

Ion equilibrium in lichen surrounding

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Abstract

In laboratory conditions, the ionic equilibriums between a solution and a cation-active layer of epiphytic lichens *Hypogymnia physodes* immersed in the solution were examined. It was found that such equilibriums, due to exchange of mobile cations: H, Na, K, Ca, and Mg, are established in natural conditions between a lichen and atmospheric water.

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1. Introduction

Studies regarding possibilities of lichens use as bioindicators concern with, among others, relations between atmospheric composition and anatomic and morphologic changes of lichens. They have been widely developed since the 1970s, when Hawksworth and Rose prepared a 10-grade lichen scale for the area of England and Wales. Such measurements indicate an approximate level of atmosphere pollution with sulphur dioxide [1], which is the main cause of acid precipitation. This research method, currently referred to as the floristic method, supplemented by anatomic-morphologic, physiologic and analytic-chemical studies, is still applied and popularised (among others, Refs. [2–12]), also in Poland (e.g. Refs. [13–20]).

In natural conditions, the equilibrium is established between cations in atmospheric water, which come from substrate (bark) and air, and cations in the cation-active layer of lichens (Fig. 1). This influence is used for assessing environment pollution with heavy metals (e.g. Refs. [21–28]).

The aim of the presented studies regarding the equilibrium was to search for dependences between pH value of atmospheric precipitation and the type, and quantity of mobile cations bound in the cation-active layer of lichens. In order to determine ion exchange preferences, particularly effect of type and level of solution salinity, on the quantity of accumulated hydrogen ions, it was necessary to examine these dependences. Therefore, this paper is focused on the issue. On this bases, the preliminary research was carried out regarding the possibility of pH value assessment of atmospheric precipitation by determining composition of cation-active layer of lichens.

Lichens, natural cation exchangers, were analysed according to the approved rules of examination of synthetic ion exchangers. During the course of studies with the use of sensitive equipment, no exchange of anions between the solution and lichens was found. However, it should be expected that anions penetrate the cation-active layer of lichens in quantity limited by the Donnan exclusion.

2. Ion exchange statics

Ion exchange statics can be described as a heterophase double displacement reaction, Donnan equilibrium or osmo-

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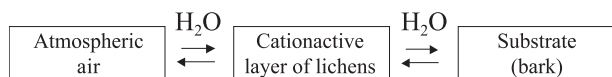
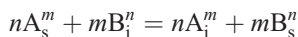


Fig. 1. Relations between environment and cation-active layer of lichens.

sis process. Ion exchange as the heterophase double displacement reaction:



is characterised by the thermodynamic constant of reaction equilibrium $K_{A/B}^0$:

$$K_{A/B}^0 = [A]_i^n [B]_s^m / [A]_s^n [B]_i^m \quad (1)$$

where: $[A]$, $[B]$ —ion activities in the solution (s) and ion exchanger (i); m , n —ion valence values.

For solutions sufficiently diluted, the concentration equilibrium constant $K_{A/B}$ can be used and then the activities are replaced by concentrations:

$$K_{A/B} = c_{A_i}^n c_{B_s}^m / c_{A_s}^n c_{B_i}^m \quad (2)$$

In order to evaluate the constant, one should determine partition coefficients on the basis of ion contents in the ion exchanger (y) and solution (x):

$$P = y/x \quad (3)$$

where: x , y are ion mole fractions in the solution (x) and ion exchanger (y), respectively. The P value is a measure of the ion affinity to ion-active layer. For ions of the same valence, the relative measure of affinity was assumed as the value of $K_{A/B}$, defined by the following formula:

$$K_{A/B} = P_B/P_A \quad (4)$$

or, on the basis of dependence (3), it can be defined with the use of mole fractions as follows:

$$K_{A/B} = (y/(1-y))((1-x)/x) \quad (5)$$

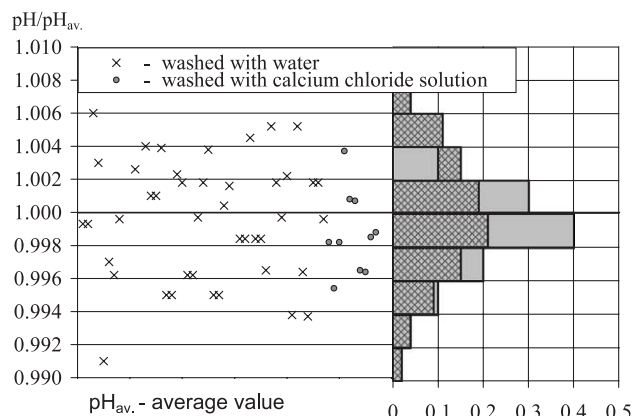
where A and B indexes denote the type of ion.

