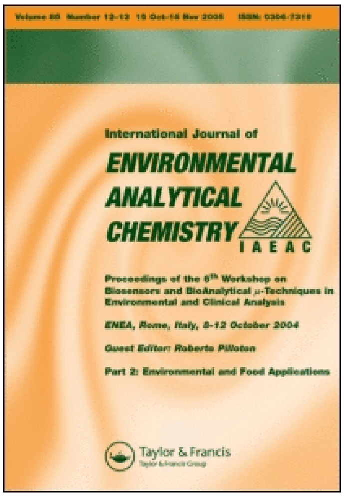

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

The Cumulation of Alkali Earths and Alkali Metals on Alga

J. Starý[a]; K. Kratzer[a]; J. Prášilova[a]
[a] Department of Nuclear Chemistry, Czech Technical University, Praha 1, Břehová 7, Czechoslavakia

To cite this Article Starý, J. , Kratzer, K. and Prášilova, J.(1983) 'The Cumulation of Alkali Earths and Alkali Metals on Alga', International Journal of Environmental Analytical Chemistry, 14: 3, 161 — 167
To link to this Article: DOI: 10.1080/03067318308071616
URL: http://dx.doi.org/10.1080/03067318308071616

Intern. J. Environ. Anal. Chem., 1983, Vol. 14, pp. 161–167
0306-7319/83/1403-0161 $18.50/0

Printed in Great Britain

The Cumulation of Alkali Earths and Alkali Metals on Alga

J. STARÝ, K. KRATZER and J. PRÁŠILOVA

Department of Nuclear Chemistry, Czech Technical University, 11519 Praha 1, Břehová 7, Czechoslavakia

(Received May 10, 1982)

The cumulation of strontium, cesium, rubidium and sodium on alga has been radiometrically investigated at different pH and at different concentrations of elements studied in the absence and in the presence of other salts. It has been found that the cumulation can be quantitatively described using the affinity constants K_M. The cumulation decreases in the order ($\log K_M$-values are given in brackets): H^+ (6.2), Ba^{2+} (4.8), Sr^{2+} and Ca^{2+} (4.6), Mg^{2+} (4.2), Cs^+, Rb^+ and NH_4^+ (2.9), K^+ (2.7), Na^+ (2.6) and Li^+ (2.4).

KEY WORDS: Alkali earths, alkali metals, alga Chlorella kessleri, Scenedesmus obliquus.

INTRODUCTION

In our previous communications a detailed study of the cumulation of chromium(III) and (VI),[1] zinc, cadmium and mercury(II),[2,3] arsenic(III) and (V), methylarsonic acid and dimethylarsinic acid[3] on different types of alga has been carried out using radiometrical method. In the continuation of these investigations the cumulation of strontium, cesium, rubidium and sodium on alga Chlorella kessleri and Scenedesmus obliquus has been studied in order to describe quantitatively the cumulation of these elements on alga.

EXPERIMENTAL

Reagents and apparatus

Unless otherwise stated, all reagents were of analytical reagent grade purity.

Hydrochloric acid and sodium hydroxide, suprapure (Merck) were applied for adjusting of pH.

Solutions of radionuclides (Swierk, Poland and Isotope, Moscow, USSR) were prepared by the dilution of the stock solution of strontium-85 chloride (specific activity 150 GBq/g Sr), cesium-137 chloride (carrier-free), rubidium-86 chloride (10 GBq/g Rb) and sodium-22 chloride (11.000 GBq/g Na). Algologically and bacteriologically pure strains of alga Chlorella kessleri (the mean geometric volume of one cell $V_a = 3.4 \times 10^{-11}\,cm^3$, the mean geometric surface of one cell $S_a = 5 \times 10^{-7}\,cm^2$) and Scenedesmus obliquus ($V_a = 5.4 \times 10^{-11}\,cm^3$, $S_a = 5.9 \times 10^{-7}\,cm^2$) were used in the experiments.

