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SHORT COMMUNICATIONS

Buffer Capacity of Surface Waters as a Geochemical Factor of Their Resistance to Acidification

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The acidification of natural waters is a serious environmental problem. The causes of water acidification can be anthropogenic factors and natural geological processes, but the main factor intensifying the process of acidification is anthropogenic acidic contamination [1].

The resistibility of natural water bodies to acidification is assayed using the criterion of acid neutralizing capacity (ANC) and buffer capacity (β).

The ANC factor, which was proposed by Henriksen et al. [2], is defined as the difference between the major cations and anions of strong acids with a correction of the ionic composition of waters for its marine constituent. In fact, ANC is a measure for the excess or deficit of hydrocarbonates or, in application to waters enriched in humic acids, their sum:

$$\mathrm{ANC} = [\mathrm{HCO_3^-}] + [\mathrm{A_{org}}] - [\mathrm{H^+}] - [\mathrm{Al^{3+}}]. \qquad (1)$$

For surface waters containing hydrocarbonates, a decrease in ANC due to hydrogen and aluminum ions is insignificant, and ANC is in fact the sum of hydrocarbonates and organic acid anions contained in salts, i.e., it can be determined from the ionic balance of water [3]:

$$\mathrm{ANC} = [\mathrm{HCO_3^-}] + [\mathrm{A_{org}}] = \Sigma[\mathrm{cat}] - \Sigma[\text{anions of strong acids}], \qquad (2)$$

where Σ[cat] is the sum of cations, including the hydrogen and ammonium ions, and Σ anions of strong acids] is the sum of the anions of strong acids (SO_4^{2-}, Cl^-, and NO_3^-).

The other criterion used to evaluate the resistance of water bodies to acidification is their buffer capacity, which indicates how the pH of the water varies with the addition of strong acids. The true buffer capacity is understood as the $\frac{db}{dpH}$ [4] differential ratio, which shows how pH changes when an infinitely small amount of a strong acid is added to the solution. It can be calculated using the classical Van Slyke equation

$$\beta = \ln 10\left\{\frac{kC_{\mathrm{tot}}[\mathrm{H^+}]}{(k+[\mathrm{H^+}])^2} + [\mathrm{H^+}] + [\mathrm{OH^-}]\right\}, \qquad (3)$$

where $[H^+]$ and $[OH^-]$ are the concentrations (in mol-equiv/l) of the H^+ and OH^- ions in the original solution, C_{tot} is the total concentration of the salt and weak acid in the solution (in mol-equiv/l), and k is the dissociation constant of the weak acid. At pH 6–8, the buffer capacity is completely controlled by the first summand in the Van Slyke equation and can be calculated by the formula

$$\beta = 2.3\frac{C_{\mathrm{tot}}10^{\mathrm{p}k-\mathrm{pH}}}{(1+10^{\mathrm{p}k-\mathrm{pH}})^2}.$$

The second summand should be taken into account for acidic waters, and the third term should be considered for alkaline waters.

A measure of buffer capacity (β) often applied in chemistry is the amount of strong acid (or alkali) needed to add to the buffer system to change its pH by one pH unit.

Natural waters of the humid zone are controlled by two systems: carbonate and humus. The buffer effect of the former is caused by the presence of hydrocarbonates and CO_2, and the action of the latter is underlain by the presence of organic acids, first of all, humic and fulvic, and their salts.

MATERIALS AND METHODS

The buffer capacity of natural waters was determined by the potentiometric titration of water samples with a strong acid, as was proposed by Nikanorov and

Lapin [5]. The titration curves were treated by a number of methods: using the method proposed by the aforementioned authors, by the direct calculation of the buffer capacity from the dependence of the pH on the amount of strong acid and by a method developed by the authors of this publication. A dependence obtained in [5] makes it possible to determine the concentration of salt (C_{salt}) and the dissociation constant of weak acids (k) if the titration curves of the salt are identical to those of a water sample:

$$\frac{[H^+]}{b - [H^+]} = \frac{k}{C_{salt}} + \frac{[H^+]}{C_{salt}}, \quad (4)$$

where b is the amount of strong acid added to the water sample, and $[H^+]$ is the equilibrium concentration of hydrogen ions upon acid addition. This equation was developed for the situation when weak acids are absent from the original solution, which is an assumption, because the concentrations of these acids can be fairly high in acidic humic waters. If the presence of weak acids in the solution is ignored, it is sometimes impossible to graphically determine the parameters of the equations, as was revealed when the titration curves were processed. To eliminate this disadvantage, we attempted to take into account the occurrence of weak acids and their salts in the solution.

