CATION-EXCHANGE CHARACTERISTICS OF WHEAT, BARLEY AND PEA DEPENDING ON THE OSMOTIC PRESSURE IN NUTRIENT SOLUTIONS OF LOW pH

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Summary. In water cultures experiment with wheat, barley and pea we studied the influence of the osmotic pressure in nutrient solutions of low pH (pH 4.5) on the content of H⁺, Ca²⁺, Mg²⁺ and K⁺ ions in water-soluble and exchange-adsorbed states and cation-exchange capacity of the above ground mass. The results obtained showed that the osmotic pressure is determinant for the changes in the cation content and also has a significant effect on the cation-exchange properties of plant tissues. The increase of the osmotic pressure in the range of 0–0.52 MPa decreased H⁺ ions and enhanced the bases content and the cation-exchange capacity of the above ground mass. The low pH of the nutrient solutions increased the share of the strongly acidic compounds in the tissues, which depended on the acidic sensitivity or tolerance of the plants.

Key words: barley, cation-exchange characteristics, nutrient solution, osmotic pressure, pea, pH, wheat

Introduction

The osmotic pressure of the nutrient substrate unites the two basic factors – salt concentration and water state that determine the normal level of the biochemical and physiological processes in plants and form the plant production (Hewith, 1966; Fedorov and Vahmistrov, 1980; Lutge and Higinbottom, 1984; Lazarov et al., 2001). In previous studies we established an osmotic pressure about 0.1 MPa, for which maximum production was obtained from cereals and leguminous plants grown on

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nutrient solutions at pH 5.5 and 4.5 (Ganev and Arsova, 1991; Arsova, 2001). This fact expanded the range of the osmotic optimum to a higher acidity of the nutrient solution, at which the balanced ion-exchange of the roots was disturbed and demonstrated that the osmotic pressure was determinant for the biomass formation from both the acidic sensitive and tolerant plants.

The mineral nutrition of plants is connected with ion-exchange processes of roots and depends on the pH of the nutrient medium. The diverse ionic groups of the biochemical structures in plant tissues participate in the ion exchange with nutrient substrate depending on its acidity and show a behavior of strongly acidic structures (polyuronic and nucleic acids) and weakly acidic structures (proteins). The specific character of ionization of the different compounds in plant tissues is expressed in the relative share of the strongly and weakly acidic positions in the cation-exchange capacity of the tissues. The acidic sensitivity of the plants is connected with the increase of the capacity of strongly acidic structures, while its decrease determines the plant tolerance (Ganev and Kalichkova, 1992).

We were interested in studying the physico-chemical properties of plant tissues as affected by the osmotic pressure in nutrient solutions of low pH. The experiment carried out with cereals and leguminous plants grown on nutrient solutions at pH 4.5 (Arsova, 2001) was used to continue the investigations in this aspect.

The aim of the present work was to study the effect of increasing osmotic pressure in nutrient solutions of low pH on the cation content and cation-exchange capacity of the above ground mass from wheat, barley and pea.

Material and methods

Plant material was taken from the water cultures experiment carried out according to the following scheme. After germination seeds of wheat, pea and barley were wrapped up by ten in rolls of filter paper in three replications and put into Erlenmaeyer flasks with distilled water for 2–3 days. The water was replaced by 200cm³ of nutrient solutions with different osmotic pressure and the only one variant was with distilled water. pH of the solutions was adjusted by a potentiometer to pH 4.5. The nutrient solutions had the following chemical composition and osmotic pressure:

Nutrient salts	I solution	solution II solution	
		mequ.l ⁻¹	
KNO ₃	4.0	12.0	60.0
$Ca(NO_3)_2$	2.0	6.0	30.0
KH ₂ PO ₄	1.0	3.0	15.0
$MgSO_4$	1.0	3.0	15.0
P, MPa	0.03	0.1	0.52

The solutions were a modification for the balanced solution of Hogland-Arnon (Hewith, 1966). The different osmotic pressure was achieved on the basis of a proportional increase in salt concentration, while the ionic ratios in the nutrient solutions were retained. The nitrogen was in the NO₃ form and the selected range of varying the osmotic pressure included the hypoosmotic and hyperosmotic conditions (0.0–0.52 MPa). For 20 days the nutrient solutions were replaced daily and adjusted by potentiometer to pH 4.5. The above ground mass was dried and ground.