Determination of equilibrium constant $K_{A/B}$ and $K_{B/C}$ enables to evaluate $K_{A/C}$ constant:

$$K_{A/C} = K_{A/B} K_{B/C} \quad (6)$$

A graphic method of description of ionic equilibria was adopted. Effective ion concentrations were calculated from the following formula: $c^* = 10^{-3} z c$ (z —ion valence); c^* has the same dimension as c , i.e., $[\text{mol}/\text{dm}^3]$ or $[\text{mol}/\text{g dm}]$. For concentrations defined in such a way, the (equivalent) equilibrium constant $K_{(E-v)A/B}$ was determined, which was equal to $K_{A/B}$ only for ions of the same charge. Assuming that $K_{(E-v)A/B}$ was independent of the ion mole fraction in the ion-active layer, and that: $\sum c^*(s) + \sum c^*(i) = \text{const.}$, it was possible to determine a curve describing the exchange equilibrium:

$$y^* = K_{(E-v)A/B} x^* / (1 + (K_{(E-v)A/B} - 1) x^*) \quad (7)$$

Fig. 2. Distribution and histograms of distributive series of relative changes of pH relative to pH_{av} .

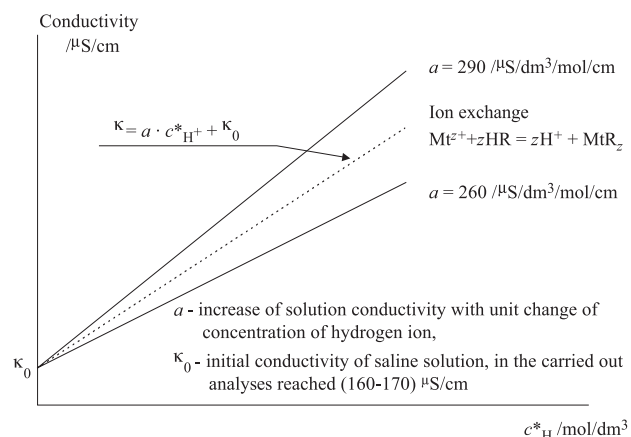
where: y^* , x^* —(equivalent) fractions in the cation-active layer and solution, respectively.

The curve is a hyperbola.

The real shape of the curve often deviates from the hyperbolic one, which indicates, among others, the influence of ion concentration in the ion-active layer on the equilibrium constant.

3. Method of sample preparation and measurements

The research was carried out on lichens *Hypogymnia physodes* sorted according to the sampling place, collected in different places from deciduous and coniferous trees. The analysis was focused on lichens separated from the substrate and other mechanical impurities. The samples were rinsed with demineralised water (conductivity $\kappa=0.1 \mu\text{S}/\text{cm}$) and dried in the temperature not exceeding 303 K. For the equilibrium studies, lichens of an averaged composition are used. Lichens were immersed in solutions of hydrochloric acid and the studied metal salt of the concentrations $c^*=0.2 \text{ mol}/\text{dm}^3$ each (of the acid as well as

Fig. 3. Ion exchange $Mt^{n+} + zHR = zH^+ + MtR_z$ as described by conductometric measurements [30].

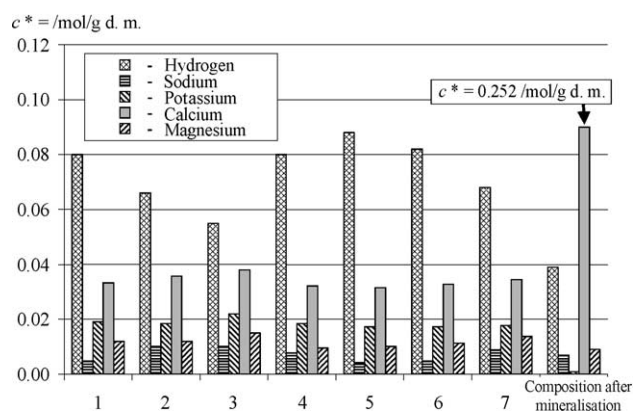


Fig. 4. Mobile cation contents in cation-active layer of 1 g of *H. physodes* lichens; numbers 1–7 denote sampling sites; the remaining bars concerned with mineralised samples of lichens.

of the salt) for 5 min (after that period of time the ion exchange equilibrium was achieved, as it was proved experimentally) and then rinsed with demineralised water. One gram of lichens prepared and then dried in such a way were next immersed in solutions (at temperature of 298 K) of different concentration ratio (Mt/H) of metal to hydro-

