Study of the Liquid Phase of the Soil as a Multicomponent Electrolyte Solution

J. CSILLAG and M. RÉDLY

Research Institute for Soil Science and Agricultural Chemistry of the Hungarian Academy of Sciences, Budapest

The liquid phase of the soil cannot be considered as pure water, characterized by the formula H_2O. It is a solution, the concentration and chemical composition of which vary in space and time /BISTRITSKAYA et al., 1981/. It contains different dissolved inorganic and organic materials, colloids and gases. The dominant inorganic cations and anions present in the soil solution are: Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, and sometimes Fe^{3+}, Al^{3+}, as well as Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, NO_3^-, HPO_4^{2-}, etc. /ADAMS, 1974; BOHN et al., 1985/.

The chemical composition of the soil solution directly determines the possibilities for and mechanisms of water and nutrient uptake by plants /ADAMS, 1974; KHASAWNEH, 1971; LINEHAN et al., 1985/, as well as the composition of adsorbed cations on the surface of soil particles according to the ion exchange equilibria /BRESLER et al., 1982; RÉDLY and DARAB, 1981; SPOSITO, 1981/. The latter, however, pointed out in the literature, significantly influences the physical properties of the soil and frequently determines its water management through the soil hydrophysical parameters /moisture potential, pF curves, hydraulic conductivity, etc./ /BRESLER et al.,1982; SHAINBERG, 1984; VÁRALLYAY, 1977/. Therefore, when determining the optimum soil ecological conditions for crops, a knowledge of the actual concentration and composition of the soil solution is of great importance.

The concentration and composition of the soil solution are influenced by the change in soil moisture content because of:

 – the simple inverse dilution effect of the liquid phase;

 – the changes in the physico-chemical processes between the solid and liquid phases of the soil /dissolution and precipitation of salts, ion-exchange and hydrolysis of adsorbed cations/ with the dilution of the soil-water system.

The total dissolved quantities of some salts may increase with an increase in soil moisture, while those of others do not change. A large number of experimental, theoretical and computational studies have been published on the characterization of these processes, to predict the effect of dilution on the chemical composition of the soil solution /CSILLAG, 1988; DARAB et al., 1956; KHASAWNEH and ADAMS, 1967; KRUPSKY et al., 1968; RÉDLY, 1977; REITEMEIER, 1946; ULRICH and KHANNA, 1972; VAN DEN ENDE, 1968/. A

knowledge of the effect of changes in soil moisture content is of interest when characterizing the liquid phase within the range of field moisture content available to plants /ADAMS, 1974/, and also when interpreting data concerning soluble salts measured in aqueous soil extracts having different soil:water ratios /BARON and TOKAREV, 1979; GILLMAN and BELL, 1978/.

The interactions between the liquid and solid phases of the soil, or between the soil solution and the plant are more complex in the case of soils having high salt concentrations, particularly in salt affected soils /BOHN et al., 1985; BRESLER et al., 1982; DARAB et al., 1980; JURINAK, 1984/; during the use of relatively concentrated nutrient solutions under greenhouse conditions /VAN DEN ENDE, 1968/; or locally in the field after the application of high fertilizer doses /NÉMETH and KÁDÁR, 1987/. The reason for the complexity of the interactions is the greater abundance of soluble salts, the occurrence of poorly soluble salts, and the decreased solubility of some salts at high alkalinity values.

In general, the concentration of the soil solution does not exceed 0.01 mol/l. However, in salt affected soils at low moisture content it may be as high as 0.1-0.5 mol/l or even, in extreme cases, 5 mol/l /International Source Book, 1967; DARAB et al., 1980/. From the physico-chemical point of view, the liquid phase of the soil is a multicomponent electrolyte solution, a "real" system, where at high concentrations it is the ion activities, not the ion concentrations which determine the rate and extent of chemical reactions. As a consequence of the interactions between the dissolved components, different "species" /such as free hydrated ions, ion-pairs, complexes or molecules/ are present in the soil solution, the physico-chemical properties of which are determined by the activity and ratio of these "species" /ADAMS, 1974; BERNHARD et al.,1986; CSILLAG and KAPOOR, 1987; DARAB et al., 1980; LINDSAY, 1979; SPOSITO, 1981; YOUNG and BACHE, 1985/.

There are theoretical limitations in the exact determination of ion activities in concentrated solutions /BERNHARD et al., 1986; MILLERO and SCHREIBER, 1982; SPOSITO, 1984/. However, a number of computerized models have been developed by applying empirical relationships describing the electrostatic interactions of ions to compute ion-pair concentrations and ion activities in soil solutions and extracts /ADAMS, 1974; AMACHER, 1984; BAHAM, 1984; CSILLAG and DARAB, 1985; MINKIN et al., 1977; PAKSHINA and RABOCHEV, 1986; PONIZOVSKY et al., 1985; SOKOLENKO, 1986/.

It has been shown that the electrostatic interactions influence the dissolution and precipitation of the sparingly soluble salts /$CaCO_3$, $CaSO_4$, $CaHPO_4$/ present in the soil or applied as fertilizers or amendments /BRESLER et al., 1982; DARAB et al., 1980; LINDSAY, 1979; SPOSITO, 1981/. It has also been proved that ion exchange processes between the solid and liquid phases of the soil are also affected by the electrostatic interactions of the ions in the solution /BRESLER et al., 1982; CSILLAG and DARAB, 1985; DARAB et al., 1980; SPOSITO, 1981/. When studying the interrelation between the soil solution and plant roots, these interactions have also been taken into account /ADAMS, 1974; KHASAWNEH, 1971; SPARKS, 1984/.

In many cases ion activities can be measured directly in soil solutions and aqueous extracts /AMACHER, 1984; DARAB et al., 1979; PONIZOVSKY et al., 1985/ or in soil suspensions /AMACHER, 1984; KRUPSKY et al., 1968; RÉDLY, 1977; SPARKS, 1984/. In addition, there have been attempts at "in situ" measurements of certain ions in wet soils by means of ion-selective electrodes /BISTRITSKAYA et al., 1981; ZYKINA, 1985/. Such measurements would make it possible to study the soil solution in a nearly natural state without shifting the equilibria between the soil phases. These methods are a promising way of showing the tendencies, but because of methodological difficulties, the interpretation of the data on absolute activity values is still the subject of discussion.