The scintillation counter with the NaI(Tl) crystal was used for the radioactivity measurements, Radiometer pH M-52 (Copenhagen, Denmark) for the determination of the equilibrium pH.

Procedure

An appropriate volume of alga suspension (containing a known amount of alga cells) was centrifuged and the supernatant was discarded. Then 5 ml of distilled water were added and the suspension was transferred into a test tube with ground glass stopper containing radionuclide investigated (initial concentration of order $10^{-7}\,mol.L^{-1}$), suitable amount of metal salts, hydrochloric acid or sodium hydroxide. The total volume was made 10 ml. The suspension was shaken for 3 hours. After an appropriate interval, 3.0 ml of the suspension was pipetted into a centrifugation tube and centrifuged for 3 min. The equilibrium pH-value, the radioactivity of alga A_a (corrected for the radioactivity sorbed on the measuring vessel) and that of the medium A_m were measured and the cumulation factor F was calculated according to equation

$$F = \frac{A_a}{A_m \cdot N_a \cdot V_a} \qquad (1)$$

where N_a denotes the number of alga cells in $1\,cm^3$, V_a — the mean geometric volume of one cell in cm^3.

All experiments were carried out at $22 \pm 1°C$.

RESULTS AND DISCUSSION

The cumulation factors F of strontium on alga Chlorella kessleri at different pH, at different strontium concentration and at different concentration ($mol.L^{-1}$) of cation M (present as chloride or nitrate) are given on Figure 1. The maximum value of the cumulation factor F_0 was reached at pH 7–10 at lowest concentration of strontium: $F_0 = 1.500 \pm 300$

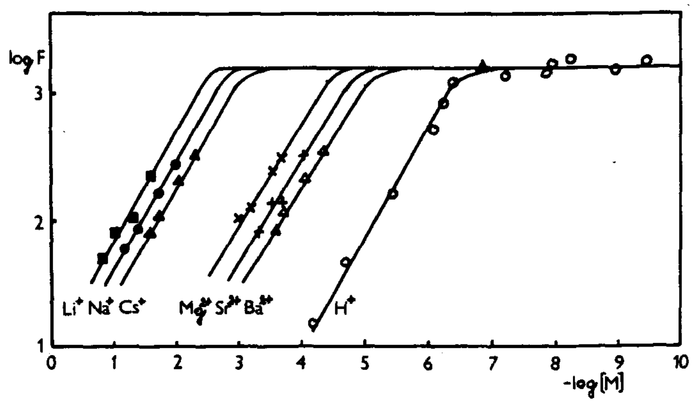

FIGURE 1 The cumulation factor F of strontium on alga Chlorella kessleri ($N_a = (8-12) \times 10^6$ cells.mL^{-1}) at different equilibrium concentrations (mol.L^{-1}) of cations M.

($\log F_0 = 3.2 \pm 0.1$). The cumulation decreases with the increase of hydrogen ion concentration and with the increase of strontium and other metal salts concentrations (pH = 7–8). The curve $\log(F_0/F - 1)$ vs. $\log[M]$ (where $[M]$ denotes the equilibrium concentration of cation M) has a slope equal to one which does not depend on the charge of M (see Figure 2).

These results can be interpreted as follows: strontium ion (the charge is omitted) reacts with alga A according to