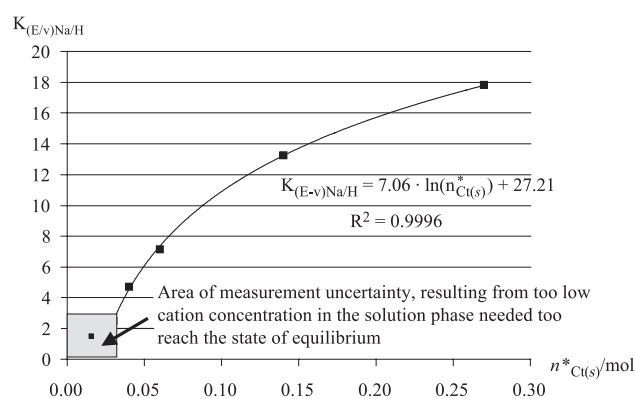


Fig. 5. Equilibrium constant $K_{(E-v)Na/H}$ dependence on total of cation contents $n^*_{Ct(s)}$ in the solution.

gen ions. Each time, the process was brought to the state of equilibrium, characterised by stability of solution pH value (determined with pH-meter [Elmetron CP-551, Zabrze, PL]) and conductivity as measured with conductometer (Elmetron CC-551, Zabrze, PL). On the basis of changes related to concentration of hydrogen ions in the solution, its composition in the state of equilibrium was

Table 1

Equilibrium constants and partition coefficients of Na/H equilibrium series for 200 cm³ of solution and 1 g of lichens immersed in the solution

$n^*_{Ct(s)}/(\text{mol})$	$c^*_{\text{init.H(i)}}/(\text{mol/g d.m.})$	x^*_{H}	1	0.9	0.8	0.6	0.5	0.4	0.2	0.1	0	$K_{(E-v)\text{av.}}$
0.27	0.09	$K_{(E-v)}$	–	–	–	–	–	129	35	17.98	17.67	17.82
		P^*	–	–	–	–	–	4.85	5.18	7.11	8.83	
0.14	0.09	$K_{(E-v)}$	–	–	41	20	13.53	13.66	13.27	13.55	13.38	13.25
		P^*	–	–	2.41	2.95	3.26	3.80	4.52	5.77	6.20	
0.14	0.05	$K_{(E-v)}$	37	20	19	13.67	13.59	13.50	12.87	12.65	12.92	7.14
		P^*	2.92	3.27	3.70	4.17	5.15	6.00	6.22	7.60	8.75	
0.06	0.09	$K_{(E-v)}$	7.21	7.13	7.43	7.00	6.97	6.68	7.30	7.03	7.51	4.72
		P^*	1.93	2.10	2.29	2.50	2.73	2.76	3.14	3.47	3.80	
0.04	0.09	$K_{(E-v)}$	4.70	4.75	4.64	4.74	4.74	4.78	4.89	4.70	4.51	2.47
		P^*	1.81	1.90	1.95	2.12	2.23	2.32	2.48	2.59	2.65	
0.03	0.09	$K_{(E-v)}$	2.39	2.43	2.38	2.44	2.49	2.55	2.52	2.41	2.52	1.67
		P^*	1.51	1.54	1.59	1.62	1.68	1.72	1.76	1.76	1.79	
0.02	0.09	$K_{(E-v)}$	2.08	0.99	1.63	2.23	0.89	2.34	2.99	0.83	1.01	
		P^*	1.21	1.35	1.80	2.07	1.90	1.99	2.11	1.01	1.36	

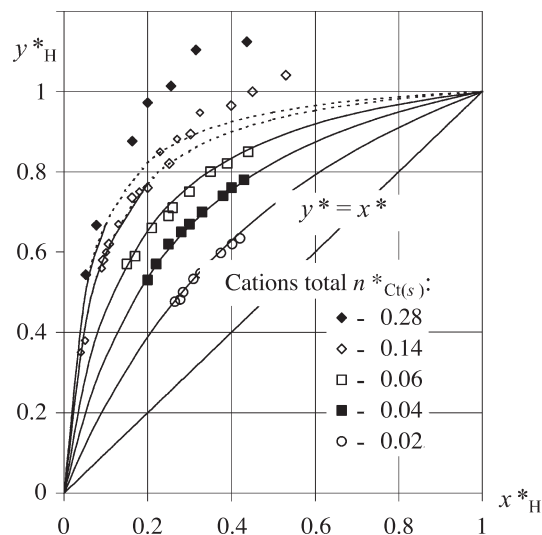


Fig. 6. Equilibrium of the Na/H ion system exchange—1 g of lichens in 200 cm³ of solution.

determined. Knowing the ion exchange capacity and initial composition of lichens, the mole fraction of cations in lichens was determined. Metals' content in the samples was determined using SOLAAR 969 Unicam atomic absorption (and emission) spectrometer. Previous error analyses [29] indicated that the uncertainty of pH measurement resulting from the methodology, uncertainty of meter indications and differences in repeatability of composition ion-active layer averaging of examined lichens equals to: $\Delta\text{pH}=0.04$. Fig. 2 shows distribution and histograms of distributive series of relative change of pH relatively to pH_{av} for series of examined lichens.

