ACTIVITY COEFFICIENTS OF SOME SODIUM AND POTASSIUM PHOSPHATES*

by

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There is a considerable body of evidence which suggests a rather close relationship between the uptake of potassium, the uptake of phosphate, and the utilization of glucose by cells, tissues and micro-organisms[1]. The uptake of glucose is thought to be associated with its phosphorylation at the cell surface[2,3]. Potassium ion has been found to enhance specifically the activity of certain phosphorylating enzymes, in particular, phosphoferase and fructokinase[4]. In addition there is more direct chemical evidence indicating that the interaction of sodium and potassium with certain polyphosphates is rather specific[5,6]. In considering the carrier hypothesis of ion transport across cell membranes and the biological specificity of sodium and potassium, knowledge of the chemical interaction of these two ions with various organic and inorganic phosphoric acids seems highly desirable.

The ionic interaction of sodium and potassium with various organic phosphoric acid esters, inorganic pyrophosphoric acid and polyphosphoric acid in aqueous solution were measured. An electrochemical cell with liquid junction incorporating a collodion cation-exchange membrane prepared according to the method of GREGOR AND SOLLNER[7] was employed. This electrochemical cell may be designated as follows:

$$\underset{}{\text{Ag, AgCl,}} \quad \underset{(1)}{\text{Me}^+ \text{Cl}^-} \;\vdots\; \underset{M}{} \;\; \underset{(2)}{\text{Me}^+ \text{P}^{-z}} \;|\; \underset{J}{} \quad \text{sat. KCl, } Hg_2Cl_2\text{, Hg}$$

Me^+ is either sodium or potassium ion, P^{-z} is the phosphate anion, M is the collodion cation-exchange membrane, and J, the liquid junction. The potential of this cell is given by

$$E = E_o' - \frac{RT}{F} \ln \frac{m_{Me_2} \cdot \gamma_{Me_2}}{m_{Me_1} \cdot \gamma_{Me_1}}$$

in which E_o' is taken as the measured potential when solution (2) is identical with solution (1), m is the concentration in moles per kilogram of water and γ is the activity coefficient. This electrochemical cell is found to give reliable measurements in the concentration range 0.001 M to 0.1 M if the pH is greater than 6.5. All measurements are made at 25.4° C.

The ionic interactions, interpreted as $-\log \gamma$, occurring in the solutions of sodium and potassium glucose-1-phosphate, glucose-6-phosphate, and glycerophosphate were found to be quantitatively accounted for in terms of the DEBYE-HÜCKEL ion attraction theory. In solutions of the fructose 1,6-diphosphates and adenosine triphosphates the correct theoretical limiting slope was apparently approached, but at higher concentrations deviations from theory occurred. These deviations were of such a nature as to indicate that, for theoretical fit, the molecules are best considered as divalent ions at twice their actual weight formal concentration. The behaviour of the inorganic pyrophosphates did not appear to be adequately explained in terms of the DEBYE-HÜCKEL theory. In the case of all of these salts the degree of interaction with sodium and with potassium ion was nearly identical, the differences being in general only slightly greater than experimental error.

The interaction of sodium and potassium with inorganic polyphosphate, prepared according to the method of LAMM AND MALMGREN[5], was most conveniently interpreted in terms of a mass action dissociation constant, assuming activity coefficients of the "free" ions comparable to that of sodium and potassium chloride solutions at the same activity and assuming independent behaviour of the phosphate unit residues. The pK's calculated in this manner were found to vary between values of 2 and 3 in the concentration range investigated, the variation being an almost linear function of the square root of the free ion concentration. In contrast to previous investigators[6],

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the pK values for the sodium salt and the potassium salt were found to differ only slightly, varying from 0.2 to 0.3, the value for the sodium salt being the greater.

These results indicate that within the latitude of interpretation possible from behaviour in aqueous solution, the compounds mentioned above are probably not directly involved as carriers in a biological mechanism serving to transport and concentrate the alkali ions. Nor does it appear possible that these substances bind intracellular potassium specifically.