Several methods can be applied to separate the liquid phase of the soils, including the use of pressure or suction apparatus, a high-speed centrifuge, or the displacement of the soil solution by various organic solvents /e.g. ethanol, dioxane/ /DARAB et al., 1956; GILLMAN and BELL, 1978; KHASAWNEH and ADAMS, 1967; REITEMEIER, 1946; SKRINNIKOVA, 1977/. The concentrations of the different ions are influenced by the separation procedure, but very few data are available at present in the literature on the comparison of the different separation methods /ADAMS et al., 1980; ELKHATIB et al., 1986; REITEMEIER and RICHARDS, 1944; SATO et al., 1981/. Hardly any publications can be found on the energy state of separated soil solutions. The present work is an attempt to obtain more information on soil solution fractions with different energy states.

Materials and methods

In order to predict the actual concentration and chemical composition of the soil solution throughout the range of field moisture content, moisture fractions obtained from the soil at different moisture potentials /between pF ≃ 0 and pF ≃ 3.4/ were analysed. The soil samples were taken from the B_1 horizons of a soda solonchak-solonetz /Apaj/ and a shallow meadow solonetz /Hortobágy/, as well as from the A horizon of a chernozem soil /Debrecen/. The main soil characteristics are given in Table 1 and Fig. 1. These solonetz soils differ in salt content, texture and ESP /exchangeable sodium percentage/. The shape of the pF curves of these soils is similar, and in the low suction range /pF 0-2.3/ relatively small changes in the moisture content can be found. By contrast, in the case of the chernozem soil, which has favourable physical and water management properties, a wider range of moisture content was observed for the pF range studied /Fig. 1/.

Table 1

Main physical and chemical characteristics of the studied soils

Soil properties	Soda solonchak-solonetz /Apaj/	Shallow meadow solonetz /Hortobágy/	Chernozem soil /Debrecen/
pH (H_2O)	10.3	9.8	6.0
$CaCO_3$ content, %	16.3	1.7	0.1
Organic matter, %	0.8	1.0	3.1
Total soluble salts, %	0.60	0.24	0.09
Cation exchange capacity (CEC), me/100 g soil	17.1	26.1	28.3
Exchangeable sodium percentage (ESP)	78.1	47.6	2.0
Saturation percentage (SP)	38.7	43.3	43.7
Particle size < 0.002 mm, %	21.7	37.2	27.4
Bulk density, g/cm^3	1.59	1.70	1.22

In the case of salt affected soils , studies were made on changes caused by dilution in the concentration and chemistry of water soluble salts, while for the chernozem soil changes in the concentration of certain nutrient elements were also studied.
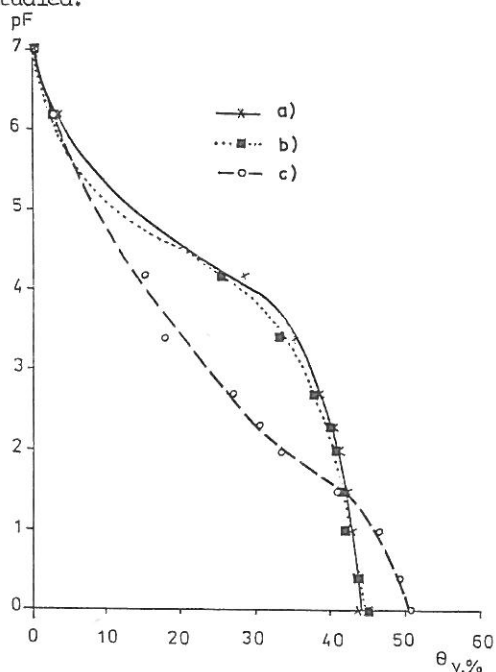

Fig. 1

pF curves of the studied soils. $\theta_{v.\%}$: Soil moisture content as volume percentage. a/ Soda solonchak-solonetz, Apaj; b/ Shallow meadow solonetz, Hortobágy; c/ Chernozem soil /Debrecen/

Air-dry samples of each soil /one kg each/ were moistened with deionized water to different pF values in the range between pF 3.4 and pF 0. Soil pastes having moisture contents higher than that of water-saturated soil /pF 0/ were also prepared from the solonchak-solonetz soil. /The highest water:soil ratio was about 0.5:1./ The wet soil samples were kept in airproof plastic vessels at room temperature and were stirred occasionally over a period of two weeks. After reaching equilibrium, the liquid phases were obtained by filtering for 48 hours with compressed air at 15 bar through cellophane membranes in pressure membrane apparatus. The exact moisture contents of the wet soil samples were measured by oven-dry method prior to pressure filtering. The solutions were analysed for pH, specific electrical conductivity /using a pipette-type micro-conductivity cell/ and ion concentrations: Na^+, K^+ /using a flame photometer/, Ca^{2+}, Mg^{2+} /using an atomic absorption spectrophotometer/, CO_3^{2-}, HCO_3^-, Cl^- /by means of alkalimetric and argentometric titration/, SO_4^{2-} /using the gravimetric method/ and NO_3^- /using distillation method/. Measurements were also made on the Na^+ and Cl^- activities in the case of the meadow solonetz soil and on Ca^{2+} and $Ca^{2+} + Mg^{2+}$ activities for the chernozem soil in the soil moisture fractions using ionselective electrodes.

660

The reproducibility of both the separation and the chemical analysis of the soil solutions was investigated on eight parallel samples for the solonchak-solonetz soil. /8 kg air-dry soil was wetted to pF 1.4, and was kept and stirred in a big airproof plastic vessel. After two weeks the wet soil was divided into eight portions and placed in eight pressure membrane apparatus, then filtered at a pressure of 15 bar./

For the solonchak-solonetz soil the sample with the highest moisture content /water:soil $\cong$ 0.5:1/ was also displaced with ethanol /by A. A. PONIZOVSKY, Institute of Soil Science and Photosynthesis, Puschino, the USSR/ and its chemical composition was compared with that obtained by the pressure membrane method.

