$ , for line OB  $\xi = \xi$ , for line OC  $\xi = \xi_0$ . Between OA and OC,  $c = c_0$ , between Oq and OB,  $c = \tilde{c}_1$ . Between OC and OB  $c$  continuously changes from  $c_0$  to  $c_1$ .

Figure 6.7b demonstrates the structure of the analytical solution for a change in the percolating solution. Equation (6.65) is valid within a region  $Eq'OA$ . The line  $q'E$  represents the front boundary formed under the percolation of the second solution. The equation of this line is  $\varepsilon x = q - q'$ .

For the further interpretation of Figure 6.7b, it seems to be useful to select the value of  $q$  corresponding to the solution input in the second phase of the experiments and an appropriate straight line  $q''N$  which is parallel to the  $x$ -axis. The movement along the straight line from  $q''$  to  $N$  has its associated movement inside the sample from the surface at the point in time when  $q''$  cm of the solution has filtered through the surface. The line  $q''N$  crosses the characteristic lines  $q'HL$ ,  $CM$ , and  $q''E$ , separating regions which obey different laws in the changes of concentrations. In the depth interval from 0 to  $x_1$  in the area  $qq'HL$  the concentration remains unchanged:  $c = \tilde{c}'_1$ ,  $c_2 = \tilde{c}'_2$  i.e. it is the same as the influent solution. In the depth interval  $[x_1, x_2]$  it is the region LHCM where the concentration changes continuously. In the depth interval the concentration is constant and equal to that which percolates across the line  $q'E$  – the front of substitution of the first solution by the second one. During this part of the process the condition is fulfilled that the sorbed amount does not change during the percolation across the substitution front. Finally, for  $x$  deeper than  $x_4$ , which is the deepness of the substitution front by the first solution, the condition in the column is the same as it was in the beginning.

Linear models represent another class of SM, having a known analytical solution of the equation systems. These systems consist of linear equations

that are of hyperbolic or parabolic type. Well known is the case of the migration of a non-sorbing migrant. When the mass-exchange between the stagnant and transmitting zones has an implicit description, the equation is:

$$\varepsilon \frac{\partial c}{\partial t} = -Q \frac{\partial c}{\partial x} + \varepsilon D \frac{\partial^2 c}{\partial x^2} \tag{6.73}$$

Solutions are known for all types of conditions at the boundary of the filtration region [CARSLAW and JAEGER 1964; BRENNER 1962]. The SM for the migration of an instantly sorbing migrant with the linear sorption isotherm  $s^0 = \varkappa c$  also gives (6.73) with the substitution of  $\varepsilon + \varkappa$  instead of  $\varepsilon$  on the left-hand side.

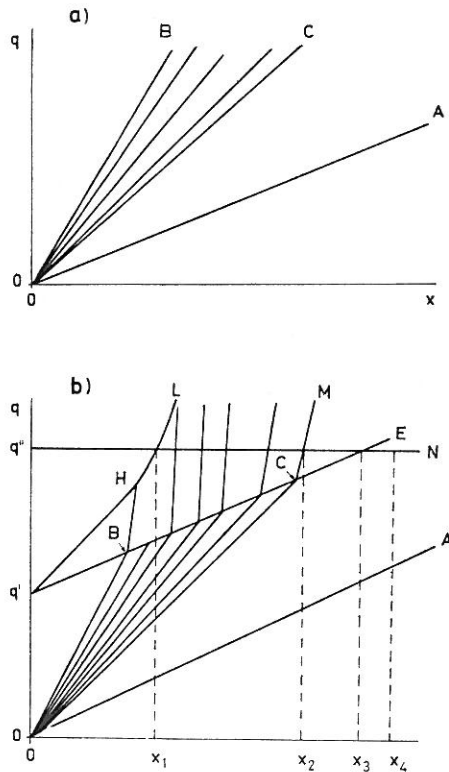


Fig. 6.7

The structure of the solution of equations of the simplest SM expressed as the variables  $q$  and  $x$  (comments in the text). a) In the case of percolating solution of constant concentration, b) in the case of percolating solution with changing concentration,  $x$  = spatial coordinate corresponding to the direction of macroscopic movement of the solution,  $m$ ;  $q$  = volume of the solution percolating through a unit cross-sectional area of the filtration region (m)

Another SM has the following system of equations:

$$\begin{aligned} \varepsilon \frac{\partial c}{\partial t} &= -Q \frac{\partial c}{\partial x} + \varepsilon D \frac{\partial^2 c}{\partial x^2} - \frac{\partial s}{\partial t} \\ \frac{\partial s}{\partial t} &= k_e (\alpha c - s); \quad c(x, 0) = \varphi_0 x; \\ s(x, 0) &= \psi_0(x); \quad \left[ \varepsilon - D \frac{\partial c}{\partial x} + Qc \right]_{x=0} = Q\tilde{c}. \end{aligned} \quad (6.73a)$$

This describes the movement of a sorbing migrant by the use of the implicit Model 1, the linear sorption isotherm and the relationship (6.45) for the sorption in time. The system (6.73a) which is exact up to  $\alpha = 1$ , corresponds to the SM for the non-sorbing migrant with Model 3. It is also suitable for SMs with Model 1 when sorption is partially instantaneous and partially continuous. Solution (6.73a) was discussed for the first time in the work of LINDSTROM and BOERSMA [1973]. However, they did not give a complete solution, and their calculation results are erroneous (disbalance of the mass by 15%). Therefore, the solution of (6.73a) is derived here, not by the application of the traditional method of inversion of the LAPLACE transformation but by the iterative solution of an auxiliary integral equation.