For highly alkaline waters whose Alk $\gg [CO_2]$ and ANC is close to the alkalinity of water, it should be assumed that all strong acid added to the solution is spent on the reaction with hydrocarbonates with the release of an equivalent amount of carbon dioxide. Let the initial concentration of salt in the solution be C_{salt}, and then the concentration of the weak acid in this solution will be $C_{acid} = \frac{C_{salt}[H^+]_{ini}}{k}$. In compliance with the aforementioned assumption, we will obtain the equation $\frac{C_{salt} - b}{\frac{C_{salt}[H^+]_{ini}}{k} + b} = \frac{k}{[H^+]}$.

After simple manipulations, we obtain the linear expression

$$\frac{b[H^+]}{[H^+] - [H^+]_{ini}} = C_{salt} - k\frac{b}{[H^+] - [H^+]_{ini}}. \quad (5)$$

The intersection point with the ordinate yields C_{salt}, and the tangent $\tan\alpha = -k$. This dependence is a particular case, and the more general situation involves a complicated system of acid–base equilibria in humic waters.

For example, the acidity of humic acids is controlled by the presence of weak acids (humic and carbon dioxide) (m_{ini}) and free hydrogen ions ($[H^+]_{ini}$):

$$Acid_{ini} = m_{ini} + [H^+]_{ini},$$

$$m_{ini} = [CO_2]_{ini} + [HA_{org}]_{ini},$$

$$m_{ini} = Acid_{ini} - [H^+]_{ini}.$$

The addition of a strong acid (b) to such natural water should result in the consumption of a certain amount of the acid by reactions with the anions of the weak acids, and the rest of the acid should be spent on an increase in the concentration of hydrogen ions equal to $([H^+] - [H^+]_{ini})$. Then the amount of the newly formed weak acids should be

$$m_{form} = b - ([H^+] - [H^+]_{ini}) = b - [H^+] + [H^+]_{ini}.$$

With regard for their initial concentrations, the overall amount should be

$$m = b + [H^+]_{ini} - [H^+] + m_{ini}$$

$$= b + [H^+]_{ini} - [H^+] - Acid_{ini} - [H^+]_{ini}$$

$$= Acid_{ini} + b - [H^+].$$

Denoting the total concentration of the salt and weak acid in the solution C_{tot}, and, with regard for the dissociation constant of the weak acid (k), we obtain $\frac{C_{tot} - m}{m} = \frac{k}{[H^+]}$.

Simple transforms yield the equation

$$\frac{[H^+]}{m} = \frac{k}{C_{tot}} + \frac{[H^+]}{C_{tot}}, \quad (6)$$

which is linear in the $\frac{[H^+]}{m}$ vs. $[H^+]$ coordinates. The tangent of the line gives $\frac{1}{C_{tot}}$, and the intersection point with the ordinate yields the absolute term $\left(\frac{k}{C_{tot}}\right)$, from which C_{tot} and k can be readily obtained. Using the classic Van Slyke equation [4], one can easily calculate the buffer capacity of water using either the first or the second equation.

For our research, we selected a number of water bodies in the basin of the Shuya (Onezhskaya) River that have various alkalinity, color index, acidity, and pH of their waters (Table 1) and should have different buffer capacities.

The alkalinity of the waters (Alk) was determined by two-point titration (to pH 4.5 and 4.2) [6, 7]. The samples were potentiometrically titrated with strong acid (0.02 N HCl solution) until the pH of the solution changed by one unit. The Ca^{2+} and Mg^{2+} ions were determined by atomic absorption [8], Na^+ and K^+ were analyzed by flame photometry [9], and NH_4^+ was determined by the indophenole method [10]. Sulfates and chlorides were analyzed by ion chromatography [11], nitrates were determined by their reduction on a Cu–Cd reducer to nitrites [12], and pH was quantified potentiometrically. All chemical analyses were conducted at

Table 1. Initial indicators of acid–base equilibrium in water samples from the natural bodies and model solutions