The cation exchange capacity /CEC/, and the mobile /exchangeable + soluble/ Na^+ and Ca^{2+} were determined by the NH_4-acetate method from the original air-dry soil samples. /In the $CaCO_3$-containing solonchak-solonetz soil the mobile Ca^{2+} concentration could only be determined by the isotope dilution method./ The amounts of exchangeable Na^+ and Ca^{2+} in the soils at different moisture contents were obtained by subtracting the quantities of dissolved Na^+ and Ca^{2+} from the mobile Na^+ and Ca^{2+} concentrations.

In order to predict the electrostatic interactions of the ions in the soil solution in the field moisture range and also at higher moisture contents, the measured pH and ion concentration values of the solution fractions were used as the input data of a computer model based on the Bjerrum ion association theory and the Debye-Hückel theory /CSILLAG and DARAB, 1985/. With a knowledge of the thermodynamic dissociation constants of ion-pairs occurring in the liquid phase of these types of soils, and by calculating the ion activity coefficients from the ionic strength values of the solutions, the ion-pair concentrations and the activities of free hydrated ions were computed. The computed Na^+, Cl^-, Ca^{2+} and Ca^{2+} + Mg^{2+} activities were compared with those measured in the soil moisture fractions.

Results and discussion

The pressure membrane method makes it possible to obtain soil moisture fractions with a physically defined energy status. The extracted solutions are retained in the soil with suctions between pF 4.2 /wilting point; 15 bar/ and pF values in the range pF 3.4-0. /These soil solution fractions can thus be considered as solutions available to plants./ Most of the methods used at present to separate soil solutions /e.g. displacement with organic solvents/ do not have this advantage because the quantity and energy status of the moisture remaining in the soil are not known.

The reproducibility of the pressure membrane method was studied in the case of the solonchak-solonetz soil at pF 1.4 /Table 2/, and was found to be fairly good.

The chemical compositions of the displaced and pressure filtered soil solutions obtained from the solonchak-solonetz soil show fairly good agreement /Table 3/. However, further investigations are necessary using soil samples with lower moisture contents, in the range between pF 0 and 3.4.

In order to study the influence of the extracting pressure on the solution concentration, in the case of the solonchak-solonetz soil a comparison was made between the concentration and composition of the saturation extract and those of the liquid phase of the soil saturation paste obtained by filtering at a pressure of 15 bar /Table 4/. The latter is about twice as concentrated as the saturation extract /consequently its sodium adsorption ratio /SAR/ value is also significantly higher/.

Table 2

Error in the preparation and chemical analysis of moisture fractions extracted from the solonchak-solonetz soil at pF 1.4 (n = 8)

pH	Electrical conductivity, mS/cm	Ion concentration							Ion activity	
		Ca^{2+}	Mg^{2+}	Na^+	K^+	Alkalinity	SO_4^{2-}	Cl^-	Na^+	Cl^-
						me/l				
8.88	10.24	0.79	0.58	115.22	0.30	70.98	34.25	16.20	69.0	16.5
9.03	10.02	0.82	0.62	114.35	0.30	66.22	33.74	16.20	68.5	16.6
9.21	10.29	0.58	0.62	116.52	0.26	71.19	34.42	16.10	67.0	17.5
9.16	10.35	0.69	0.60	116.52	0.33	71.91	35.62	16.30	65.0	18.5
9.12	10.24	0.72	0.62	116.52	0.30	61.05	34.59	15.20	66.0	18.4
9.03	10.24	0.69	0.62	116.52	0.31	68.91	34.76	16.20	68.3	19.8
9.00	10.24	0.68	0.50	116.52	0.29	70.77	33.74	15.50	67.5	21.0
9.12	10.35	0.86	0.52	116.52	0.30	70.57	34.59	15.30	68.4	16.5
$\bar{x}$	9.07	10.25	0.73	0.58	116.09	0.30	68.95	34.46	15.87	67.46	18.10
s	0.10	0.10	0.09	0.05	0.84	0.02	3.66	0.61	0.46	1.39	1.66
CV	0.12	0.99	12.20	8.21	0.72	6.69	5.31	1.76	2.89	2.05	9.17
h	0.09	0.09	0.07	0.04	0.70	0.02	3.07	0.51	0.38	1.16	1.39

n = number of data; $\bar{x}$ = mean value; s = standard deviation; CV = coefficient of variation; h = confidence limit.

The chemical composition of soil solutions obtained by displacement with ethanol /A/ and by the pressure filtration method /B/

Me-thod	$\Theta_{w.\%}$	pH	Ca^{2+}	Mg^{2+}	Na^+	Alkal-inity	HCO_3^-	SO_4^{2-}	Cl^-
						me/l			
A.	45.0	9.05	0.42	0.42	84.60	48.50	44.00	26.00	13.80
B.	46.4	9.03	0.38	0.33	81.73	43.91	35.71	21.92	10.17

$\Theta_{w.\%}$ = soil moisture content as a weight percentage

Comparison of the liquid phases of soil saturation pastes /SP = 38.7/ extracted from the solonchak-solonetz soil using the PASTEUR-CHAMBERLAIN /A/ and pressure membrane /B/ apparatus

Pres-sure, bar	pH	EC, mS/cm	Ca^{2+}	Mg^{2+}	Na^+	K^+	Alkal-inity	HCO_3^-	SO_4^{2-}	Cl^-	SAR
							me/l				
			A. PASTEUR-CHAMBERLAIN apparatus								
4-5	9.22	4.58	0.54	0.07	44.35	0.24	22.75	19.85	10.70	6.50	80
			B. Pressure membrane apparatus								
15	8.96	9.12	0.47	0.40	92.93	1.25	50.18	40.53	24.65	11.19	141

$$SAR = \sqrt{\frac{Na^+}{Ca^{2+} + Mg^{2+}}} \quad (mmol/l)^{1/2}$$

In order to investigate the effect of dilution on the concentration and composition of the soil solution, the concentrations measured for the dominant ions in the three soils are plotted against soil moisture content, i.e. against the corresponding pF values /Fig. 2/. With decreasing moisture content /i.e. with increasing suction/, the solutions extracted are more and more strongly retained and concentrated. This tendency is also shown by the electrical conductivity of the solutions /Table 5/.