$$Sr + A = SrA \tag{2}$$

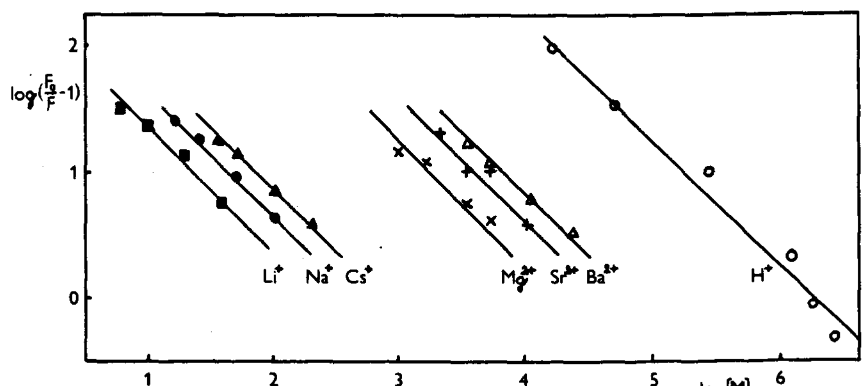

FIGURE 2 The dependence of $\log(F_0/F - 1)$ vs. $\log[M]$ for different cations M.

The affinity constant for strontium K_{Sr} can be expressed as follows:

$$K_{Sr}=\frac{[SrA]}{[Sr][A]}=\frac{F}{[A]} \tag{3}$$

where $[A]$ denotes the "free (equilibrium) capacity" of algal cells to cumulate strontium ions. At very low concentrations of strontium and hydrogen ions in the absence of other salts, the cumulation factor reaches its maximum value, i.e. F_0. In these conditions, the following equation is valid:

$$K_{Sr}=\frac{F_0}{c_A} \tag{4}$$

where c_A is the maximum "capacity" of algal cells to cumulate strontium ions.

The increase of strontium concentration leads to the decrease of the cumulation because of the decrease of the free capacity:

$$c_A=[A]+[SrA]=[A](1+K_{Sr}[Sr]). \tag{5}$$

By combination of Eqs. (3)–(5) it follows:

$$\frac{F_0}{F}-1=K_{Sr}[Sr]. \tag{6}$$

Other alkali earths and alkali metals M compete with the cumulation of strontium and the following equation is valid for the distribution of strontium present at very low concentrations at pH > 7:

$$\frac{F_0}{F}-1=K_M[M]. \tag{7}$$

The influence of hydrogen or ammonium ions can be expressed in a similar manner.

The log K_M-values calculated according to Eqs. (6) and (7) are summarized in Table I. These data are in a good agreement with K_M-values determined from our investigations of the cumulation of barium-133 on alga Scenesdesmus obliquus.[4]

The affinity constants for cesium, rubidium and sodium were also calculated from the study of the cumulation of the above elements on alga

TABLE I

The determination of the affinity constants K_M from the study of the cumulation of strontium on alga Chlorella kessleri.

Cation M	$-\log[M]$	F_0/F	$\log K_M$	$\log K_M$ mean
Ba^{2+}	4.35	4.5	4.89	
	4.03	7	4.81	4.81±0.06
	3.72	12.5	4.78	(4.90±0.03)[a]
	3.53	17.5	4.73	
Sr^{2+}	4.03	5.0	4.63	
	3.72	12	4.76	4.63±0.10
	3.53	11	4.53	(4.55±0.17)[a]
	3.31	20	4.59	
Ca^{2+}	4.03	6	4.73	
	3.72	11	4.72	4.66±0.08
	3.41	18	4.64	(4.56±0.13)[a]
	3.16	26	4.56	
Mg^{2+}	3.72	5.3	4.35	
	3.53	6.6	4.28	4.27±0.09
	3.23	13	4.31	(4.00±0.11)[a]
	3.00	15	4.15	
Cs^{+}	2.30	5	2.90	
	2.00	8	2.85	2.84±0.06
	1.70	15	2.85	
	1.52	18	2.74	
Rb^{+}	2.30	5	2.90	
	2.00	9	2.90	2.86±0.06
	1.70	14	2.81	
	1.52	22	2.84	
NH_4^{+}	2.00	9	2.90	
	1.70	15	2.85	2.82±0.07
	1.40	24	2.76	
	1.22	36	2.76	
K^{+}	2.00	7	2.78	
	1.70	11	2.70	2.66±0.10
	1.40	15	2.55	(2.75±0.07)[a]
	1.22	26	2.62	
Na^{+}	2.00	5.6	2.66	
	1.70	10	2.65	2.66±0.01
	1.40	19	2.66	(2.51±0.13)[a]
	1.22	28	2.65	