Water body	pH	Alk, mmol-equiv/l	Color idex	ANC	Acid
				mmol-equiv/l	
L. Imatozero	6.82	0.29	25	0.35	0.10
L. Pryazhinskoe	6.80	0.23	90	0.39	0.10
L. Ukshezero	7.16	0.49	25	0.55	0.02
L. Syamozero	6.93	0.15	40	0.24	0.05
L. Iso-Puhjajarvi	6.11	0.08	120	0.22	0.13
L. Soujarvi	6.08	0.05	130	0.20	0.11
Shuya R.	5.91	0.05	140	0.24	0.14
L. Lizhmenskoe	6.14	0.04	35	0.10	0.09
L. Salonjarvi	5.57	0.02	160	0.15	0.09
L. Vuontelenjarvi	4.55	<0.01	180	0.14	0.31
Model solutions					
$NaHCO_3$ 0.0625 mmol-equiv/l	6.62	0.05	–	0.06	0.05
$NaHCO_3 + CH_3COONa$ 0.125 mmol-equiv/l	6.70	0.10	–	0.25	0.05
CH_3COONa 0.0625 mmol-equiv/l	5.87	0.03	–	0.06	0.05

the certified (state standard of the Russian Federation) Laboratory of Hydrochemistry and Hydrogeology of the Institute of Water Problems of the North, Karelian Research Center, Russian Academy of Sciences, with the quality of the analyses monitored by in-laboratory and external replicate determinations. External analyses were conducted within the framework of the ICP-Waters Inernational Project [13].

RESULTS AND DISCUSSION

The potentiometric titration curves of water samples with strong acid show certain differences between individual water samples (Fig. 1). For example, they are linear for waters whose alkalinity is higher than their acidity (Alk > Acid), convex for waters with Acid > Alk, and concave when Acid ⩾ Alk. Consequently, the buffer capacity of water in the second type of samples is higher at the beginning of titration than late during its course. The situation is opposite for the third type of waters, while the buffer capacity of the first-type waters remains unchanging throughout the whole titration range of the samples. Here we consider the true buffer capacity, which is graphically determined as $\frac{db}{dpH}$ from the tangent of the titration curve slope at each of its titration points. The curves clearly demonstrate that the buffer capacity is at a maximum in highly alkaline and acidic humus-rich samples (which is obvious enough in comparison with low alkaline samples). The analysis of the dependence of $\frac{[H^+]}{[b]-[H^+]}$ on $[H^+]$ for most of the water samples demonstrates that this dependence is linear throughout the whole pH range (Fig. 2). Alkaline waters yield hyperbolic curves, whereas samples of acidic humic waters are characterized by negative ordinate values. In fact, these curves cannot be applied to determine the parameters of the straight line equation. These data also indicate that natural waters containing weak acids and their salts cannot be represented in the form of a solution of a salt of a weak acid whose titration curve is identical to that of a water sample. At the same time, the $\frac{[H^+]}{m}$ vs. $[H^+]$ graphic dependences for most of our water samples are straight lines (the correlation coefficients are >0.99), which were used to calculate (by least-square fitting) the coefficients for the

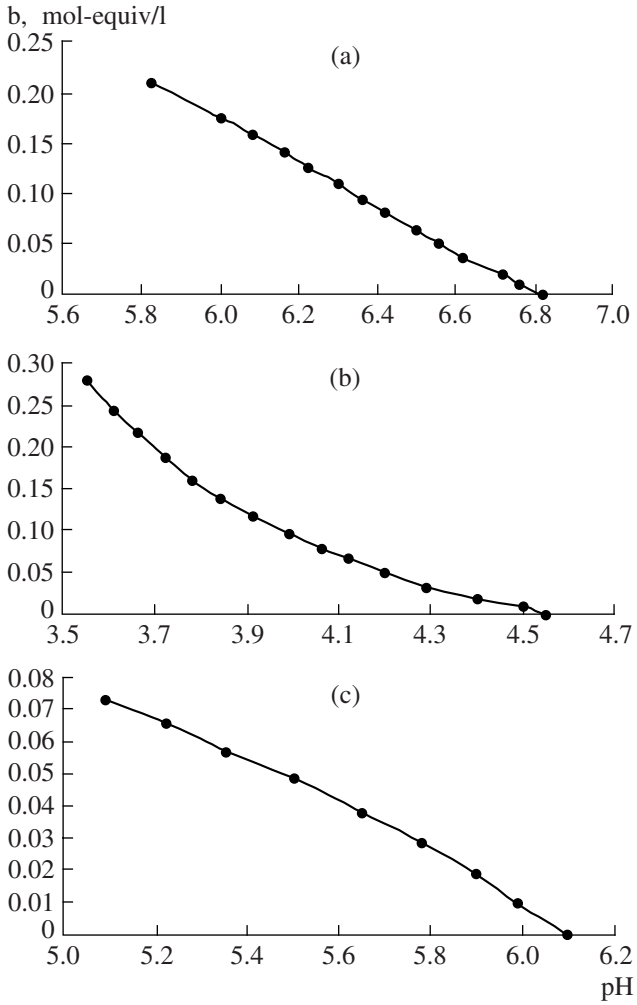

Fig. 1. Curves of potentiometric titration of water with strong acid. Water samples from (a) Lake Imatozero, (b) Lake Vuontelejarvi, and (c) Lake Ios-Puhjajarvi.