The content of H⁺, Ca^{2+} , Mg^2 and K⁺ ions and the cation-exchange capacity of the strongly acidic (CEC_{SA}) and weakly acidic (CEC_A) ion-exchange structures were determined by using the following analytical methods.

Plant sample of 1 g was saturated with 3 M glycerol, which was the most appropriate dissolving agent for mineral and organic salts and acids in tissues and extracted completely the cations in water-soluble state. In the filtrate H⁺ ions were determined by titration with 0.04 N NaOH. In aliquot parts of this filtrate Ca^{2+} and Mg^{2+} ions were determined complexometrically by titration with 0.02 N EDTA and K⁺ ions – by flame spectrophotometry method. The cations in exchange-adsorbed state were desorbed from the same plant sample with 0.5 N NaCl. In aliquot parts of the filtrate Ca^{2+} and Mg^{2+} ions were determined by titration with 0.01 N EDTA and K⁺ ions – spectrophotometrically. After subsequent saturation of the sample with mixed buffer solution of 0.5 N Na-acetate and 0.2 N Na-maleinate (pH 8.2) the exchange-adsorbed H⁺ ions were determined in the filtrate acidimetrically by titration with 0.04 N NaOH (Ganev and Arsova, 1982).

The different biochemical compounds in plant tissues react in the cation exchange as strongly acidic and weakly acidic structures depending on the degree of ionization of their H⁺ ions. The capacity values of the ion-exchange structures in plant tissues were determined on the principle of adsorption of calcium indicator ions on the strongly acidic charges (ionic groups of polyuronic, nucleic acids, etc.) and of the hydrogen indicator ions on the weakly acidic charges (proteins). For this purpose the plant sample of 1 g was boiled in 100 ml 0.5 N NaCl to set all acidic positions in Na-form. After that the sample was saturated with mixed buffer solution of 0.2 N calcium acetate and 0.2 N calcium-lactate (pH 5.0). Ca²⁺ and H⁺ ions were desorbed with mixed buffer solution of 0.4N sodium acetate and 0.2 N sodium maleinate (pH 8.2). In the filtrate H⁺ ions were determined acidimetrically by titration with 0.02 N NaOH and Ca²⁺ ions complexometrically by titration with 0.01 N EDTA. The capacity values of the weakly acidic and strongly acidic ion-exchange structures were calculated on the base of the H⁺ and Ca²⁺ content, respectively (Ganev and Arsova, 1989).

Results and discussion

The influence of the osmotic pressure of the solutions on plant productivity is a summary effect from its impact upon the physico-chemical parameters.

Table 1 presents the content of cations in water-soluble and exchange-adsorbed state in the above ground mass of wheat, pea and barley depending on the osmotic pressure in nutrient solutions at pH 4.5.

Table 1. Content of cations in water-soluble and exchange-adsorbed state in the tissues of wheat, pea and barley depending on the osmotic pressure (P, MPa) in nutrient solutions of pH 4.5 (Values are given as mean average from three replications)

	H^+	Ca^{2+}	Mg^{2+}	K^+	Σ	H^+	Ca ²⁺	Mg^{2+}	\mathbf{K}^+	CEC
P, MPa	in water-soluble state in exchange-adsorbed state									
	cmol ⁺ .kg ⁻¹					cmol ⁺ .kg ⁻¹				
					Wheat					
0.00	58.4	24.0	2.1	85.9	170.4	12.2	21.0	3.1	1.5	37.8
0.03	45.2	38.0	2.5	146.3	205.0	10.4	23.5	3.3	3.4	40.6
0.10	41.2	41.0	2.6	172.3	257.1	9.8	28.5	3.5	3.8	45.6
0.52	40.3	52.0	3.0	240.3	335.6	8.6	31.6	3.7	4.4	48.3
					Pea					
0.00	62.6	38.5	1.5	50.6	153.2	16.8	28.5	1.8	1.0	48.1
0.03	58.4	45.8	1.6	115.1	220.9	13.6	32.8	1.8	1.4	49.6
0.10	56.3	50.6	1.8	140.3	249.0	10.5	38.9	1.9	1.6	52.9
0.52	52.5	54.6	2.0	230.2	339.3	8.6	42.3	2.3	2.1	55.3
Barley										
0.00	52.8	42.0	2.2	76.7	173.7	16.0	22.3	1.8	1.5	41.6
0.03	45.6	46.4	2.5	115.1	245.6	14.6	25.4	2.1	1.9	44.0
0.10	41.2	48.5	2.7	188.5	280.9	13.8	28.9	2.6	2.7	48.0
0.52	39.6	51.5	3.1	232.5	326.7	12.6	30.9	2.9	3.9	50.3
LSD 1%	2.15	2.40	0.22	3.27		1.20	0.75	0.35	0.27	
5%	1.31	1.65	0.12	2.02		0.87	0.49	0.25	0.15	

