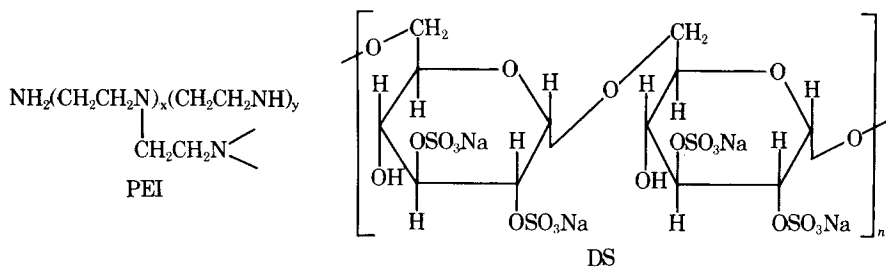


Polyelectrolyte Complex of Sodium Dextran Sulfate with Polyethyleneimine

This paper reports a novel chemical reaction of sodium dextran sulfate and polyethyleneimine leading to a polyelectrolyte complex. The aqueous solution of sodium dextran sulfate (DS) coreacted in an aqueous solution of polyethyleneimine (PEI) to form a water-insoluble precipitate which Miekka¹ called "polysalt."

The structures of PEI and DS estimated by Tokyo Kasei Co., Ltd., or by Meito Sangyo Co., Ltd., Japan, is as follows:



The experimental conditions, yield, and elemental analyses for the polyelectrolyte complexes are given in Table I. As seen in the table, the mole ratios of N/S in structural units of the polyelectrolyte complexes formed in the higher pH range or those formed in the larger amount of PEI were greater than those in the lower pH range because of lower dissociation of PEI solution or greater than those in the smaller amount of PEI. Thus, PEI and DS contents and pH in both solutions played an important role in determining the composition ratio of PEI to DS in the polyelectrolyte complex produced. In addition, the sodium and chlorine contents in the polyelectrolyte complexes compared with those in PEI and DS decreased considerably. These results indicate that the amine groups participate in the binding of DS, probably its OSO_3 group.

None of the polyelectrolyte complexes dissolved in water, most of them having swelled to a limited extent.

We were unable to find a solvent for our polyelectrolyte complexes. Thus, all the polyelectrolyte complexes were found to be insoluble, even when heated in a ternary solvent mixture such as water/dioxane/hydrochloric acid (5:47:48 wt-%) or in dimethylformamide, or in formic acid, or in dimethyl sulfoxide alone, though the polyelectrolyte complexes formed at pH 2.3 were only partially soluble when heated in the ternary solvent mixture water/acetone/potassium bromide (60:20:20 wt-%).

The colorimetric reaction by toluidine blue appeared throughout the interior of the polyelectrolyte complex, indicating an even dispersion of DS in the polyelectrolyte complex (expts. A-1, A-2, A-3, and B-1).

The mechanism of polyion interaction, the probable structures of the polyelectrolyte complexes, and their properties have been investigated in considerable detail by Michels et al.^{2,3}

A typical experimental procedure was as follows. The DS (molecular weight 640,000, sulfur content 18.6% as determined at the Meito Sangyo Co., Ltd., Japan) and the PEI (molecular weight 45,000, nitrogen content 30.5%, mole ratio of primary amine to secondary amine to tertiary amine 1:2:1 as determined at the Tokyo Kasei Co., Ltd., Japan) were from Meito Sangyo Co., Ltd., and Tokyo Kasei Co., Ltd.

DS solution was adjusted to pH 2.3 by passing through columns containing the cation exchange resin (Dowex 50W-X8) in the hydrogen form; and DS solution without passing through the cation exchange resin was adjusted to pH 7.0 or 10.4 by the use of sodium hydroxide solution. PEI solution which passed through columns containing the anion exchange resin (Amberlite 400) in the hydroxide

TABLE I
 Experimental Conditions,^a Polymer Yields, and Elemental Analyses of
 Polyelectrolyte Complexes^b

Expt. no.	Amount of PEI solution, ml PEI/100 ml DS	Mole ratio of N/S in solution	Yield of polymer, g	Nitrogen content, %	Sulfur content, %	Mole ratio of N/S in the polyelectrolyte complex
A-1 ^c	125	5:1	0.113	9.76	14.00	1.6
A-2 ^{c,f}	25	1:1	0.104	8.83	15.89	1.3
A-3 ^c	5	1:5	0.016	8.34	15.88	1.2
B-1 ^d	125	5:1	0.151	10.45	13.16	1.8
B-2 ^d	25	1:1	0.067	10.06	14.67	1.6
B-3 ^d	5	1:5	0.011	10.39	15.24	1.6
C-1 ^e	125	5:1	0.118	11.80	13.01	2.1
C-2 ^{e,g}	25	1:1	0.019	10.35	14.93	1.6
C-3 ^e	5	1:5	trace	—	—	—

^a Concentration of DS and PEI, 1 g/1000 ml.

^b The analyses were performed at the Rikagaku Research Institute, Japan.

^c Both DS and PEI solutions were adjusted to pH 2.3.

^d Both DS and PEI solutions were adjusted to pH 7.0.

^e Both DS and PEI solutions were adjusted to pH 11.0.

^f Carbon content, 25.82%; hydrogen content, 5.66%; chlorine content, 0.03%.

^g Carbon content, 26.71%; hydrogen content, 5.89%; sodium content, 0.015%.

form was adjusted to pH 2.3, 7.0, or 10.4 with hydrochloric acid solution. A solution of PEI was added dropwise to the DS solution at a rate of about 3 ml/min and stirring of the reaction system. The solution containing the polyelectrolyte complex was then kept for 30 min at room temperature. When the solution of DS was added dropwise to the PEI solution, a gelatinous precipitate formed under the experimental condition and could not be filtered out. There are primary amine, secondary amine, and tertiary amine groups in each molecule of PEI, i.e., four different basic groups which are reflected in the form of the titration curves. However, the inflection point of the amine groups was not detectable by potentiometric titration⁴ of PEI base.

The elucidation of the detailed structures and the antithrombogenic character of the polyelectrolyte complexes are currently under investigation.

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