Changing the variables we obtain:

$$\begin{aligned} y &= c - \tilde{c}, \quad z = s - \alpha\tilde{c}, \quad \varphi(x) = \varphi_0(x) - \tilde{c} \\ \psi(x) &= \psi_0(x) - \tilde{c}, \quad \beta = Q/\varepsilon, \quad \alpha^2 = D, \quad \lambda = k_e, \quad \nu = 1/\varepsilon, \\ \frac{\partial y}{\partial t} &= \alpha^2 \frac{\partial^2 y}{\partial x^2} - \beta \frac{\partial y}{\partial x} - \nu \frac{\partial z}{\partial t}; \quad \frac{\partial z}{\partial t} = \lambda (\alpha y - z) \\ \left[ -\beta y + \alpha^2 \frac{\partial y}{\partial x} \right]_{x=0} &= 0; \quad y(x, 0) = \varphi(x); \quad z(x, 0) = \psi(x) \end{aligned} \quad (6.74)$$

Then  $z$  is excluded from the second equation:

$$z(x, t) = \psi(x)e^{-\lambda t} + \lambda \int_0^t d\tau e^{-\lambda(t-\tau)} y(x, \tau) \quad (6.75)$$

The following equation remains for  $y$ :

$$\frac{\partial y}{\partial t} - \alpha^2 \frac{\partial^2 y}{\partial x^2} + \beta \frac{\partial y}{\partial x} + \nu y = \nu \lambda z \quad (6.76)$$

$\nu_1 = \nu \lambda$ . According to TIKHONOV and SAMARSKY [1966] the solution of (6.76) may be given in the following form:

$$y(x, t) = \int_0^\infty d\xi G(x, \xi, t) \varphi(\xi) + \nu \lambda \int_0^t d\tau \int_0^\infty d\xi G(x, \xi, t - \tau) z(\xi, \tau) \quad (6.77)$$

where  $G(x, \xi, t)$  is GREEN'S function for equation (6.76) with  $z = 0$ . The concrete expression of this function depends on the boundary conditions and will be defined later. Here it should be noted that the result of the solution

will not depend on the choice of  $G$ . Only the general property of such functions is used:

$$y(x, t + t_1) = \int_0^\infty d\xi G(x, \xi, t + t_1) y(\xi, t_1)$$

If (6.75) is put into (6.77) it is found that

$$y(x, t) = y_\varphi(x, t) + \nu\lambda \int_0^t e^{-\lambda(t-\tau)} y_\varphi(x, \tau) d\tau + Q[y] \quad (6.78)$$

where  $y_\varphi$  and  $y_\psi$  are solutions of (6.76) for  $\lambda = 0$  and initial distributions  $\varphi(x)$  and  $\psi(x)$ :

$$y_\varphi(x, t) = \int_0^\infty G(x, \xi, t) \varphi(\xi) d\xi,$$

$$y_\psi(x, t) = \int_0^\infty G(x, \xi, t) \psi(\xi) d\xi$$

and  $Q[y]$  is an integral operator:

$$Q[y] = \Lambda \int_0^t d\tau \int_0^\infty G(x, \xi, t - \tau) d\xi \int_0^\tau d\tau_1 e^{-\lambda(\tau-\tau_1)} y(\xi, \tau_1)$$

where  $\Lambda = \nu\lambda$ .

Let us divide  $y$  into two parts  $y = y_I + y_{II}$ :

$$y_I = y_\varphi + Q[y_I], \quad y_{II} = \nu\lambda \int_0^t e^{-\lambda(t-\tau)} y_\varphi(x, \tau) d\tau + Q[y_{II}].$$

These equations are solved using a method of successive approximations:

$$y_I^{(0)} = y_\varphi$$

$$y_I^{(1)} = y_\varphi + Q[y_I^{(0)}] = y_\varphi + Q[y_\varphi]$$

$$y_I^{(2)} = y_\varphi + Q[y_I^{(1)}] = y_\varphi + Q[y_\varphi] + Q^2[y_\varphi]$$

$$y_I = y_\varphi + \sum_{k=1}^\infty Q^k[y_\varphi]$$

It is easy to find that

$$\begin{aligned} Q[y_\varphi] &= \Lambda \int_0^t d\tau \int_0^\infty G(x, \xi, t - \tau) d\xi \int_0^\tau d\tau_1 e^{-\lambda(t-\tau_1)} y_\varphi(\xi, \tau_1) = \\ &= \Lambda \int_0^t d\tau \int_0^\tau d\tau_1 e^{-\lambda(\tau-\tau_1)} y(x, t - \tau + \tau_1) = \Lambda \int_0^t d\tau e^{-\lambda\tau} y_\varphi(x, t - \tau) \int_\tau^t d\tau_1 = \\ &= \Lambda \int_0^t \tau e^{-\lambda(t-\tau)} y_\varphi(x, \tau) d\tau. \end{aligned}$$