The amount of the hydrogen ions in water-soluble state for the three plants decreases with the rise of the osmotic pressure. H⁺ ions are released from the carboxyl groups of organic acids (RCOOH). This means that their quantity is diminished as well. At the same time the electrolytic content (S - summary content of the cations in water-soluble state) increases to a much higher extent, mainly regarding the potassium ions. It could be noticed that the ionic ratios in the electrolytic phase are changed significantly with the rise of osmotic pressure of the solutions. For instance, the ratio between the monovalent ions of potassium and hydrogen increases as follows: K⁺/H⁺ (wheat) = 1.47 (0.0 MPa); 3.23 (0.03 MPa); 4.18 (0.1 MPa); 5.96 (0.52 MPa); K⁺/H⁺ (barley) = 1.45 (0.0 MPa); 2.52 (0.03 MPa); 4.57 (0.1 MPa); 5.87 (0.52 MPa); K⁺/H⁺ (pea) = 0.80 (0.0 MPa); 1.97 (0.03 MPa); 2.50 (0.1 MPa); 4.40 (0.52 MPa).

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The smallest changes were observed for the pea which confirms the fact that leguminous crops possess a greater capability for regulating the balance of their mineral composition. The rise of the salt concentration in liquid phase of plant tissues with the increase of the solutions' osmotic pressure is a result of the selective mechanisms of ion uptake (Fedorov and Vahmistrov, 1980).

Thus, the higher osmotic pressure of the solution activates the neutralization with basic cations of the organic acids. It is very probable that this process could cause an increase of the internal osmotic pressure in the phloem sap of plant tissues, which varies within 1 to 3 MPa according to published data (Lutge and Higinbottom, 1984).

The adsorption phase of the tissues is comparatively more protected than the liquid one from the impact of external factors. Because of that the changes in the content of the exchange-adsorbed cations for the three plant species are expressed more weakly. The same trends of changes caused by the increasing osmotic pressure are observed (Table 1). Namely, the concentration of hydrogen ions diminishes and that of the basic cations increases. The total content of the exchange-adsorbed cations expresses the cation-exchange capacity of the above ground mass (CEC). Most probably, the high capacity value under osmotic stress conditions is due to the formation of new ion-exchange structures and, respectively, to the availability of new adsorption sites. The above ground mass of pea features had the highest capacity (CEC_{pea} 48.1–55.3 cmol⁺.kg⁻¹) for all osmotic levels, which is characteristic for the leguminous crops.

We found out analogous changes in the content of cations in water-soluble and exchange-adsorbed state in the tissues of wheat, pea and barley in nutrient solutions of pH 5.5 (Ganev and Asrsova, 1991), which confirms the dominant role of the osmotic pressure in this case.

Fig. 1, 2 and 3 show the content of cations in liquid and absorption phases in the tissues of wheat, pea and barley, expressed, respectively, as percentages of the electrolytic content and cation-exchange capacity depending on the osmotic pressure. The osmotic pressure does not influence the character of the relative distribution of cations, which are arranged in the following orders:

Liquid phase: $K^+ \% > H^+ \% > Ca^{2+} \% >> Mg^{2+} \%$

Adsorption phase: $Ca^{2+}\% > H^+\% > Mg^{2+}\% > K^+\%$

Table 2 shows the capacity values of the strongly acidic (CEC_{SA}) and weakly acidic (CEC_A) structures and the cation-exchange capacity (CEC_{SA+A}) of the above ground mass of wheat, pea and barley depending on the osmotic pressure of the nutrient solutions of pH 4.5. The rising osmotic pressure increases the strongly acidic positions and diminishes the weakly acidic positions. These changes are expressed most significantly for the pea where the osmotic stress (P-0.52 MPa) causes a rise of CEC_{SA} with 26% compared to the variant with distilled water. The low pH of the nutrient solution results in a larger share of the strongly acidic positions. Thus, for all three plant species the capacity of the strongly acidic structures is higher than the capacity of the weakly