An important element of the analyses was the comparison of pH value and conductivity during the process. It was found [30–32] that the course of ionic exchange: $\text{Mt}^{z+} + z\text{HR} = z\text{H}^+ + \text{MtR}_z$ can be characterised by conductiv-

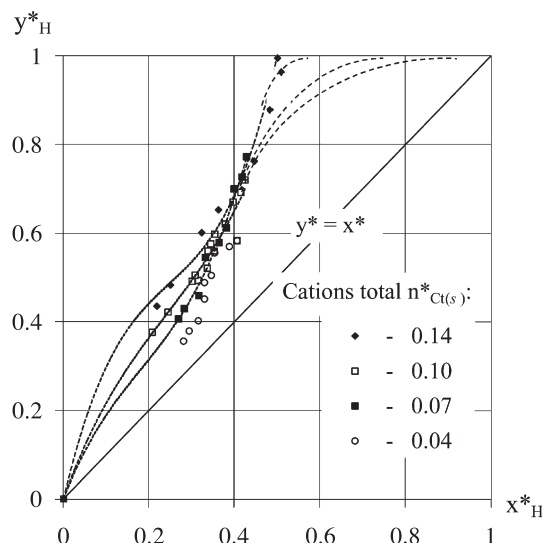


Fig. 7. Equilibria of Mg/H ion exchange.

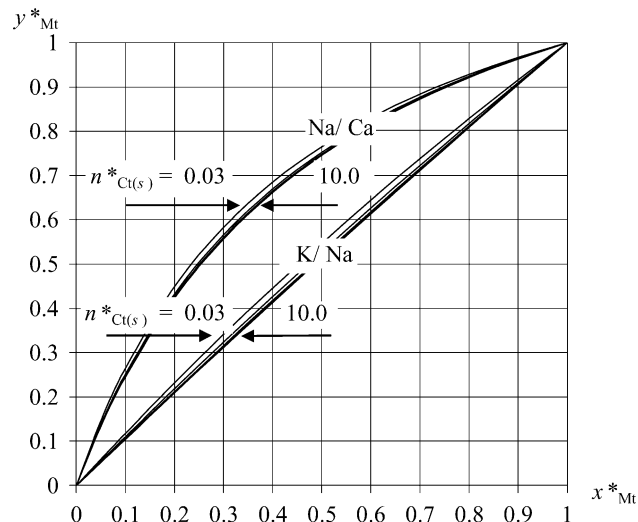


Fig. 8. Equilibria of ion exchange Na/Ca and K/Na.

ity κ measurements. The $\kappa=f(c^*)$ dependence is a straight line: $\kappa = ac^*_{\text{H}} + \kappa_0$, where the a value was usually within empirically determined limits: $a \in (260; 290)$. Any deviations could result from, among others, competitive processes of sorption or desorption of anions or dissolution of ionic substances. The graphic description of the dependence is shown in Fig. 3.

4. Results

4.1. Influence of environment on the type and quantity of mobile cations sorbed in lichens

The study focused on *H. physodes* lichens, collected from different trees growing in Poland: in the Tatra Mountains, the Table [Stołowe] Mountains, the Drawskie

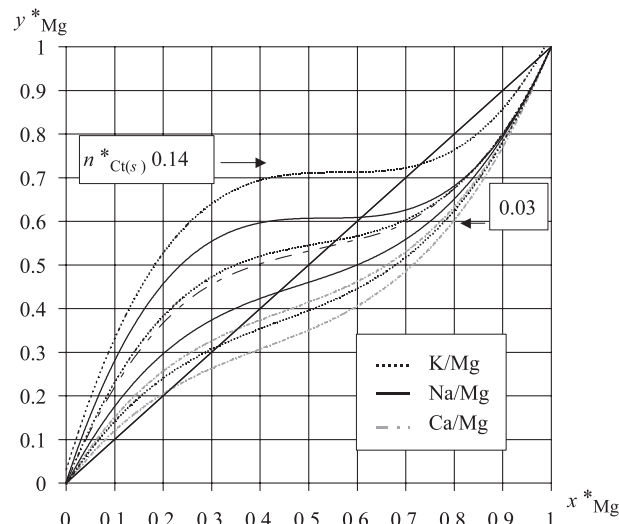


Fig. 9. Equilibria of ion exchange K/Mg, Na/Mg and Ca/Mg.

Table 2

Statistic assessment of errors in the determination of equilibrium constant for Na/H, Ca/H and K/H as well as partition coefficient for Mg/H

Parameter	Na/H					Ca/H					K/H					Mg/H
$n^*_{\text{Ct(s)}/\text{mol}}$	0.27	0.14	0.06	0.04	0.03	0.14	0.07	0.05	0.04	0.14	0.07	0.04	0.03	0.03	P^*	
σ	0.05	0.12	0.09	0.03	0.03	0.16	0.07	0.03	0.03	0.08	0.33	0.12	0.03	0.03		
$\sigma_{(\text{series})}$			0.13			0.05				0.10						0.10
R^2			0.9979			0.9959				0.9974						0.8180

Lake District as well as in the forests of the Opole Province. The results are shown in Fig. 4.