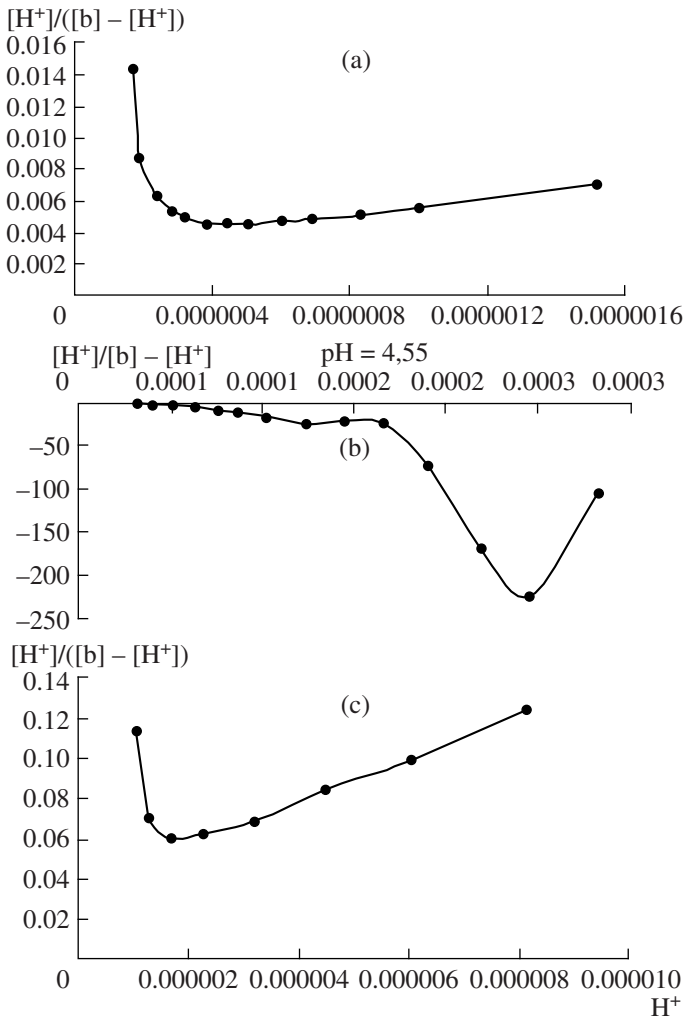

Fig. 2. Dependence of $\frac{[H^+]}{b - [H^+]}$ on $[H^+]$ for water samples from (a) Lake Imatozero, (b) Lake Vuontelejarvi, and (c) Lake Ios-Puhjajarvi.

line (Fig. 3). The later values were used to calculate the C_{tot} and pK (Table 2). The exceptions from the above dependence are water samples from Ukshezero Lake. These waters are highly alkaline and low acidic (Fig. 4). At the same time, this water shows a linear dependence according to Eq. (5). The statistical treatment of the titration curves allowed us to determine the values of C_{salt} and k and to calculate the initial concentration of weak acid and C_{tot}, i.e., parameters analogous to those in Eq. (6), which can be further used to calculate the buffer capacity of the water.

The C_{tot} of alkaline waters is, in fact, equal to the sum of their alkalinity and acidity, and the pK of these waters is close to the pK of carbonic acid according to its first dissociation reaction. The salt concentrations correspond to the alkalinity of water, and the concentration of weak acid corresponds to the acidity of the solution. The relations obtained for the alkalinity of waters is consistent with the following general rule: strong acid first of all titrates anions of weaker acids. In our situation, these are hydrocarbonates but not the anions of humic acids. The buffer capacity of water in these solutions is caused by the carbonate system of acid–base equilibria. With reference to humic acids, the calculated value of C_{tot} is close to the acidity of the water, and the concentration of the salt of weak acid is higher than the alkalinity but much lower than the concentrations of the anions of humic acids. The calculated pK value is higher than the pK of humic acids but lower than the pK of carbonic acid. In this situation, natural water can be envisioned as a two-component buffer system containing salt and acid in a solution, with the pK of the acid having an intermediate pK value between those of carbonic acid and humic acids. A situation resembling that