Fig.1. Relative distribution of cations in wheat depending on the osmotic pressure in nutrient solutions of pH 4.5

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Fig. 2. Relative distribution of cations in pea depending on the osmotic pressure in nutrient solutions of pH 4.5



Fig. 3. Relative distribution of cations in barley depending on the osmotic pressure in nutrient solutions of pH 4.5

61%

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P, MPa	CEC _{SA}	CECA	CEC _{SA+A}	CEC _{SA}	CECA
		cmol ⁺ .kg ⁻¹			in % of CEC _{SA+A}
			Wheat		
0.0	19.5	19.0	38.5	50.6	49.3
0.03	20.5	18.6	39.1	52.4	47.5
0.10	27.7	17.1	44.8	61.8	38.1
0.52	31.0	16.5	47.5	65.2	34.7
			Pea		
0.0	29.4	18.6	48.0	61.2	38.7
0.03	37.2	12.0	49.2	74.6	24.4
0.10	44.4	8.0	52.4	84.7	15.3
0.52	47.8	7.0	54.8	87.2	12.7
			Barley		
0.0	22.6	19.4	42.0	53.8	46.1
0.03	24.2	19.0	43.2	56.0	43.9
0.10	29.0	18.5	47.5	61.0	38.9
0.52	34.4	15.2	49.6	69.3	30.6
LSD 1%	1.30	0.45			
5 %	0.95	0.21			

Table 2. Capacity of strongly acidic (CEC_{SA}) and weakly acidic (CEC_A) structures and cation exchange capacity (CEC_{SA+A}) of the above ground mass of wheat, pea and barley depending on the osmotic pressure (P, MPa) in nutrient solutions of pH 4.5 (Values are given as mean average from three replications)

acidic structures ($CEC_{SA} > CEC_A$). The difference between the capacity values of the two types of acidic structures is greatest under condition of osmotic stress, where CEC_{SA} attains maximal values. The increase of the strongly acidic capacity value provides an additional adsorption of cations under high salt concentration and low pH of the solution, which is probably an adaptive reaction of the plants to the complex impact of both the osmotic and acidic factor in the nutrient medium.

Pea, which is an acidic sensitive plant, is characterized by the largest share of strongly acidic positions in the cation-exchange capacity, which varies within the range from 61.2% to 87.2% depending on the osmotic pressure. This share is lowest for the wheat, which is tolerant to high acidity conditions and varies between 50.6% and 65.2% of the total capacity of the above ground mass.

The behavior of some biochemical compounds as strongly acidic structures is determining for the mineral nutrition of plants in acid medium. The increase of the cationexchange capacity of the above ground mass also is a consequence of the higher capacity of the strongly acidic structures at higher osmotic pressure of solutions. This supports the hypothesis of providing new adsorption sites for cation exchange under these conditions. Maximal values of CEC_{SA+A} (48.0–54.8 cmol⁺.kg⁻¹) are observed for pea, which confirms the fact that leguminous crops are characterized by high cation-exchange ability.

The close values of the capacity $\text{CEC}_{\text{SA+A}}$ to those which are defined as a sum of the exchange-adsorbed cations (CEC) in Table 1 is a logical consequence of the character of the applied analytical methods.

Conclusion

The increase of the osmotic pressure in nutrient solutions of pH 4.5 leads to the following changes in the cation-exchange characteristics of the tissues of wheat, barley and pea:

- decrease in H⁺ ions content;
- increase in bases content;
- increase in the share of strongly acidic structures;
- increase in the cation-exchange capacity.

Under conditions of osmotic stress (P - 0.52 MPa) a maximal cation-exchange capacity of the above ground mass is obtained, which provides an additional adsorption of cations and improves the mineral nutrition at low pH of the nutrient solutions.

The low pH of the nutrient solutions results in domination of the strongly acidic structures in the whole range of variation of the osmotic pressure, which is determined by the acidic sensitivity of plants and is best observed for pea.

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