The above diagram shows that lichens collected at different places vary in content of individual cations. The fraction of hydrogen ions (calculated on the base of pH data of the solutions after proton exchange by CuSO_4) in lichens $x^*_{\text{H(i)}} \in (0.4; 0.7)$ is influenced by the substrate in which the lichens grow as well as by composition of atmospheric precipitation. Lichen sample composition averaging is possible through bathing in saline solutions ($x^*_{\text{H(i)}}=0.3$). This treatment is very important in case of the lichen exposition method used in the environment quality monitoring. The exposition method of lichens transplanted to industrial areas as well as in so-called “lichen deserts” is used in numerous studies (e.g. Refs. [33–39]).

4.2. Equilibriums between solution and cation-active layer of lichens

Examination of the equilibriums was carried out on lichens with the averaged composition. The total concentration of mobile cations (H^+ , Na^+ , K^+ , Ca^{2+} and Mg^{2+}) in 1 g of lichens, $c^*_{\text{Ct(i)}}$, i.e. its sorption (ion exchange) capacity, was evaluated by pH measurements of the total amount of hydrogen ions accumulated in lichens as desorbed by 30 min (during the lapse of time the ion equilibrium was achieved) in the solution of copper sulphate (the copper ion affinity to lichens is several times bigger than those of the mobile cations) of the concentration $c^*=2.0 \text{ mol/dm}^3$ and determining the other cations by desorbing them in the solution of hydrochloric acid of the same (i.e. 2.0 mol/dm^3) concentration. The total concentration of mobile cations determined in this way ($c^*_{\text{Ct(i)}}=0.145 \text{ mol/g dm}$) has been equal to the average mobile cation content calculated from

the data presented in Fig. 4, viz. in samples 1–7. Change of equilibriums $K_{(\text{E-v})\text{M/H}}$ were examined for two cases: $\sum n^*_{\text{Ct(s)}} + \sum n^*_{\text{Ct(i)}} = \text{const.}$ and $\sum n^*_{\text{Mt(s)}} = \text{const.}$, where $n^* [\text{mol}] = 10^{-3}zn$; the n is the content of metal ion and z is its valence value. The (s) and (i) indexes refer to the solution and ion-active layer of lichen, respectively, while the Ct index refers to the total contents of cations.

4.2.1. Equilibriums in case of $\sum n^*_{\text{Ct(s)}} + \sum n^*_{\text{Ct(i)}} = \text{const.}$

The averaged sample of lichens (1 g) were immersed in solutions of metal salts (Na, K, Ca, and Mg) and hydrochloric acid mixed in different proportions, with constant concentration of cations $c^*_{\text{Ct(s)}}$ for successive measurement series. On the basis of pH and conductivity measurements, the partition coefficients P^* and equilibrium constants $K_{(\text{E-v})\text{M/H}}$ were determined. The calculation was carried out according to dependences (3) and (5), assuming the following sorption capacity of lichens $c^*_{\text{Ct(i)}}=0.145 \text{ mol/g dm}$, *vide super*. The results of the Na/H series are presented in Table 1, the other two systems (K/H and Ca/H) have exhibited similar behaviour, while the Mg/H system has showed a different relationship (Fig. 7).

In Table 1, the figures in italic refer to data for which dependence (7) is not valid. Deviations from the stoichiometric ion exchange are checked by comparing the measured data with those presented in Fig. 3. The dependence: $K_{(\text{E-v})} = f(n^*_{\text{Ct(s)}})$ for the system Na/H is shown in Fig. 5, it is valid for $K_{(\text{E-v})} > 1$, the lower range is characterised by a considerable measurement uncertainty due to very small cation concentration in the solution as compared with the number of cations bound by cation-active layer of lichens. However, in the upper range concentration the pH value is a significant factor. It was found that significant deviations from the results anticipated by dependence (7) arose, if the

Table 3

Change of concentration of hydrogen ions in 200 cm^3 of solution depending on salt concentration and pH stock solution