TABLE I (continued)

Cation M	$-\log[M]$	F_0/F	$\log K_M$	$\log K_M$ mean
Li^+	1.60	7	2.38	
	1.30	15	2.45	2.36 ± 0.07
	1.00	23	2.34	
	0.77	33	2.28	
H^+	6.4	1.5	6.10	
	6.25	1.9	6.20	
	6.10	3.3	6.46	6.25 ± 0.15
	5.45	11	6.45	$(6.15 \pm 0.06)^a$
	4.7	35	6.23	
	4.2	100	6.20	

[a]Mean value of log K_M obtained from the study of the cumulation of barium on alga Scenedesmus obliquus.

Scenesdemus obliquus at different concentrations of metal studied. The following $\log K_M$-values were obtained: ~ 3, 2.8 and 2.6 for cesium, rubidium and sodium, respectively.

The maximum capacity of alga Chlorella kessleri used to cumulate strontium ions can be calculated from experimentally determined K_M and F_0-values using Eq. (4): $c_A \sim 0.04\,\mathrm{mol.L^{-1}}$. Approximately the same value was calculated directly from the maximum concentration of strontium ion on alga at pH > 7.

Under the assumption that c_A value is constant for all alkali earths and alkali metals it follows from Eq. (4):

$$\frac{K_{Sr}}{K_M} = \frac{F_{0,Sr}}{F_{0,M}} \tag{8}$$

F_0-values depend on the size of algal cells,[1] however, the product $F_0 \cdot V_a \cdot S_a^{-1}$ is approximately constant for all alga species.[3] Thus, the log F_0-values for alga Chlorella kessleri used decrease in the order ($\log F_0 \cdot V_a \cdot S_a^{-1}$ are given in brackets): 3.4 (−0.8) for barium, 3.2 (−1.0) for strontium and calcium, 2.8 (−1.4) for magnesium, 1.5 (−2.7) for cesium, rubidium and ammonium ions, 1.3 (−2.9) for kalium, 1.2 (−3.0) for sodium and 1.0 (−3.2) for lithium ions.

Experimentally determined $\log F_0$-value for barium equals 3.5 ± 0.1 using alga Scenedesmus obliquus ($V_a = 3.1 \times 10^{-11}\,\mathrm{cm^3}$, $S_a = 5.2 \times 10^{-7}\,\mathrm{cm^2}$, $\log F_0 \cdot V_a \cdot S_a^{-1} = -0.7$).[4] F_0-values for alkaline metals are very small and cannot be determined with a sufficient precision. The following log F_0-values were determined using alga Scenedesmus obliquus: ~ 2, 1.7 and 1.0 for cesium, rubidium and sodium, respectively.

The strong tendency of algal cells to cumulate hydrogen ions[2,3] suggests that the c_A-value for hydrogen ions is at least one order higher than that of alkali earths and alkali metals. From that reason the $\log F_0$-value for hydrogen ions should be higher than 5.8 ($\log F_0 \cdot V_a \cdot S_a^{-1} > 1.6$) for alga Chlorella kessleri used.

Acknowledgement

The authors express their thanks to Mrs. T. Vrbská for her technical assistance.

References

1. J. Starý, B. Havlík, A. Zeman, K. Kratzer, J. Prášilová and J. Hanušová, *Acta Hydrochim. Hydrobiol.* **10,** 251 (1982).
2. J. Starý, B. Havlík, K. Kratzer, J. Prášilová and J. Hanušová, *Acta Hydrochim. Hydrobiol.*, in press.
3. J. Starý and K. Kratzer, *Intern. J. Environ. Anal. Chem.*, **10,** 65 (1982).
4. J. Starý, B. Havlík, K. Kratzer, J. Prášilová and J. Hanušová, *Acta Hydrochim. Hydrobiol.*, in press.