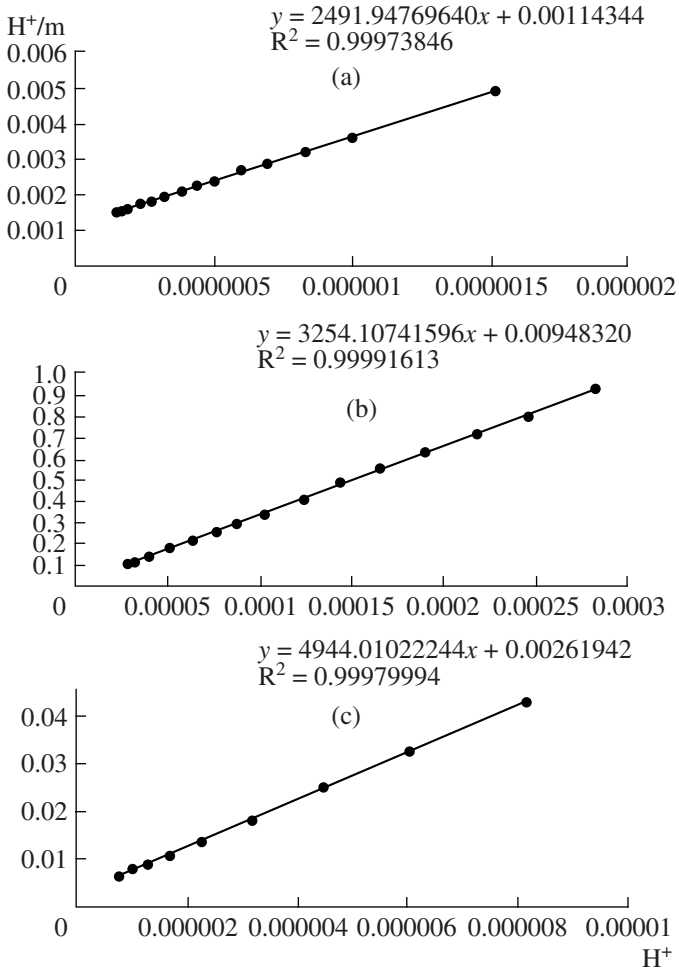

Fig. 3. Dependence of $\frac{[H^+]}{m}$ on $[H^+]$ for water samples from (a) Lake Imatozero, (b) Lake Vuontelejarvi, and (c) Lake Ios-Puhjajarvi.

with natural waters occurs with $NaHCO_3$, $NaHCO_3$ + $NaCH_3COO$, and $NaCH_3COO$ model solutions (Table 2).

We have demonstrated that the method of potentiometric titration can be used to determine the buffer system to which a natural water corresponds which has strong-acid titration curves analogous to those of the buffer solution.

The calculated buffer capacity values of alkaline waters with relatively low color indices are lower than the alkalinity and ANC (Table 2). The β values of highly humic waters is higher than their alkalinity but lower than ANC. The buffer capacity of natural waters increases with increasing alkalinity and humus contents of the waters. In acidic humic waters, a significant contribution to their buffer capacity is made by free hydrogen ions. The comparison of the value of β calculated according to Van Slyke with the treatment of potentiometric titration curves with the β_{exp}, which is determined from the tangent of the titration curve slope (b vs. pH) during the initial stage (β_{0exp}), demonstrates their almost complete identity.

The buffer capacity according to Van Slyke of alkaline waters from lakes Imatozero, Pryazhinskoe, and Syamozero and acidic humic waters from lakes Salonjarvi and Vuontelejarvi is lower than the buffer capacity of waters during a change of their pH by one unit (β_{1exp}), whereas the situation with low alkaline waters is opposite. In the latter case, the low concentration of hydrocarbonates in the solution results in the rapid exhaustion of the alkalinity potential of the water when strong acid is added to it.