$n^*_{\text{Mt(s)}/\text{mol}}$	$x^*_{\text{H init.}}$	0	0.1	0.2	0.4	0.5	0.6	0.8	0.9	1
0.14	$\text{pH}_{\text{init.}}$	5.73	5.00	4.75	4.58	4.33	4.14	4.00	3.90	3.73
	Δc^*_{H}	−0.058	−0.052	−0.045	−0.038	−0.019	0.005	0.028	0.052	0.109
0.10	$\text{pH}_{\text{init.}}$	—	—	4.85	4.48	4.30	4.18	4.00	3.87	—
	Δc^*_{H}	—	—	−0.040	−0.023	−0.009	0.004	0.035	0.069	—
0.07	$\text{pH}_{\text{init.}}$	5.51	5.23	4.71	4.39	4.19	4.06	3.87	3.74	3.63
	Δc^*_{H}	−0.042	−0.039	−0.027	−0.009	0.010	0.031	0.073	0.111	0.153
0.05	$\text{pH}_{\text{init.}}$	5.90	5.12	4.63	4.41	4.21	4.14	4.03	3.84	3.70
	Δc^*_{H}	−0.039	−0.032	−0.020	−0.007	0.013	0.022	0.042	0.088	0.133
0.03	$\text{pH}_{\text{init.}}$	—	—	4.66	4.38	4.31	4.20	4.09	3.98	—
	Δc^*_{H}	—	—	−0.014	0.001	0.007	0.019	0.036	0.058	—

pH value in the equilibrium state is less than 3.9, which was probably caused by the thallus destruction. Similar effect is observed if $\text{pH}_{\text{equilibr.}} > 8.0$.

For comparison, the measurements were repeated for series of 1 g lichen samples put into 1000 cm³ of solution and the similar results were obtained. On the basis of function $K_{(\text{E-v})} = f(n^*_{\text{Ct(s)}})$ drawn in Fig. 5 according to dependence (7), the course of changes of proton contribution in cation-active layer of lichens and in the solution phase was calculated. The numerical data from Table 1 were placed on hyperbolas drawn in the aforementioned way. The equilibrium is presented in Fig. 6.

In the same manner, the equilibrium constants and partition coefficients were determined for the K/H, Ca/H and Mg/H system equilibria. The equilibrium changes for the K/H and Ca/H systems are analogous to those of the Na/H ion system (cf. Fig. 6). The Mg/H equilibrium (Fig. 7) are not described by dependence (7), which may result from the aforementioned influence of concentration of magnesium ions in the lichen ion-active layer on the equilibrium constant. Linear part for the Mg/H equilibrium (Fig. 7) dependence: $y^* = f(x^*)$, it has a slope value $P^* = y^*/x^* = 1.6477$; $R^2 = 0.818$.

According to dependence (6), taking the empirical parameters of $K_{(\text{E-v})} = f(n^*_{\text{Ct(s)}})$ function for the K/H and Ca/H systems ($K_{(\text{E-v})\text{K/H}} = 7.51 \ln(n^*_{\text{Ct(s)}}) + 29.17$) and $K_{(\text{E-v})\text{Ca/H}} = 7.51 \ln(n^*_{\text{Ct(s)}}) + 9.12$), the equilibria data of ion exchange for the solutions of Na/Ca and K/Na were determined and presented in Fig. 8. Similarly, taking the parameters of the function $K_{(\text{E-v})} = f(n^*_{\text{Ct(s)}})$ from Fig. 7 for examined range of Mg/H concentrations, the calculated parameters of equilibria of ion exchange are shown in Fig. 9 for the K/Mg, Na/Mg and Ca/Mg solutions.

On the basis of research carried out, chemical affinity series of examined cations to cation-active layer of lichens were established as follows: $\text{K} < \text{Na} < \text{Ca} < \text{H}$ and $\text{Mg} < \text{H}$. The magnesium affinity in relation to cations of other metals changes depending on their contribution to solution phase because dependence (7) is not held for the Mg/H system. Table 2 includes the data concerned statistic assessment of the obtained results.

Due to the averaged composition of samples (cf. Fig. 2), the pH measurements are characterised by uncertainty

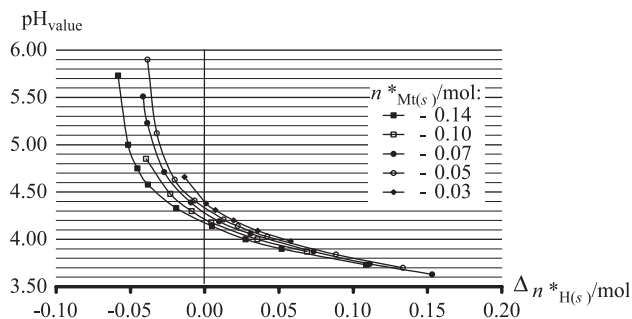


Fig. 10. Determination of pH value for which the system lichen-solution is in equilibrium, at the given value of $n^*_{\text{Mt(s)}}$.