The ion concentrations in the extracts of the solonchak-solonetz soil /Apaj/ are higher than those of the meadow solonetz soil /Hortobágy/, but their ion composition is similar: in both soils Na_2CO_3 and $NaHCO_3$ are the dominant salts. Because of the high alkalinity of these soils, the Ca^{2+} and Mg^{2+} concentrations are very low, so they are not represented on the figure. The increase in ion concentrations with decreasing moisture content is more pronounced at moisture contents corresponding to higher pF values and depends on the ion in question: highest increase is observed in the case of the prevailing Na^+ ion.
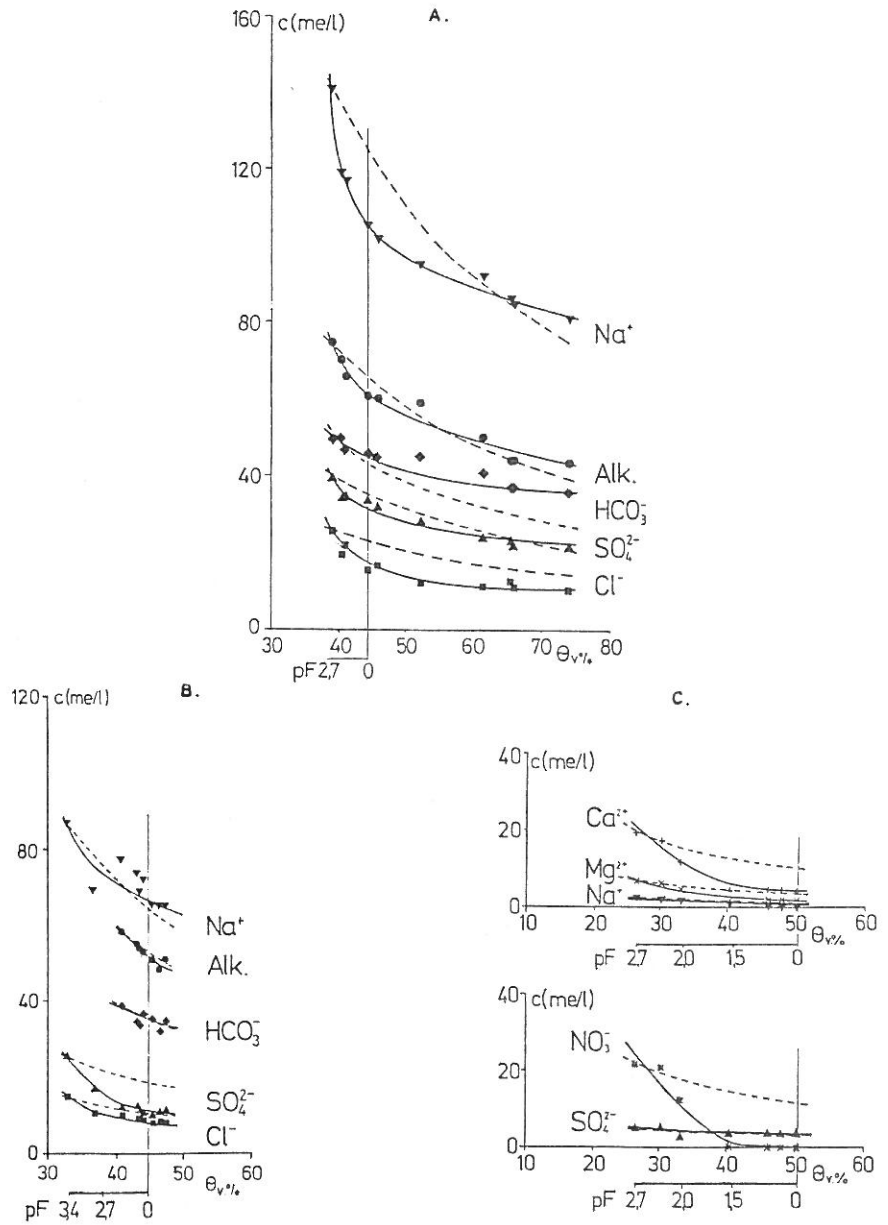
Fig. 2

Measured ion concentrations as functions of soil moisture content /solid
lines/, and the curves of the inverse relation of simple dilution /dashed
lines/. A. Soda solonchak-solonetz /Apaj/; B. Shallow meadow solonetz /Hor-
tobágy/; C. Chernozem soil /Debrecen/. $\theta_{v\%}$: soil moisture content as
volume percentage

Table 5
Specific electrical conductivity values in certain
moisture fractions of the solonchak-solonetz soil

pF range	$\Theta_{v.\%}$	EC mS/cm
2.7–4.2	39.1	12.84
0–4.2	44.5	10.12
–	73.8	7.52

$\Theta_{v.\%}$ = soil moisture content as volume percentage

     It is clear that the concentration of the soil solution is significant-
ly less for the chernozem soil than for the salt affected soils, and that
Ca^{2+} and Mg^{2+} salts /mainly $Ca(NO_3)_2$/ are present in relatively higher con-
centration. The field moisture range studied /between pF 0 and 2.6/ is much
wider than for the solonetz soils, and the rapid increase in Ca^{2+} and NO_3^-
concentrations in the solution fractions at above pF 1.5 is remarkable.
     In the case of all three soils and for every ion, the shape of the con-
centration curves differs from the inverse relations of simple dilution /Fig.
2/. This dissimilarity can be explained by changes caused by dilution in the
physico-chemical processes between the solid and liquid phases of the soil.
     In the studied wide moisture range of the solonchak-solonetz soil,
when evaluating the quantity of dissolved salts as a function of soil mois-
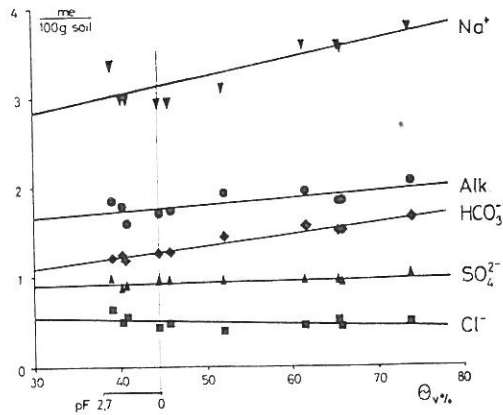ture content /Fig. 3/, it is found that:

Fig. 3
The quantities of ions of dissolved salts /expressed in me/100 g oven-dry
soil/ as functions of soil moisture content in the soda solonchak-solonetz
soil. $\Theta_{v.\%}$: See Fig. 1

- Na^+ and HCO_3^- show a slight increase with the increase of moisture content. The reason for this is that $NaHCO_3$, the dominant salt in the solon-chak-solonetz soil, is a relatively less soluble salt, the dissolved quantity of which increases with moisture content.