Similarly

$$Q^2[y_\varphi] = \frac{1}{2} A^2 \int_0^t \tau^2 (t - \tau) e^{-\lambda(t-\tau)} y_\varphi(x, \tau) d\tau$$

$$Q^3[y_\varphi] = \frac{1}{12} A^3 \int_0^t \tau^3 (t - \tau)^2 e^{-\lambda(t-\tau)} y_\varphi(x, \tau) d\tau$$

Inductive inference leads to the formula:

$$Q^n[y_\varphi] = \frac{A^n}{(n-1)! n!} \int_0^t \tau^n (t - \tau)^{n-1} e^{-\lambda(t-\tau)} y_\varphi(x, \tau) d\tau$$

Consequently

$$y_I = y_\varphi + \sum_{n=1}^{\infty} \frac{A^n}{(n-1)! n!} \int_0^t \tau^n (t - \tau)^{n-1} e^{-\lambda(t-\tau)} y_\varphi(x, \tau) d\tau =$$

$$= y_\varphi + \int_0^t d\tau e^{-\lambda(t-\tau)} y_\varphi(x, \tau) \left[ \sqrt{\frac{A\tau}{t-\tau}} I_1[2\sqrt{A\tau(t-\tau)}] \right]$$

where  $I_1(x)$  is a modified BESSEL function of the first kind, index 1.  $y_{II}$  is determined in the same way. As a result we get:

$$y(x, t) = y_\varphi + \int_0^t d\tau e^{-\lambda(t-\tau)} y_\varphi(x, \tau) \left[ \sqrt{\frac{A\tau}{t-\tau}} I_1[2\sqrt{A\tau(t-\tau)}] + \right.$$

$$\left. + \nu\lambda \int_0^t dt e^{-\lambda(t-\tau)} y_\varphi(x, \tau) I_0[2\sqrt{A\tau(t-\tau)}] \right]$$

Then, according to (6.75)

$$z(x, t) = \psi(x) e^{-\lambda t} + \nu\lambda \int_0^t d\tau y_\varphi(x, \tau) I_0[2\sqrt{A\tau(t-\tau)}] e^{-\lambda(t-\tau)} +$$

$$+ A \int_0^t d\tau e^{-\lambda(t-\tau)} y_\varphi(x, \tau) \left[ \sqrt{\frac{t-\tau}{A\tau}} I_1[2\sqrt{A\tau(t-\tau)}] \right]$$

Finally  $y(x, t)$  is defined. GREEN's function for this case is:

$$G(x, \xi, t) = e^{-\nu t} \left[ \frac{1}{2\alpha\sqrt{\pi t}} e^{-\left(\frac{\xi-x+\beta t}{2\alpha\sqrt{t}}\right)^2} + \frac{1}{2\alpha\sqrt{\pi t}} e^{-\left(\frac{\xi+x+\beta t}{2\alpha\sqrt{t}}\right)^2} e^{\frac{\beta}{\alpha^2} x} - \right.$$

$$\left. - \frac{\beta}{\alpha^2} e^{\frac{\beta}{\alpha^2} x} \operatorname{erfc} \left( \frac{x + \xi + \beta t}{2\alpha\sqrt{t}} \right) \right]$$

where

$$\operatorname{erfc}(z) = \frac{2}{\sqrt{\pi}} \int_z^\infty e^{-t^2} dt$$

Analysing the case when the initial distribution is a jump function:

$$y(x, 0) = \varphi(x) = \begin{cases} c_0 - \bar{c} & 0 < x \leq L \\ 0 & x > L \end{cases} \quad (6.79)$$

$$z(x, 0) = \psi(x) = \kappa \varphi(x) = \begin{cases} \kappa(c_0 - \bar{c}) & 0 < x \leq L \\ 0 & x > L \end{cases}$$

After integrating in (6.77) it is finally found that:

$$y_{\varphi}(x, t) = (c_0 - \bar{c})e^{-\nu t} \left\{ \frac{1}{2} \operatorname{erfc} \left( \frac{\beta t - x}{2\alpha\sqrt{t}} \right) - \frac{2\beta\sqrt{t}}{\alpha\sqrt{\pi}} e^{-\left(\frac{\beta t + x}{2\alpha\sqrt{t}}\right)^2} + \right.$$

$$+ \frac{1}{2} \left[ 1 + \frac{2\beta}{\alpha^2} (\beta t + x) e^{\frac{\beta}{\alpha^2} x} \operatorname{erfc} \left( \frac{\beta t + x}{2\alpha\sqrt{t}} \right) - \frac{1}{2} \operatorname{erfc} \left( \frac{\beta t - x + L}{2\alpha\sqrt{t}} \right) + \right.$$

$$\left. \left. + \frac{2\beta\sqrt{t}}{\alpha\sqrt{\pi}} e^{-\left(\frac{\beta t + x + L}{2\alpha\sqrt{t}}\right)^2} e^{\frac{\beta x}{\alpha^2}} - \frac{1}{2} \left[ 1 + \frac{2\beta}{\alpha^2} (\beta t + x + L) \right] e^{\frac{\beta}{\alpha^2} x} \operatorname{erfc} \left( \frac{\beta t + x + L}{2\alpha\sqrt{t}} \right) \right] \right\}$$