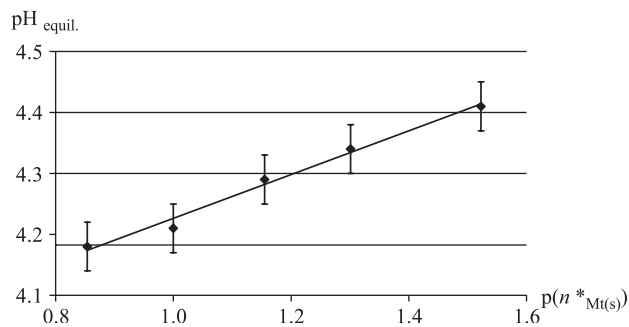


Fig. 11. Influence of $p(n^*_{\text{Mt(s)}})$ on equilibrium pH.

$\Delta\text{pH} = 0.04$, and the average standard deviation $\sigma_{(s)}$, empirically determined for a given dependence: $K_{(\text{E-v})} = f(n^*_{\text{Ct(s)}})$, does not exceed 0.14.

4.2.2. Equilibria in case of $\sum n^*_{\text{Mt(i)}} = \text{const.}$

Assuming that solution salinity comes mainly from substrate where lichens grow, it is worth considering the equilibria with constant level of salinity.

In the experiment, contribution of metal cations in the solution were selected on the basis of portions of metal ions (Mg, Ca, Na, and K) present in the solution after rinsing the substrate where lichens used to grow. The following was assumed in the prepared solutions: $n^*_{\text{K(s)}}/n^*_{\text{Ca(s)}}/n^*_{\text{Na(s)}}/n^*_{\text{Mg(s)}} = 1.00:0.85:0.73:0.61$.

In the analysed measurement series with constant $n^*_{\text{Mt(s)}}$ (0.03–0.14 mol in 200 cm³ of solution), $n^*_{\text{H(s)}}$ was changed within the range of pH from 3.5 to 6.0. An important parameter of the relation considered in such a way is the state of equilibrium of the solution, where $\text{pH}_{\text{initial}} = \text{pH}_{\text{final}}$. The results of measurements of solution pH as well as difference in concentration of hydrogen ions $\Delta c^*_{\text{H(s)}}$ before and after the process of sorption are presented in Table 3 and shown in Fig. 10.

Fig. 11 depicts dependence of the equilibrium pH on concentration of metal cations in the solution phase, expressed as: $p(n^*_{\text{Mt(s)}}) = -\log(n^*_{\text{Mt(s)}})$. Measurement uncertainty of equilibrium pH is 0.04; it is marked in the figure.

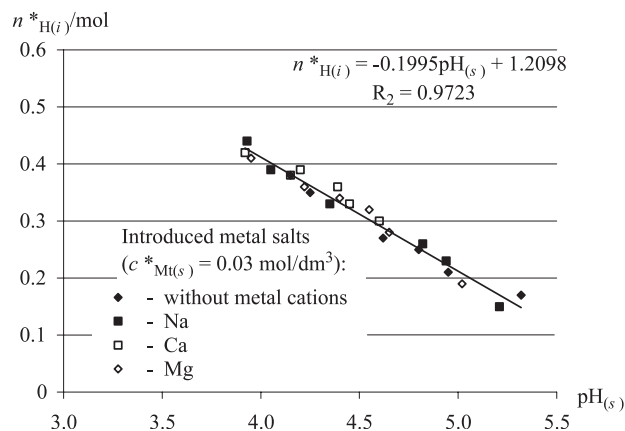


Fig. 12. Influence of pH of solution saturated with CaF_2 on the concentration of hydrogen ions in the cation-active layer of lichens.

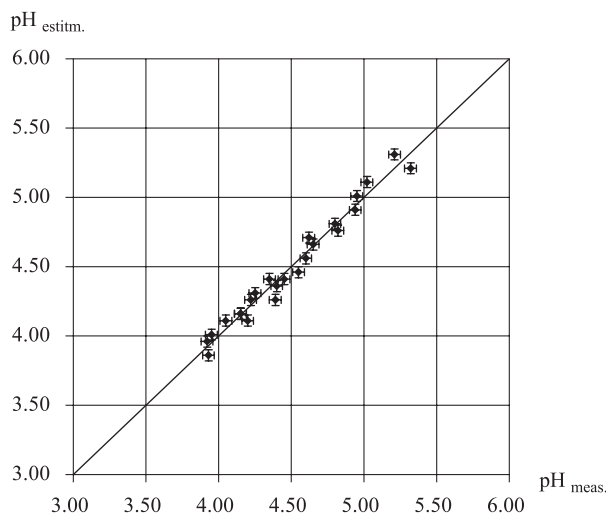


Fig. 13. Comparison of measured pH value of the solution with the pH data determined on the basis of lichen studies with the method proposed here.