- CO_3^{2-}, SO_4^{2-} and Cl^- are present in this soil in the form of readily soluble sodium salts; they are dissolved even at low moisture content, their quantity dissolved shows practically no change with moisture content.

- If the examinations are restricted to the narrow moisture range between pF 0 and 3.5, changes in the quantity of dissolved salts are negligible in the case of both solonetz soils.

In salt affected soils the equilibria between the phases of the soil may be influenced by the electrostatic interactions of the ions present in the liquid phase. These interactions are stronger in the case of divalent
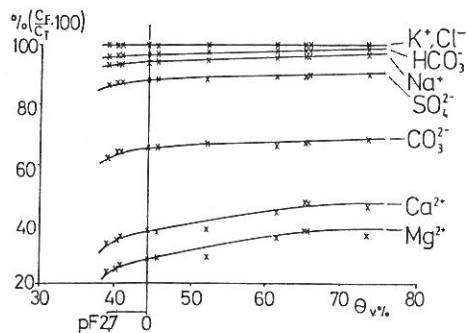

Fig. 4

Free ion concentrations (c_F) in the percentage of total, measured ion concentrations (c_T) plotted against soil moisture content in the soda solonchak-solonetz soil. $\theta_{v.\%}$: See Fig. 1

c_F /at Na^+, e.g. $c_{F_{Na^+}} = c_{T_{Na^+}} - \Sigma c_{NaCO_3^-} + c_{NaHCO_3^0} + c_{NaSO_4^-}/$ computed with the model published by CSILLAG and DARAB /1985/.
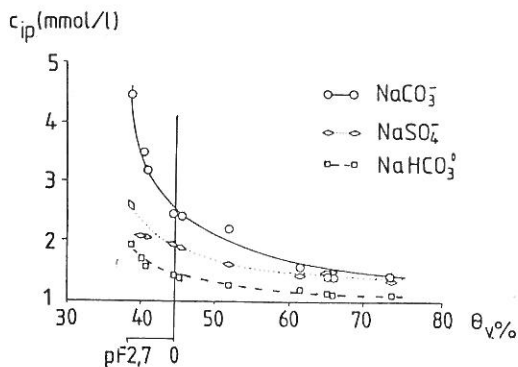

Fig. 5

Dependence of ion association on soil moisture content in the soda solonchak-solonetz soil. $\theta_{v.\%}$: See Fig. 1.; c_{ip}: ion-pair concentration, computed with the model published by CSILLAG and DARAB /1985/

666

ions than for monovalent ones. Therefore, the free ion concentrations expressed as a percentage of the measured values are much lower for the divalent ions /Fig. 4/. As it is represented for the solonchak-solonetz soil, the decrease in this value with the decrease in moisture content is also more pronounced for divalent ions, as a consequence of their higher ability for ion-pairing.

Due to the high concentration of Na^+ in the liquid phase of the solonchak-solonetz soil, ion-pairs containing Na^+ / $NaCO_3^-$, $NaSO_4^-$, $NaHCO_3^0$/ dominate among the ion-pairs. With a decrease in soil moisture content, the short-range electrostatic interactions of the ions, and consequently, the ion-pair concentrations, increase significantly /Fig. 5/. The concentration of $NaCO_3^-$, for example, is nearly twice as high at pF 2.7 than at pF 0.

Using saturation extracts of solonchak and solonetz soils as an example it was previously shown /CSILLAG and DARAB, 1985/ that, as a consequence of the short- and long-range electrostatic interactions of ions, the activities of free hydrated ions were significantly less than measured ion concentrations. This tendency is more pronounced in the soil solution, especially in salt affected soils. The difference increases with decreasing moisture content because in a more concentrated solution the electrostatic interactions are stronger /Fig. 6A/. This increase is especially great in moisture fractions obtained at higher pF values in the case of the prevailing Na^+ ion and also of the divalent anions.
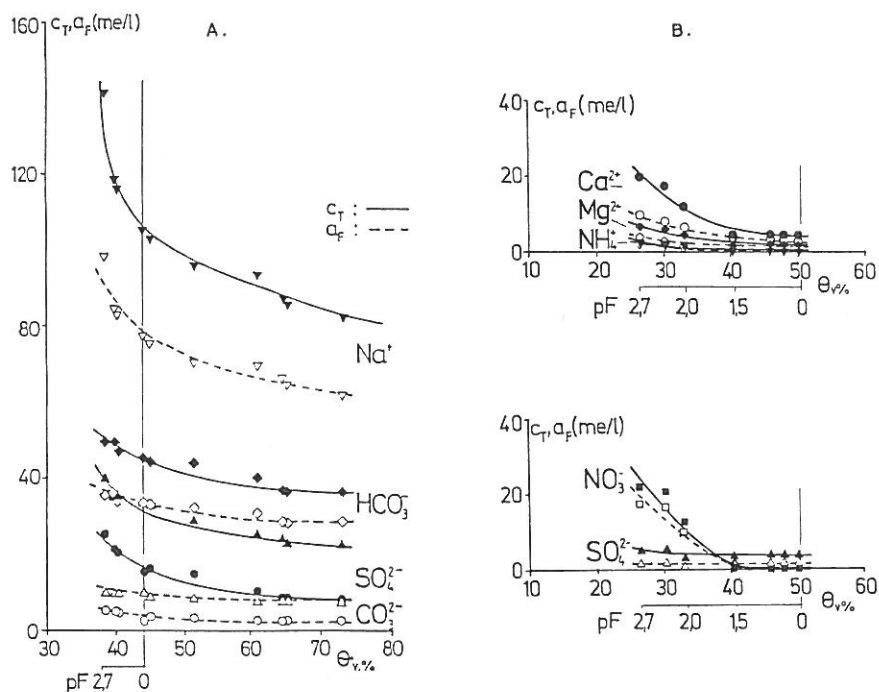

Fig. 6

The effect of the short- and long-range electrostatic interactions of ions as a function of soil moisture content in the soda solonchak-solonetz soil /A/ and chernozem soil /B/. c_T: measured, total ion concentration; a_F: free ion activity /computed with the model published by CSILLAG and DARAB /1985//. $\Theta_{v.\%}$: See Fig. 1.