Appendix 1 contains programme MIGR 1 for the calculation of the filtrate composition at depth  $L$  for SM (6.73a) taking into account (6.79). An example for the application of the programme is given in Figure 6.8 where

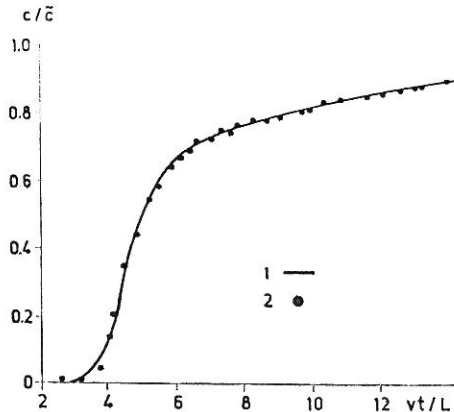


Fig. 6.8

Linear SM calculation of soil column saturation with a sorbing migrant (atrazine). 1. calculated values, 2. measured values [ELRICK et al., 1966]

calculated and measured compositions of filtrate are represented on the basis of soil column experiments for atrazine saturation [ELRICK et al. 1966]. Calculations were carried out assuming instantaneous sorption with a linear isotherm. The programmes in Appendix 1 also work for SM equations (6.73).

The analytical solution is also known for SM (6.73a) with the condition:  $D = 0$ . The analysis of such a SM is appropriate under the condition that

molecular diffusion and hydrodynamic dispersion in a wide range of parameters common for soils do not essentially influence the solution of the migration problems. Comparing solutions obtained with approximate  $D$  values (exact to an order of magnitude) and if  $D = 0$ , the influence of the choice of  $D$  value on the solution can be estimated and in certain cases the precise determination of  $D$  can be neglected, reducing the volume of experimental work. A solution of (6.73a) with  $D = 0$  cannot be obtained with  $D \rightarrow 0$ . It can be carried out with other methods, for instance that of MIRONENKO and PACHEPSKY [1976]: where  $\varphi(x) = c_0$ ,  $\psi(x) = \alpha c_0$  the solution of system (6.74) equivalent to (6.73a) is expressed as:

$$\begin{aligned} y(\xi, t) &= \bar{c} + (c_0 - \bar{c}) R(\tau, \xi) \\ z(\xi, t) &= \alpha c_0 + \alpha(\bar{c} - c_0) R(\xi, \tau) \end{aligned} \quad (6.80)$$

where

$$\xi = \frac{\nu \lambda \alpha}{\beta} x, \quad \tau = \lambda \left( t - \frac{x}{\beta} \right),$$

$$R(\xi, \tau) = \int_0^\tau I_0(2\sqrt{\xi q}) e^{-\xi - q} dq.$$

Using the programme MIGR 2 it is possible to calculate the filtrate composition at a depth  $L$  in accordance with the solution (6.80) (see Appendix 2).

For SMs which include non-linearities (for example, non-linear isotherms of the ion exchange or sorption) and transfer processes other than convection and which do not have analytical solutions, a numerical approach is necessary. For example, the SM given by equations (6.45) and (6.58)–(6.60), the process of the transformation of the system of SM equations to the type suitable for numerical computation, is given below.

The case of migration of two ions is analysed, for which the SM is presented by equations (6.45) and (6.58)–(6.60). The ion exchange and the constancy of surface charges:  $s_1 + s_2 = S$  are taken into account.

Summarizing equations (6.58) for  $j = 1$  and  $j = 2$  under the condition:  $S = \text{const.}$  the following equation is obtained for total concentration  $C$ :

$$\frac{\partial \hat{C}}{\partial t} = D \frac{\partial^2 \hat{C}}{\partial x^2} - \frac{Q}{\hat{\varepsilon}} \frac{\partial \hat{C}}{\partial x} - \frac{\bar{\varepsilon}}{\hat{\varepsilon}} \frac{\partial \bar{C}}{\partial t} \quad (6.81)$$

Similarly from (6.59) when  $j = 1$  and  $j = 2$  it can be obtained that

$$\frac{\bar{\varepsilon}}{\hat{\varepsilon}} \frac{\partial \bar{C}}{\partial t} = k_s (C - \bar{C}) \quad (6.82)$$

Using (6.45) the following equations can be derived:

$$\frac{\partial \hat{s}_1}{\partial t} = k_e (s_1^0 - \hat{s}_1) \quad (6.83)$$

$$\frac{\partial \bar{s}_1}{\partial t} = k_e (\bar{s}_1^0 - \bar{s}_1) \quad (6.84)$$