A detailed report of the techniques employed and the results obtained in this investigation will be published elsewhere. The author is greatly indebted to Professor F. O. SCHMITT for his advice in this investigation.

REFERENCES

1 H. B. STEINBACH, *Ann. Rev. Physiol.*, 13 (1951) 21.
2 J. SACKS, *Cold Spring Harbor Symp. Quant. Biol.*, 13 (1948) 180.
3 M. D. KAMEN AND S. SPIEGELMAN, *Cold Spring Harbor Symp. Quant. Biol.*, 13 (1948) 151.
4 H. A. LARDY, *Phosphorus Metabolism*. W. D. MCELROY AND B. GLASS, Editors, Baltimore, 1951.
5 O. LAMM AND H. MALMGREN, *Z. anorg. Chem.*, 245 (1941) 103.
6 J. R. VAN WAZER AND D. A. CAMPANELLA, *J. Am. Chem. Soc.*, 72 (1950) 655.
7 H. P. GREGOR AND K. SOLLNER, *J. Phys. Chem.*, 50 (1946) 53.

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ZUR WIRKUNGSWEISE VON WUCHS- UND HEMMSTOFFEN

III. DIE WECHSELWIRKUNG VON INDOL-3-ESSIGSÄURE UND EOSIN IN LICHT UND DUNKELHEIT

von

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Die an früherer Stelle[1,2] geschilderten Versuche mit Lanolinpasten, welche sowohl Indol-3-essigsäure als auch Eosin in verschiedenen Mengenverhältnissen enthielten, betrafen Pasten, deren Herstellung bzw. Mischung bei Tageslicht erfolgt war, so dass eine photochemische Zerstörung oder Inaktivierung der Indol-3-essigsäure nicht auszuschliessen war. Es konnte eingewendet werden, dass sich die beobachtete Wuchsstoff-Hemmstoff-Wechselwirkung nicht am lebenden System (der Testpflanze) selbst abspielen müsse, sondern dass die gegenseitige Bewirkung von Wuchs- und Hemmstoff sich bereits vorher, auf rein chemischem Wege in der Paste selbst vollziehe, in dem durch die durch das Eosin ausgeübte Photosensibilierung eine teilweise Inaktivierung der Indol-3-essigsäure erfolgen könne. Für eine solche Annahme sprachen vor allem Versuche, welche im Institut von SKOOG (Madison, Wisc.) unter Verwendung des WENT'schen Agartestes durchgeführt worden sind. Dass die Verhältnisse im Pastentest jedoch anders liegen und die Belichtung der beide Stoffe enthaltenden Pasten keinen entscheidenden Einfluss auf den Ausfall der Versuche ausübt, zeigt die Fig. 1, welche sich auf einen in dreifacher Wiederholung ausgeführten Vergleichsversuch von Pasten bezieht, die teils dem Licht ausgesetzt, teils in Dunkelheit hergestellt und getestet wurden. Die Herstellung der Dunkelpasten erfolgte dabei so, dass eine Indol-3-essigsäure-Paste $2 \cdot 10^0$% sowie eine $2 \cdot 10^0$%ige Eosin-Paste bei schwachem künstlichen Licht eingewogen und angerührt wurde. Daraus wurden (ebenfalls im Licht) durch Vermischen mit entsprechenden Mengen reiner Lanolinpaste Verdünnungen $2 \cdot 10^{-1}$, $2 \cdot 10^{-2}$ und $2 \cdot 10^{-3}$% hergestellt. Nunmehr erfolgte die Vermischung jeweils gleicher Mengen von Indol-3-essigsäure- und Eosin-Pasten bei völliger Dunkelheit. Die Aufbringung der Pasten auf die Testpflanzen erfolgte im Schatten der weitgehend abgedunkelten Dunkelkammerlampe mit dem für Wuchsstoffarbeiten üblichen SCHOTT'schen Gelbfilter, wobei die