Partly as a consequence of the different ability of mono- and divalent ions to form ion-pairs /comp. Fig. 4/ and, partly due to their differing activity coefficients, their ratio in the solution is really higher, and increases much more with decreasing soil moisture content than expected from the different solubilities of their salts /Fig. 7/. The sodium adsorption ra-
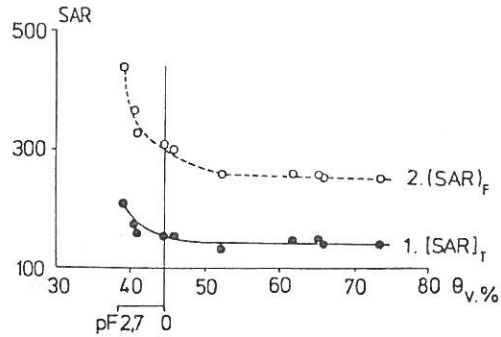

Fig. 7

The effects of electrostatic interactions of ions on the sodium adsorption ratio of the soil solution in the soda solonchak-solonetz soil. SAR: See Table 4.; $[SAR]_m$: SAR calculated from measured cation concentrations; $(SAR)_F$: SAR calculated from free cation activities. $\Theta_{v.\%}$: See Fig. 1
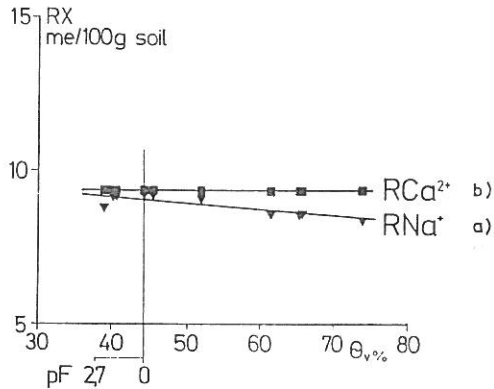

Fig. 8

The amounts of exchangeable Na^+ and Ca^{2+} as functions of soil moisture content in the soda solonchak-solonetz soil. a/ Determined with the NH_4-acetate method; b/ determined with the isotope dilution method. $\Theta_{v.\%}$: See Fig. 1

tio /SAR/ of the soil solution is influenced by the electrostatic interactions of the ions. Higher values are obtained if it is calculated from free cation activities than are expected from the cation concentrations measured. This difference increases with decreasing moisture content. This means that the true Na^+ /divalent cation ratio is higher in soil solutions at field moisture content and when the electrostatic interactions of the ions are considered than is to be expected from the analyses of the more diluted soil-water extracts.

668

The increase in the absolute and relative sodium concentrations of the soil solution with decreasing soil moisture content shifts ion exchange processes in favour of sodium /Fig. 8/, thus promoting solonetz-forming processes.

For the chernozem soil /Fig. 6B/ the concentration-activity difference is the highest for the prevailing divalent ion Ca^{2+} /at pF 2.6 it is about 10 me/l/. This is in agreement with literature data /ADAMS, 1974; KHASAWNEH, 1971/ indicating that when evaluating the interactions between the soil solution and plant roots, the activities and not the concentrations of the nutrient ions should be taken into account.

The activity values of Na^+ and Cl^- /in the case of the meadow solonetz soil/, and of Ca^{2+} and $Ca^{2+} + Mg^{2+}$ /in the case of the chernozem soil/ were also measured in the soil moisture fractions using ion-selective electrodes. A similarly good agreement with the computed activities in the soil solutions /Table 6/ was obtained, as previously in more than a hundred soil saturation extracts /DARAB et al., 1979/. In the case of Cl^- the concentration and activity values are the same within the error of the determination /Table 2/. The differences between the computed and measured mean pX values /negative logarithms of ion activities/ are within the confidence limit of routine pH determinations for soil solutions and aqueous soil extracts /<0.1 pX/ /Table 6/. It would appear that the model presented by CSILLAG and DARAB /1985/ is suitable for the determination of SO_4^{2-}, CO_3^{2-} and HCO_3^- activities, which are important in soil chemical processes, but cannot be measured directly.

Conclusions

The change observed in the concentration and composition of the soil solution with a decrease in soil moisture content in salt affected soils results in the following:

- An increase in the concentration leads to an increase in the osmotic potential of the soil moisture, so the water uptake of the plants will be hindered and the moisture reserves available to the plants become limited;

- With the absolute and relative increase in sodium ion concentration in the soil solution, the ESP value of the soil increases. The electrostatic interactions of the ions further increase this tendency, creating less favourable conditions with respect to the shift of ion exchange processes in favour of sodium;

- The increase in sodium saturation may exert an unfavourable influence on soil physical properties /soil structure deteriorations, swelling, etc./ and on water management characteristics /increase in moisture retention, decrease in water and ion transport coefficients/;

- By contrast, irrigation with good quality irrigation water leads to beneficial changes in the actual concentration and composition of the soil solution.

Based on the analysis of the soil solutions of a chernozem soil it was found that:

- The concentrations of Ca^{2+} and NO_3^- ions at field moisture content are much higher than is to be expected from the analysis of more diluted extracts;

- Therefore, when evaluating the quantities of these ions available for plants, the strengthening of electrostatic interactions with the decrease in soil moisture content must be taken into account.