And, finally, for  $c_1$ , as a consequence of (6.58) and (6.59),

$$\frac{\partial \hat{c}_1}{\partial t} = D \frac{\partial^2 \hat{c}_1}{\partial x^2} - \frac{Q}{\hat{\varepsilon}} \frac{\partial \hat{c}_1}{\partial x} - \frac{k_s}{\hat{\varepsilon}} (\hat{c}_1 - \bar{c}_1) - \frac{1}{\hat{\varepsilon}} \cdot \frac{\partial \hat{s}_1}{\partial t} \quad (6.85)$$

$$\frac{\partial \bar{c}_1}{\partial t} = \frac{k_s}{\bar{\varepsilon}} (\hat{c}_1 - \bar{c}_1) - \frac{1}{\bar{\varepsilon}} \cdot \frac{\partial \bar{s}_1}{\partial t} \quad (6.86)$$

are valid.

At the boundaries of the migration region

$$\hat{c}_1(0, t) = \bar{c}_1; \quad \hat{C}(0, t) = \bar{C}; \quad \left. \frac{\partial \hat{c}_1}{\partial x} \right|_{x=L} = 0; \quad \left. \frac{\partial C}{\partial x} \right|_{x=L} = 0 \quad (6.87)$$

It should be recalled that (6.81)–(6.87) were derived from equations of the mass balance for a layer of finite thickness assuming that  $\Delta x, \Delta t \rightarrow 0$ . For the numerical solution (6.81)–(6.82) a reverse operation is carried out: by the approximation of finite differences differential equations are transformed into equations of the mass balance in layers of finite thickness. If we have  $N$  layers with equal thickness  $\Delta x = L/N$  in the filtration zone, and the coordinates of the sections are enumerated from 0 to  $N$ :  $x_i = i\Delta x$ . Introducing discrete time intervals:  $t_n = t_0 + n\Delta t$ , the values of any variable in (6.81)–(6.87) at a moment of time  $t_n$  at the point  $x = x_i$  are indicated by using subscript  $i$  and superscript  $n$ . For example,  $C(x_i, t_n) = C_i^n$ ,  $s_1(x_{i+1}, t_n) = s_{1,i+1}^n$ , etc.

In equations (6.81) and (6.82) finite difference approximations of the derivatives give:

$$\begin{aligned} & \Delta x [\hat{\varepsilon}(\hat{C}_i^{n+1} - \hat{C}_i^n) + \bar{\varepsilon}(\bar{C}_i^{n+1} - \bar{C}_i^n)] = \\ & = \hat{\varepsilon} D \Delta t \left[ h \frac{\hat{C}_{i+1}^n - 2 \cdot \hat{C}_i^n + \hat{C}_{i-1}^n}{\Delta x} + (1-h) \frac{\hat{C}_{i-1}^{n+1} - 2 \cdot \hat{C}_i^{n+1} + \hat{C}_{i-1}^{n+1}}{\Delta x} \right] - \\ & - Q \Delta t \left[ h \frac{\hat{C}_i^n - \hat{C}_{i-1}^n}{\Delta x} + (1-h) \frac{\hat{C}_i^{n+1} - \hat{C}_{i-1}^{n+1}}{\Delta x} \right] \end{aligned} \quad (6.88)$$

$$\bar{\varepsilon}(\bar{C}_i^{n+1} - \bar{C}_i^n) = k_s \Delta t [h(\hat{C}_i^n - \bar{C}_i^n) + (1-h)(\hat{C}_i^{n+1} - \bar{C}_i^{n+1})] \quad (6.89)$$

Equation (6.88) expresses the balance of the total mass of migrants in the solution in a layer of  $\Delta x$  thickness between the sections  $x = x_i$ ;  $x_i = x_{i+1}$ . The total mass of migrants changes due to the inflow of the solution into the section  $x = x_i$  and the outflow from the section  $x = x_{i+1}$  during the time  $\Delta t$ . The average flow through each of the sections for time  $\Delta t$  is calculated accord-

ing to the formula:  $J = hJ^n + (1 - h)J^{n+1}$ ,  $0 \leq h \leq 1$ . Nothing can be assumed about the value of  $h$  a priori; it is usually selected according to the conditions of exactness of the calculations. Equation (6.89) expresses the law for changing the total mass of dissolved migrants in the stagnant zone of section  $x_i$ . This change is proportional to the difference between the average values of total concentration in two zones for an interval of time  $\Delta t$ . The average concentration for a time  $\Delta t$  is derived according to formula  $C = hC^n + (1 - h)C^{n+1}$ , where  $h$  is the same as in (6.89).

