Selective Interaction of Dextran Sulfate with Inorganic Cations

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The counterion fixation by the polyion may be attributed to the tremendous values of electrical forces caused by a highly-charged polyelectrolyte. However, some differences in the counterion fixation could be observed; they may be attributed to the different radii of the hydrated counterions.[1] Though it is well known that the selective accumulation of potassium ions takes place in the living cell, the substance performing such a high selective accumulation has, unfortunately, never been found within the cell. On the other hand, the accumulation of potassium ions[2] takes place in some connective tissue, which has been said to be the one of the least active parts of the living system. The chondroitin sulfate is known as a polyelectrolyte, carrying many ionizable sulfate and carboxyl groups, and is also known as the main constituent of the connective tissues. It is of interest in this connection to see whether the accumulation of potassium ions can be attributed to the physico-chemical basis or to the metabolic basis.

TABLE 1. CRITICAL CONCENTRATIONS (M) OF CATIONS REQUIRED FOR THE PRECIPITATION OF ONE PER CENT DEXTRAN SULFATE SOLUTION*

Sample	M^+	K^+	Cs^+	M^{2+}	Ba^{2+}	M^{3+}
DS-1 (2.0)	—	0.35	0.28	—	0.015	—
DS-2 (0.2)	—	0.40	—	—	0.002	—
DS-3 (0.75)	—	—	—	—	0.006	—
DS-4 (2.0)	—	0.43	0.69	—	0.012	—
DS-5 (2.5)	—	0.26	0.39	—	0.016	—
DS-6 (1.0)	—	—	—	—	—	—
Chondroitin sulfate (0.5)	—	—	—	—	—	—
Alginate (0)	—	—	—	<0.01	<0.01	<0.01

* The sign, —, indicates no precipitation occured even when the concentrations of inorganic electrolyte reached 2 M. M^+ includes lithium, sodium and choline ion, M^{2+}, magnesium, calcium, strontium, nickel(II), cobalt(II), manganese(II) and cadmium ion, and M^{3+} aluminum and ferric ion. Dextran sulfate was abbreviated as DS and the smaller sample number indicates the higher molecular weight. The numericals in the brackets indicate the average number of sulfate ion per hexose ring.

TABLE 2. CRITICAL CONCENTRATION OF CATIONS REQUIRED FOR THE PRECIPITATION OF 12 PER CENT DEXTRAN SULFATE SOLUTION*

Added electrolyte	Critical concn., M
NaCl	6.0
KCl	0.28
RbCl	0.52
CsCl	0.44
$BaCl_2$	0.026

* The intrinsic viscosity of the dextran sulfate (DS-5) in 1 M sodium chloride solution was 0.028. The incipient aggregation of the dextran sulfate did not occur with the addition of saturated lithium chloride solution and in the presence of the 2 M solutions of the other ions described in Table 1.

In order to compare the effects of sulfate and carboxyl groups separately, sodium dextran sulfate and sodium alginate were chosen as species with these ionizable groups.

The sodium chondroitin sulfate and alginate used were commercial products. Ten kinds of sodium dextran sulfates, with various sulfate contents and molecular weights, were kindly supplied by the Meito Sangyo Co., Ltd. The inorganic electrolytes were all chlorides. The 2 M inorganic electrolyte solution was added to a one per cent solution of polyelectrolytes until the precipitation began to occur; the critical minimum concentration of electrolytes required for an incipient precipitation was taken as a measure of the ion interaction. The experiments were carried out at room temperature, 20±2°C. The results are summarized in Tables 1 and 2.

It may be seen in Table 1 that K^+, Cs^+ and Ba^{2+} showed a specific interaction with dextran sulfate, while the other ions examined had no specificity. It is likely that the formation of a precipitate in the presence of these ions may be attributed to their smaller hydrated ionic radii[1] or to the nature of their electron shells and to the resulting conformation of the salts.

Further, it may be seen in Table 1 that either the higher sulfate ion density or the higher molecular weight of the dextran sulfate is required for the specific interaction with the inorganic cations. For example, by comparing the behavior of DS-3

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1) I. Kagawa and H. P. Gregor, *J. Polymer Sci.*, **23**, 477 (1956).

2) N. R. Joseph, M. B. Engel and H. R. Catchpole, *Nature*, **192**, 1175 (1961).

with that of DS-4, the former has a higher molecular weight than the latter, although the former is smaller than the latter in the S-content; it may thus be seen that the higher sulfate ion density per monomer enhances the interaction. On the other hand, by comparing the behavior of DS-2 with that of DS-6, it may be seen that the molecular weight plays a greater role than the S-content.

On the other hand, the alginate exhibited no selective interaction with cations with the same charge, and the chondroitin sulfate, no any specific interaction with any of the inorganic ions examined. Though some specific interaction between the alginate and the inorganic ions could be observed,(3) this may be regarded as minor as compared with the specific interaction reported in this paper.

It can be seen in Table 2 that the effect of potassium, rubidium, and cesium ions is remarkably stronger than that of sodium ions. The results reported in this paper indicate that the polymeric structure of the hexose sulfate ion is responsible for the specific interaction.

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3) A. Katchalsky, R. E. Cooper, J. Upadhyay and A. Wasserman, *J. Chem. Soc.*, **1961**, 5198.