Table 6

Measured and computed free ion activities (mol/1·10³) and the mean values of the negative logarithms of free ion activities (mol/1) in moisture fractions obtained from the meadow solonetz soil /Hortobágy/ and chernozem soil /Debrecen/ at different moisture potentials

Meadow solonetz soil /Hortobágy/

θ_{v}%	pF	Na⁺ Measured	Na⁺ Computed	Cl⁻ Measured	Cl⁻ Computed
32.7	3.5	66.0	64.5	16.0	11.1
36.7	2.9	39.5	51.7	11.0	7.8
40.9	1.8	46.5	57.5	9.5	7.5
43.3	0.8	48.0	55.0	9.0	6.6
43.6	0.6	48.2	51.3	9.0	6.6
44.2	0.3	50.0	54.0	8.5	6.6
45.5		48.0	49.4	6.9	6.2
47.5		47.0	49.3	7.5	6.2
46.6		49.0	49.4	6.6	6.5
x̄		49.1	53.6	9.3	7.2
sd		1.6		0.5	
t		2.8		4.4	
px̄		1.31	1.27	2.05	2.15
d		0.04		0.10	

Chernozem soil /Debrecen/

θ_{v}%	pF	Ca²⁺ Measured	Ca²⁺ Computed	Ca²⁺ + Mg²⁺ Measured	Ca²⁺ + Mg²⁺ Computed
26.5	2.6	4.7	4.6	6.8	6.2
30.3	2.3	4.1	4.1	6.5	5.5
33.1	2.1	3.5	3.1	4.9	4.3
40.4	1.6	1.4	1.3	1.9	1.8
46.0	1.0	1.2	1.3	2.0	1.8
48.0	0.7	1.2	1.3	1.8	1.7
50.2	0.1	1.2	1.2	1.9	1.7
x̄		2.5	2.4	3.7	3.3
sd		0.1		0.1	
t		1.3		3.2	
px̄		2.68	2.69	2.50	2.55
d		0.01		0.05	

at n = 9   t5% = 2.31;   t1% = 3.36;   t0.1% = 5.04

at n = 7   t5% = 2.45;   t1% = 3.71

Free ion activities are computed with the model published by CSILLAG and DARAB /1985/.
d: differences between measured and computed mean pX values;
θ_{v}%: soil moisture content as volume percentage.

Summary

In order to predict the actual concentration and chemical composition of the soil solution over the entire range of field soil moisture content, the moisture fractions of a chernozem soil and two salt affected soils /solonchak-solonetz and shallow meadow solonetz/ were extracted and analysed. The separation of the liquid phases was carried out in pressure membrane apparatus by filtering at 15 bar through cellophane membranes from the wet soils moistened to different degrees according to the pF curve /between pF≃ 0 and ≈3.4/. By this method, soil moisture fractions with a definite energy status can be obtained: they are retained in the soil with suctions ranging between pF 4.2 /15 bar/ and the pF value in question.

In the case of the solonchak-solonetz soil at pF 1.4, the reproducibility of the separation and the chemical analysis of the soil moisture fractions was fairly good. The concentration and chemical composition of displaced and pressure filtered soil solutions were compared, as were those of the soil saturation extract /obtained at 4-5 bar/ and the pressure filtered /15 bar/ solution.

It was shown that the change in the quantity of dissolved salts was negligible in the limited moisture range between pF 0-3.5, but at higher moisture contents the quantity of dissolved $NaHCO_3$ somewhat increased, With a decrease in soil moisture content /i.e. with increasing suction/, the concentrations of the ions and the degree of electrostatic interactions in the solution increase: the dependence of ion-pair concentrations and free ion activities from soil moisture content were represented. It was proved that the computed free ion activity values agreed well with those measured by Na^+, Cl^-, Ca^{2+} and $Ca^{2+} + Mg^{2+}$ ion-selective electrodes in the soil moisture fractions.

As a consequence of the electrostatic interactions of ions, the true SAR value in the moisture fractions of the salt affected soils is higher and increases much more with decreasing soil moisture content than is to be expected from the cation concentrations measured. This means that the sodium saturation of salt affected soils is really higher than expected from an analysis of dilute aqueous soil extracts.

The ion concentrations of the moisture fractions of the chernozem soil were much lower than those of salt affected soils. The tendency for Ca^{2+} and NO_3^- concentrations to increase with a decrease in soil moisture content was similar. The role of the electrostatic interactions of ions cannot be ignored even in the case of soil solutions of non-salt affected soils.

References

ADAMS, F., 1974. Soil solution. In: The Plant Root and Its Environment. /Ed.: CARSON, E. W./. 441-481. University Press of Virginia. Charlottesville. USA.

ADAMS, F. et al., 1980. A comparison of column-displacement and centrifuge methods for obtaining soil solutions. Soil Sci. Soc. Am. J. 44. 733--735.

AMACHER, M. C., 1984. Determination of ionic activities in soil solutions and suspensions: principal limitations. Soil Sci. Soc. Am. J. 48. 519-524.

BAHAM, J., 1984. Prediction of ion activities in soil solutions: computer equilibrium modeling. Soil Sci. Soc. Am. J. 48. 525-531.

BARON, V. A. and TOKAREV, N. I., 1979. Computation of equilibrium composition of the soil solution and the solid phase of salts from the data of aqueous extracts.) [In Russian.] Pochvovedenie. /4/ 37-45.

BERNHARD, M., BRINCKMAN, F. E. and SADLER, P. J. /Eds./, 1986. The Importance of Chemical "Speciation" in Environmental Processes. Springer-Verlag. Berlin.

BISTRITSKAYA, T. L., VOLKOVA, V. V. and SNAKIN, V. V., 1981. (Soil solutions in chernozems and grey forest soils.)[In Russian.] Nauka. Moscow.

BOHN, H. L., McNEAL, B. L. and O'CONNOR, G. A., 1985. Soil Chemistry. 2nd edition. J. Wiley and Sons, New York.

BRESLER, E., McNEAL, B. L. and CARTER, D. L., 1982. Saline and Sodic Soils. Principles-Dynamics-Modeling. Springer-Verlag. Berlin.

CSILLAG, J., 1988. The chemical composition of the soil solution extracted from solonetz soils by pressure membrane method. Proceedings, Int. Symp. on Solonetz Soils. Problems, Properties , Utilisation. 256-261. Osijek, Yugoslavia.

CSILLAG, J. and DARAB, K., 1985. (New results in the study of the electrostatic interactions of ions in soil saturation extracts.)[In Hungarian.] Agrokémia és Talajtan. 34. 27-52.

CSILLAG, J. and KAPOOR, B. S., 1987. The importance of the study of chemical speciation in natural waters and soil solutions. Clay Research. 6. /2./ /In press/.

DARAB, K., CSILLAG, J. and PINTÉR, I., 1980. Studies on the ion composition of salt solutions and of saturation extracts of salt affected soils. Geoderma. 23. 95-111.