The diagrams presented in Figs. 10 and 11 indicate that the number of hydrogen ions accumulated in lichens, at $n^*_{\text{Mt(s)}} = \text{const.}$, is proportional to their concentration in the solution phase and changes along with the change of salinity level. Therefore, to specify interrelations between pH value of atmospheric precipitation and accumulation of hydrogen ions in the cation-active phase of lichens, a steady salinity level of the solution sample is required. Hence, it was attempted to average the content of salt in the prepared precipitation. The experiment consisted in allowing the 1 dm³ artificial precipitation with known pH and salinity level to permeate through fine, slightly soluble salt. This solution was used for rinsing lichens until establishment of a dynamic equilibrium, which was indicated by constant read-out of solution conductivity and pH. Due to large affinity of large metal cation to cation-active layer of lichens in the experiment, we made use of calcium fluoride (solubility product $L = 4.9 \times 10^{-11}$), whose concentration in the solution corresponded to examined cation concentrations ($n^*_{\text{Ca(s)}} = 0.14$ mol in 200 cm³ of solution). Preliminary results of the research are shown in diagrams (Figs. 12 and 13).

Due to constant concentration of calcium ions in the solution used for rinsing lichens, which exceeded concentration of cations in examined atmospheric precipitation several times, the influence of other metal cations on Mt/H equilibrium was diminished, which was indicated by the linear arrangement of points in Fig. 12.

The difference between the actual pH value and the value determined on the basis of analysis of lichen content (desorption of hydrogen ions in the solution of copper sulphate) does not exceed 0.2 of pH unit, which is depicted in the diagram (Fig. 13).

After detailed studies, particularly of the process kinetics, this type of pH determination of atmospheric precipitation can be used in lichenoidication methods consisting in exposition of the lichens transplanted on the so-called “lichen deserts”.

5. Discussion and conclusions

The results of this study indicate that the concentration of mobile cations in cation-active layer of lichens depends on their concentration in the lichen direct environment. The reached state of equilibrium, which results from heterophase double displacement reaction, can be described by the thermodynamic equilibrium constant, which determines the partition coefficients and cation affinities to cation-active layer of lichens. This interpretation is valid for pH values in the range of $3.9 < \text{pH}_{\text{equil.}} < 8.0$. Exceeding the limits it leads to irreversible changes in lichen structure, which results in a change in number of ions in the solution as evidenced by solution conductivity data (cf. Fig. 3). Another restriction results from the static method of analysis; the minimal cation contents in the solution is determined as $c^* = 0.03$ mol/dm³, below which the state of equilibrium cannot be reached, considering the determined sorption capacity of lichens ($c^*_{\text{Ct(s)}} = 0.145$ mol/g dm) and composition of cation-active layer.

On the basis of experimental results considering the above criteria, it was found that:

- for pairs of cations of K/H, Na/H and Ca/H, dependence (7) was valid. Therefore, in the case of constant number of cations in the solution, equilibrium constant does not change due to change of cation contribution in the solution (Fig. 6). According to the Eq. (6), the same dependence is true for any combination of these cations (Fig. 8),
- it was demonstrated that, along with change of magnesium contribution in relation to other cations, dependence (7) was not valid (Figs. 7 and 9), which meant that equilibrium constant might depend on contribution of magnesium ions in the cation-active layer of lichens.
- proposed method of analysis of change in contribution of cations in the solution and cation-active layer of lichens, due to proper repeatability of the samples, is characterised by uncertainty of pH measurement of approximately: $\Delta \text{pH} = 0.04$ and average standard deviation of $\sigma_{(s)}$, empirically determined for specified dependences: $K_{(E-v)} = f(n^*_{\text{Ct(s)}})$ is less than 0.14.
- for the identified, constant content of metal cations in the solution, it is possible to determine the solution pH value in the state of equilibrium with the cation-active layer of lichens (Figs. 10 and 11). Then, $\Delta n^*_{\text{H(s)}} = 0$.

The studies revealed that the ion-active properties of lichens could be used for determining acidity of atmospheric precipitation. In the laboratory conditions, the linear dependence was determined between concentration of hydrogen ions in cation-active layer of lichens, desorbed in the solution of copper sulphate of concentration $c^* = 2.0$ mol/dm³, and pH value of prepared precipitation (Fig. 12), provided that the salinity of the precipitation was averaged. The averaging was carried out by allowing the prepared

solution (artificial precipitation with known pH value and salinity) to permeate through fine calcium fluoride and then directing the solution on a sample of lichens. Difference between the measured pH value of the solution and the value determined on the basis of analysis of lichen constitution (Fig. 13) did not exceed 0.2 of pH value, regardless of the type and initial content of salt in the solution.

Concluding, the concentration of hydrogen ions accumulated in the cation-active layer of lichens growing in natural environment is linearly dependent on the pH value of atmospheric precipitation to which the lichens have been exposed. The H^+ concentration can be determined by the standard pH measurements carried out for the solution of constant salinity in which the lichen sample is immersed for the time needed to attain the ionic equilibrium.

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