Equations (6.83)–(6.87) are approximated in the same way as (6.81) and (6.82). As a result the system of non-linear equations (6.81)–(6.87) is a finite difference analogue, which connects the values of the unknowns in the upper time layer (at  $t=t_{n+1}$ ), i.e.  $\hat{c}_i^{n+1}$ ,  $\hat{c}_i^{n+1}$ ,  $\hat{c}_{1,i}^{n+1}$ ,  $\hat{c}_{1,i}^{n+1}$ ,  $\hat{s}_{1,i}^{n+1}$ ,  $\hat{s}_{1,i}^{n+1}$  ( $i = 1 \div N$ ), with their values at the same points in a lower time layer (where  $t = t_n$ ). As the initial values of the unknown functions are given for  $t = t_0$ , then, solving equations of the finite difference analogue and considering the values at  $t = t_1$  as unknown then for  $t = t_2$ , etc., one can find a solution for any  $T > t_0$ . The method of solving the non-linear system of equations is combined from the processes of linear algebra and successive approximation for (6.83), (6.84) and (6.87). Appendix 3 gives the programme RASNA to solve the system of finite difference equations that replace (6.81)–(6.87).

The problem of the identification of models for certain processes consists in the discovery of the parameters and functions given in (6.61). Some of them, such as  $\varepsilon$ ,  $Q$ ,  $S$  and  $s^0$  can usually be measured directly. However, it should be kept in mind, that in some cases methods of determining parameters from disturbed samples may give wrong information regarding the values of model parameters. For example, the number of adsorption sites in the disturbed sample may differ from those in undisturbed ones, etc.

Other parameters and functions of the above-mentioned in (6.61), such as  $\hat{\varepsilon}$ ,  $k_s$  and  $\varphi(z)$ , are determined by solving the systems of SM equations and by a comparison of experimental and calculated values. For instance, applying the system of SM equations (6.45), (6.58) and (6.60) for the description of the movement of a single migrant, values  $d$ ,  $s^0$ ,  $\varepsilon$ ,  $Q$ ,  $\beta$ ,  $D_\mu$  and the function  $f_n(\eta)$  are known from experimental values;  $\hat{\varepsilon}$ ,  $k_s$  and  $k_e$  from (6.61) are subject to determination. Measured concentrations of migrant in the effluent at the points of time  $t_1, t_2, \dots, t_n$ ;  $\hat{c}_{m,1}, \hat{c}_{m,2}, \dots, \hat{c}_{m,n}$  are assumed to be known. Values of  $\hat{c}$  at  $x = L$  at the same moments of time may be calculated, and they depend not only on  $t$ , but on the values of unknown parameters  $k_s, k_e, \hat{\varepsilon} : \hat{c} = \hat{c}(L, t, k_s, k_e, \hat{\varepsilon})$ .

Introducing the function:  $\Phi(k_s, k_e, \hat{\varepsilon}) = \sum_{i=1}^n [\hat{c}_{m,i} - \hat{c}(L, t_i, k_s, k_e, \hat{\varepsilon})]^2$ , optimal values of  $k_s, k_e$ , and  $\hat{\varepsilon}$  will correspond to the minimum of function  $\Phi$ . The search for the minimum of such functions is usually carried out with the combination of several methods of non-linear programming [POLYAK and SKOKOV 1967]. In the determination of parameters the greatest difficulties arise for the models of non-essential processes. When parameters of less important processes vary, the value of  $\Phi$  changes slightly, and experimental errors in the values of  $\hat{c}_{m,i}$  may be regarded as the reason why values for the parameters of non-essential processes are obtained which are far from correct.

Such situations are undesirable because the necessity of unjustified complication of the search methods for parameters reduces the rate of the

search. The error in determining parameters is not too high as long as the corresponding processes are not essential; however, one cannot consider such parameters as fully valid.

Some *a priori* conclusions on the significance of this or other processes can be drawn, if analytical solutions are used and dimensionless parameters, characterizing the relation of characteristic periods of certain processes, are introduced. For instance, the degree of influence of molecular diffusion and hydrodynamic dispersion can be estimated by the value of the BRENNER number  $B = \frac{QL}{\hat{\varepsilon}D} = \frac{L^2/D}{\hat{\varepsilon}L/Q} = \tau_c/\tau_d$ , where  $\tau_c$  and  $\tau_d$  are characteristic periods of the convective transfer and the diffusive-dispersive transfer. The SM equation for a non-sorbing migrant in the flowing zone is similar to (6.73). Dividing both of its parts by  $Q/L$  and determining  $t' = tQ/\hat{\varepsilon}L$ ,  $x' = x/L$  we get:

$$\frac{\partial c}{\partial t'} + \frac{\partial c}{\partial x'} = \frac{1}{B} \cdot \frac{\partial^2 c}{\partial x'^2} \tag{6.90}$$

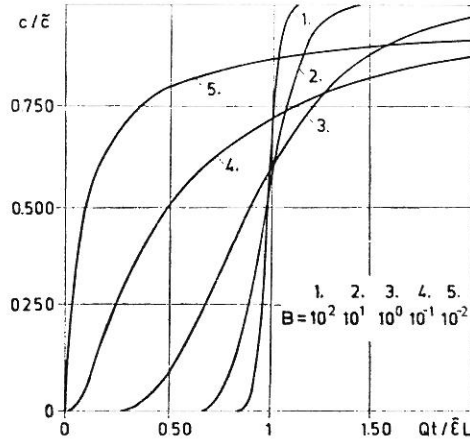


Fig. 6.9

Influence of BRENNER number (B) on the form of the break-through curve

If the BRENNER number is small, it can be assumed that the diffusive and dispersive transport have only a slight influence on the solution. This can be seen in Figure 6.9, which represents the influence of value  $B$  on the filtrate composition – time function for  $x' = 1$ , i.e. with  $x = L$ .