DARAB, K., KISS, K. and MEDVEGY, J., 1956.(Methods for the analysis of the soil solution on alkali soils of the Trans-Tisza Region.)[In Hungarian.] Agrokémia és Talajtan. 5. 395-404.

DARAB, K., RÉDLY, M. and CSILLAG, J., 1979. (Ion activity measurements and calculations in the saturation extracts of salt affected soils.)[In Hungarian.] Agrokémia és Talajtan. 28. 399-410.

ELKHATIB, E. A. et al., 1986. A centrifuge method for obtaining soil solution using an immiscible liquid. Soil Sci. Soc. Am. J. 50. 297-299.

GILLMAN, G. P. and BELL, L. C., 1978. Soil solution studies on weathered soils from tropical North Queensland. Aust. J. Soil Res. 16. 67-77.

International Source-Book on Irrigation and Drainage of Arid Lands in Relation to Salinity and Alkalinity, 1967. FAO/UNESCO.

JURINAK, J. J., 1984. Salt affected soils: Thermodynamic aspects of the soil solution. In: Soil salinity under irrigation. /Eds.: SHAINBERG, I. and SHALHEVET, J./. 15-31. Springer-Verlag. Berlin.

KHASAWNEH,F.E., 1971. Solution ion activity and plant growth. Soil Sci. Soc. Amer. Proc. 35. 426-436.

KHASAWNEH,F. E. and ADAMS, F., 1967. Effect of dilution on calcium and potassium contents of soil solutions. Soil Sci. Soc. Amer. Proc. 31. 172-176.

KRAPSKY, N. K., ALEXANDROVA, A. M. and LAPKINA, Yu. I., 1968. (Dependence of sodium ion activity in the soil on its moistening degree.) [In Russian.] Pochvovedenie. /3/ 70-80.

LINDSAY, W. L., 1979. Chemical equilibria in soils. J. Wiley and Sons. New York.

LINEHAN, D. J., SINCLAIR, A. H. and MITCHELL, M. C., 1985. Mobilisation of Cu, Mn and Zn in the soil solutions of barley rhizospheres. Plant and Soil. 86. 147-149.

MILLERO, F. J. and SCHREIBER, D. R., 1982. Use of the ion-pairing model to estimate activity coefficients of the ionic components of natural waters. Am. J. Sci. 282. 1508-1540.

MINKIN, M. B., ENDOVITSKY, A. P. and LEVCHENKO, V. M., 1977.(Ion associations in soil solutions.)[In Russian.] Pochvovedenie./2/ 49-58.

NÉMETH, T. and KÁDÁR, I., 1987. (Accumulation of sulphate and "total salt" content in a soil profile as affected by 11-year NPK fertilization.)

[In Hungarian.] In: Chemical products in agriculture. '87 Conference. Keszthely, 1987. /Ed.: BLASKE, Z./. 95-100. Keszthely.

PAKSHINA, S. M. and RABOCHEV, G. I., 1986. (Calculation of ion activity in soil solutions and mineralized waters.) [In Russian.] Pochvovedenie. /11/ 96-104.

PONIZOVSKY, A. A., MIRONENKO, E. V. and PACHEPSKY, Ya. A., 1985. Calculations of ion activities in soil solutions from humic horizons. Geoderma. 36. 37-44.

RÉDLY, M., 1977. Modern methods for the determination of total concentration and ionic composition of the water soluble salt content of soils. In: Proc. Indo-Hungarian Seminar on the Management of Salt Affected Soils. 71-84. C.S.S.R.I. Karnal, India.

RÉDLY, M. and DARAB, K., 1981. The evaluation of physico-chemical processes from the point of view of alkali soil amelioration. Agrokémia és Talajtan. 30. Suppl. 178-188.

REITEMEIER, R. F., 1946. Effect of moisture content on the dissolved and exchangeable ions of soils of arid regions. Soil Sci. 61. 195-214.

REITEMEIER, R. F. and RICHARDS, L. A., 1944. Reliability of the pressure-membrane method for extraction of soil solution. Soil Sci. 57. 119-135.

SATO, S. et al., 1981. Comparative studies on the chemical composition of soil solution in land used for various purposes. 2. Relationships between the pH of the soil solution and the methods for separating the soil solution. Memoirs of the Faculty of Agriculture, Hokkaido University. Sapporo, Japan. 12. 211-221.

SHAINBERG, I., 1984. The effect of electrolyte concentration on the hydraulic properties of sodic soils. In: Soil Salinity Under Irrigation. /Eds.: SHAINBERG, I. and SHALHEVET, J./ 49-64. Springer-Verlag. Berlin.

SKRINNIKOVA, I. N., 1977. (Methods for the investigation of the chemical composition of the liquid phase of soil.)[In Russian.] In: Methods of steady-state study of soils. /Eds.: Rode, A. A. et al./ 3-40. Izd. Nauka. Moscow.

SOKOLENKO, E. A. /Ed./, 1986. Water and Salt Regimes of Soils: Modeling and Management. A. A. Balkema. Rotterdam.

SPARKS, D. L., 1984. Ion activities: an historical and theoretical overview. Soil Sci. Soc. Am. J. 48. 514-518.

SPOSITO, G., 1981. The Thermodynamics of Soil Solutions. Clarendon Press. Oxford.

SPOSITO, G., 1984. The future of an illusion: ion activities in soil solutions. Soil Sci. Soc. Am. J. 48. 531-536.

ULRICH, B. and KHANNA, P. K., 1972. Description and dissolution of salts from soils as a function of soil:water ratio. Soil Sci. 114. 250-253.

VAN DEN ENDE, J., 1968. Analysis of greenhouse soils by means of aqueous extracts. In: Proc. of the VIth Colloquium of the International Potash Institute, Florence, Italy. 246-255. IPI. Berne.

VÁRALLYAY, G., 1977. Moisture status and flow phenomena in salt affected soils. In: Proc. Indo-Hungarian Seminar on the Management of Salt Affected Soils. 85-102. C.S.S.R.I. Karnal. India.

ZYKINA, G. K., 1985. (Determination of the ionic composition of soil solutions using ion-selective electrodes.) [In Russian.] Pochvovedenie. /4/ 104-107.

YOUNG, S. D. and BACHE, B. W., 1985. Aluminium-organic complexation: formation constants and a speciation model for the soil solution. J. Soil Sci. 36. 261-269.