The reason for the elevated resistance of acidic humic waters to acidification is the acidic chemistry of these waters. These waters are characterized by a significant contribution of the second summand in the Van Slyke equation to the buffer capacity. At the same time, the ANC index does not reflect these relations and cannot be directly used as an indicator of the acid-neutralizing capacity of waters. The parameter adequately

Table 2. Calculated parameters of model solutions

Water body	pH	C_{tot}	C_{salt}	C_{acid}	$\beta_{Van\ Slyke}$	β_{0exp}	β_{1exp}
		mmol-equiv/l					
L. Imatozero	6.34	0.401	0.302	0.099	0.17	0.22	0.21
L. Pryazhinskoe	6.40	0.304	0.212	0.092	0.14	0.13	0.16
L. Ukshezero	6.44	0.570	0.479	0.091	0.18	0.22	0.28
L. Syamozero	6.15	0.214	0.157	0.053	0.10	0.12	0.12
L. Iso-Puhjajarvi	6.28	0.202	0.077	0.125	0.11	0.09	0.07
L. Soujarvi	6.30	0.168	0.056	0.112	0.09	0.06	0.06
Shuya R.	6.22	0.197	0.058	0.139	0.10	0.07	0.06
L. Lizhmenskoe	6.52	0.131	0.041	0.090	0.06	0.05	0.04
L. Salonjarvi	5.90	0.118	0.032	0.086	0.07	0.08	0.11
L. Vuontelenjarvi	5.54	0.307	0.033	0.274	0.12	0.12	0.28
Model solutions							
$NaHCO_3$ 0.0625 mmol-equiv/l	6.43	0.11	0.06	0.05	0.06	–	0.04
$NaHCO_3$ +CH_3COONa 0.125 mmol-equiv/l	6.41	0.13	0.08	0.05	0.07	–	0.06
CH_3COONa 0.0625 mmol-equiv/l	5.73	0.10	0.05	0.05	0.06	–	0.05

reflecting the true resistance of waters to their acidification is the buffer capacity of these waters but not their formal ANC index. Proceeding from the data presented above for the buffer capacity, it can be concluded that water bodies with waters of elevated alkalinity and acidic humic waters are the most resistant to acidification, while low-alkalinity waters are weakly resistant to acidification.

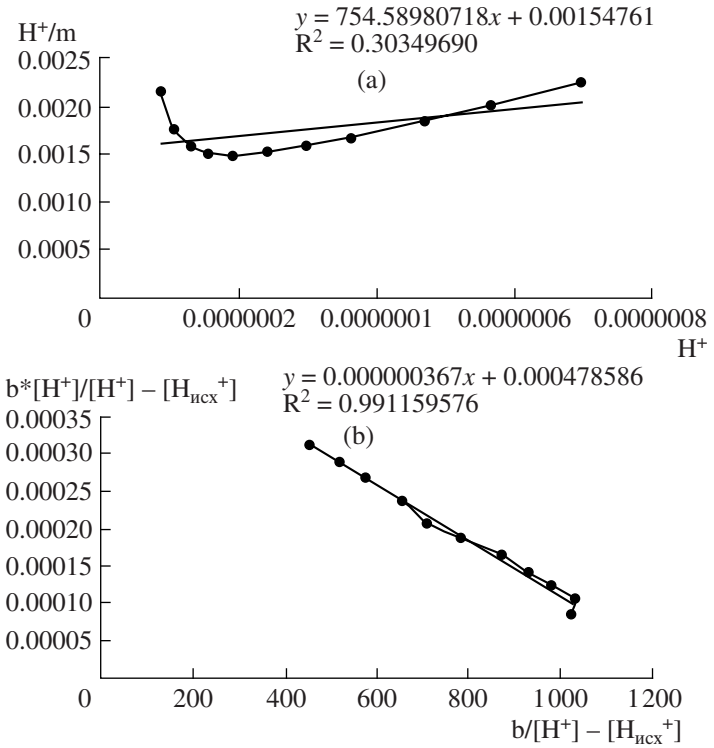

Fig. 4. Dependences of (a) $\frac{[H^+]}{m}$ on $[H^+]$ and (b) $\frac{b[H^+]}{[H^+] - [H^+]_{ini}}$ on $\frac{b}{[H^+] - [H^+]_{ini}}$ for water from Vkshezero Lake.

CONCLUSIONS

1. Based on the theoretical and experimental research, we determined that natural water with a complicated composition of components of acid–base interactions can be envisioned as a two-component buffer system containing a salt and acid, whose curves of titration with a strong acid are analogous to the curves of the original water.

2. The processing of data on water titration curves with a strong acid allowed us to calculate the concentration of salt in the solution and the dissociation constant for the weak acid. The parameters thus obtained can be used to determine the true buffer capacity of the water according to Van Slyke.

3. It was determined that buffer capacity reflects the actual resistibility of waters to acidification, in contrast to the currently widely applied indicator of the acid-neutralizing capacity of waters.

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