Another parameter, characterizing the relative rate of the processes is the parameter:  $\zeta = \frac{k_e L}{Q}$ . SM equations for a single sorbing migrant with a linear isotherm of sorption, ignoring the stagnant zone, in variables  $t'' = \frac{Qt}{L}$ ,  $x'' = \frac{x\varepsilon}{L}$  is as follows:

$$\frac{\partial(\kappa c)}{\partial t''} + \frac{\partial(\kappa c)}{\partial x''} = -\frac{\kappa}{\varepsilon} \cdot \frac{\partial s}{\partial t''}; \quad \frac{\partial s}{\partial t''} = \zeta(\kappa c - s) \tag{6.91}$$

The rate of approach to the equilibrium is governed by the value of  $\zeta$ . The influence of values  $\zeta$  and  $\nu = \frac{\zeta}{\varepsilon}$  on the filtrate composition vs. time function for  $x'' = 1$  is shown in Figure 6.10.

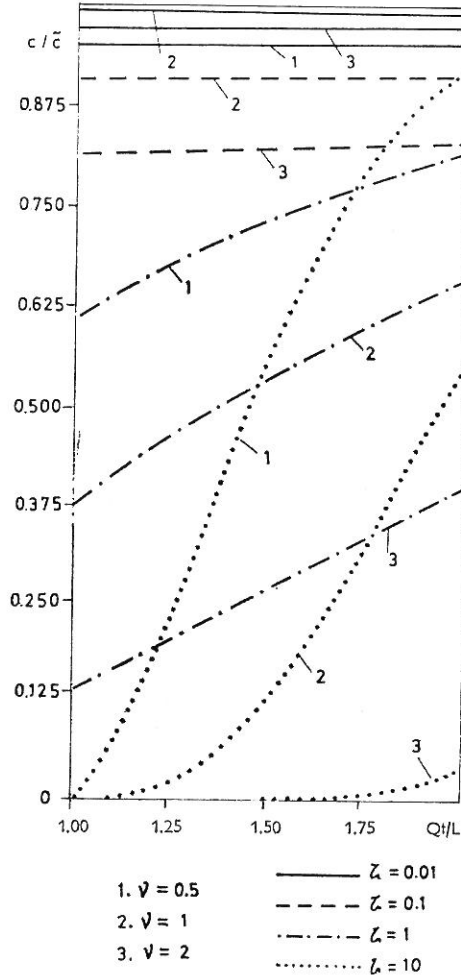


Fig. 6.10

Influence of values of parameters  $\zeta$  and  $\nu$  on the form of a break-through curve

### List of Symbols for Chapters 6 and 7.2

The symbols in Chapters 6 and 7.2 to identify physical values are given below with an indication of their dimensions. These are based on the International System of Measuring Units, and all deviations from the latter caused

by the need for a more compact way of recording values in the range of values normally used in research papers, are specially mentioned. In particular, as a time-measuring unit suitable for the description of migration processes in the soil, 24 hr (one day) is selected. Chemical symbols, when used as indexes, mean that the value in question relates to a specific ion or chemical compound. The superscripts  $g$ ,  $e$  and  $s$  denote the mass of the migrant in the gaseous phase of the soil, in exchange form on the surface of the solid phase, and in crystalline salts, respectively. The superscript 0 refers to the state of equilibrium.

To complete these symbols the following superscripts are used:

$\wedge$	for the transfer zone of the interparticle space
$\sim$	for the stagnant zone of the interparticle space
$\sim$	for values related to the solution percolating into the migration region, together with the subscript 0 for the initial values in the water migration area, the subscript w for values connected with the water in pores, and the subscripts indicating the process, as follows:
$c$	convective transfer
$d$	molecular diffusion
$h$	hydrodynamical dispersion
$s$	mass exchange between stagnant and transfer interparticle space zones
$e$	ion exchange or sorption.

If the symbol has a special significance and it alters the dimension of the value, this is indicated immediately after those symbols by an additional sign.

$B$	BRENNER number
$C$	total average mass concentration of a mixture of the migrants being studied in the interparticle solution [ $\text{kg}/\text{mole}/\text{m}^3$ ( $\text{kg-ion}/\text{m}^3$ )]
$D$	coefficient to describe the effects of diffusion-type processes [ $\text{m}^2/\text{day}$ (24 hours)]
$D_d$	coefficient of molecular diffusion in the soil
$D_h$	coefficient of hydrodynamic dispersion
$D_s$	a "structural diffusion coefficient", to describe mass-exchange between stagnant and transfer zones
$D^\mu$	coefficient of molecular diffusion in the solution
$\bar{D}$	coefficient of molecular diffusion in micropores
$E$	dimensionless relation between the CEC of the solid phase of the soil, and that of the salt content in the soil solution
$F$	the ratio of the volume of effluent to the total solution volume in the sample
$I$	the rate of sorption of a stagnant mass of migrant [ $\text{kmole}/\text{m}^3/\text{day}$ ( $\text{kg-ion}/\text{m}^3/\text{day}$ )]
$I_s$	the transfer rate of migrant from the stagnant to the transfer zone
$I_w$	the rate of decrease in solution volume [ $\text{day}^{-1}$ ]
$J$	the flow rate of the mass of migrant in the soil liquid phase per unit time through a unit cross-sectional area [ $\text{kmole}/\text{m}^2/\text{day}$ ( $\text{kg-ion}/\text{m}^2/\text{day}$ )]
$J_c$	flow due to convective transfer
$J_d$	flow due to molecular diffusion
$J_h$	flow due to hydrodynamic dispersion



$J_s$	fictive "structural flow" to describe mass exchange from the stagnant zone to the transfer zone
$K$	equilibrium constant of salt-exchange reactions between the soil phases
$L$	the length of the migration zone under study [m]
$M$	the quantity of migrants capable of remaining in the solid phase.
$N$	the number of migrants being investigated at any moment
$Q$	the water flux through a unit cross-sectional area [m/day]
$R$	effective depth of dead-end pores of the stagnant phase, [m]
$S$	CEC value of the soil [kgeq/m <sup>3</sup> ]
$T$	total exchange capacity
$U$	the average rate of infiltration in the interparticle space [m/day]
$V$	ratio of the volume of percolating solution to the total moisture capacity of the filtration region
$X$	sodium percentage in the solution
$Y$	the degree of sodium saturation (D.S.S.)
$a$	thermodynamic activity of the ion (salt)
$c$	average concentration of migrant in the interparticle solution [kmole/m <sup>3</sup> (kg-ion/m <sup>3</sup> )]
$\hat{c}$	average concentration for the interparticle space transfer zone
$\bar{c}$	average concentration for the interparticle space stagnant zone
$\tilde{c}$	concentration in the solution percolating into the migration region
$c_0$	initial concentration in the migration area
$d$	average diameter of macro-aggregates, m
$g$	total mass of an individual migrant in a soil volume containing one m <sup>3</sup> of interparticle solution [kmole/m <sup>3</sup> (kg-ion/m <sup>3</sup> )]
$k$	salt-exchange velocity constant [day <sup>-1</sup> ]
$k_c$	ion-exchange velocity constant
$k_s$	mass-exchange velocity constant from the stagnant zone to the transfer zone
$m$	amount of migrant in the interparticle solution per unit soil volume [kmole/m <sup>3</sup> (kg-ion/m <sup>3</sup> )]
$m^l$	amount of migrant in the liquid phase of the soil volume unit
$n_+, n_-$	the number of positive and negative ions
$p_{CO_2}$	partial pressure of carbon dioxide, atm.
$q$	volume of the solution percolating through a unit cross-sectional area of the filtration region [m]
$s$	average content of migrant in the solid phase of a unit soil volume exposed to ion-exchange or sorption processes [kmole/m <sup>3</sup> (kg-ion/m <sup>3</sup> )]
$\hat{s}$	for the transfer zone
$\bar{s}$	for the stagnant zone
$t$	time [days]
$\Delta t$	the time interval for which the balance is calculated [days]
$x$	spatial coordinate corresponding to the direction of macroscopic movement of the solution [m]
$\Delta x$	thickness of the layer [m]
$y$	coordinate perpendicular to the direction of the main water flow [m]
$z_+, z_-$	the charges of positive and negative ions, respectively
$\alpha$	activity coefficient of the monovalent ion [1000 kg H <sub>2</sub> O/kmole]
$\beta$	tortuosity factor

$\beta_f$	shape factor
$\gamma$	activity coefficient [1000 kg H <sub>2</sub> O/kmole (kg-ion)]
$\varepsilon$	the interparticle solution volume in unit soil volume
$\hat{\varepsilon}$	in the transfer zone
$\bar{\varepsilon}$	in the stagnant zone
$\zeta$	ratio between the characteristic times of convective transfer and mass-exchange
$\eta$	ratio between the characteristic times of convective transfer and molecular diffusion in macropores
$\theta$	moisture content in volume percentage
$\kappa$	distribution coefficient of linear sorption
$\lambda$	auxiliary variable
$\Lambda$	auxiliary variable
$\mu$	the ionic strength of the solution [kmole/m <sup>3</sup> ]
$\nu$	ratio between solution volumes in the stagnant and transfer zones
$\xi$	self-similarity coordinate
$\Pi$	ratio of the filtrate volume to the field moisture capacity
$\rho$	the weight of a unit volume of interparticle solution [1000 kg/m <sup>3</sup> ]
$\tau$	the characteristic duration of the process [days]
$\varphi$	a function indicating the availability of the exchanger surface to the ions of the solution
$\chi$	coefficient in the modified equation of the ion exchange isotherm
$\psi$	auxiliary function
$\omega$	the cross-sectional area of the migration region vertical to the $x$ -axis [m]
$\bar{\omega}$	cross-sectional area of the section of dead-end and micro-pores serving as a path for mass-exchange between the stagnant and transfer zones in a unit of soil volume [1/m]