Interaction of Sodium and Potassium Ions with Ionic Dextran Derivatives in Aqueous Solution with and without Added Salt

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Received November 7, 1972

ABSTRACT: The interactions of alkali ions with the ionic dextran derivatives—carboxymethyldextran, sulfopropyldextran, and dextran sulfate—were studied by measuring the counterion activity coefficients, the sound velocity and electric conductivity in aqueous solutions of polyelectrolytes with and without an added salt. In solutions without added salt, the counterion activity coefficients for the derivatives are fairly constant over the concentration range from 0.007 to 0.04 equiv per l., and decrease with an increase of the degree of substitution. The activity coefficients of Na$^+$ and K$^+$ ions for carboxymethyldextran have the same value, but the activity coefficient of the Na$^+$ ion is larger than that of the K$^+$ ion for dextran sulfate and the situation is reversed for sulfopropyldextran. The additivity of cationic activities holds for mixtures of the derivatives and simple salt except for the dextran sulfate–KCl system. For dextran sulfate having a degree of substitution 2.54 the activity coefficient of potassium ion is only 0.16 and the additivity of activity does not hold. This suggests that there exists a particular high degree of site binding of potassium ion to sulfate groups, in addition to the usual electrostatic diffuse binding. The existence of such a specific site binding of K$^+$ ion to sulfate groups was also demonstrated by measurements of the sound velocity and conductivity in solutions containing dextran sulfate and potassium chloride.

Single-ion activities of counterions in polyelectrolyte solution have been studied experimentally or theoretically and an additivity rule for counterion activities in mixtures of polyelectrolytes and simple salts has been reported by many authors.[2-12] Many kinds of polyelectrolytes, *e.g.*, carboxymethylcellulose, polyacrylate, poly(styrenesulfonate), poly(vinylsulfonate), and DNA, have been used for the measurements, but in most cases only the activities of Na$^+$ counterions were measured.

The degree of binding of cations to polyelectrolytes has also been studied by a variety of experimental methods. Strauss and Ross[13] reported that the counterion association by polyphosphate ions decreases in the order, Li$^+$ > Na$^+$ > K$^+$ > Cs$^+$ as determined by conductivity, electrophoresis, and membrane equilibrium measurements. Strauss and Leung[14] also tried to determine the degree of site binding of counterions—Li$^+$, Na$^+$, K$^+$, Mg^{2+}, and Ca^{2+}—to polyelectrolyte having different kinds of ionizable group by dilatometry. However, by this method it was impossible to determine quantitatively the degree of counterion binding to polyelectrolytes and consequently it was difficult to reach definite conclusions as to the dependence of the counterion activities on the nature of the polyion.

Recently it has become possible to use reliable cation-selective glass electrodes for the measurements of the activities of several cations. Podlas and Ander[10] measured the Na$^+$ and K$^+$ ions activities in carrageenan solutions, and found K$^+$ ion activity coefficient, γ_{K^+}, to be larger than γ_{Na^+} for both κ- and λ-carrageenan.

In our investigations of ionic polysaccharides, that is, dextran sulfate, carboxymethyldextran, and sulfopropyldextran having different degrees of substitution, the interaction of Na$^+$ and K$^+$ ions with these derivatives in aqueous solution has been systematically studied by a potentiometric technique using cation-sensitive glass electrodes, conductivity, and sound velocity measurements. The purpose of this paper is to compare the binding affinity of Na$^+$ and K$^+$ ions to different ionizable groups on the polyelectrolytes, which should contribute to an understanding of polyelectrolyte behavior and may help to elucidate certain biological phenomena.

Experimental Section

Materials. Three ionic dextran derivatives, dextran sulfate, carboxymethyldextran, and sulfopropyldextran, with different degrees of substitution, were used. These purified derivatives were kindly supplied by Research Institute of Meito Sangyo Co., Ltd., Nagoya. The properties of the dextran derivatives used in this study are summarized in Table I. The parent dextran, an anhydroglucose polymer mainly containing α-1,6-glucoside linkages, of these residues has a mean molecular weight of 50,000, determined by viscometry. An aqueous solution of about 1 per cent concentration of sodium salts of derivatives were passed through a mixed-bed ion-exchange resin column (Amberlite IR-120 and IRA-400). Completeness of the conversion was assured by a flame test and the acid form polymers thus obtained were neutralized with sodium or potassium hydroxide by potentiometric titration. The polyelectrolyte concentration was calculated from the potentiometric data.

Activity Measurement. Activities of sodium ion were determined with a Beckman 39278 and Horiba 1512 sodium ion electrodes. Potassium ion activities were determined with a Beckman 39173 cationic electrode. As a reference electrode a Beckman frit junction reference electrode was used.

The following procedure was employed in order to minimize the diffusion of KCl from the frit junction at the tip of the electrode which affects the results of activity measurements. The reference electrode was immersed in a saturated KCl solution in a glass tube (*ca.* 20 mm in diameter) with a branch and the saturated KCl solution is connected through a polyethylene tube to another glass tube (*ca.* 5 mm in diameter) with an orifice which operates instead of the frit junction of the reference electrode. The orifice at the tip of this glass tube was made in such a way that the electric resistance of saturated KCl solution through this orifice was 7–10 × 10^4 ohms at room temperature.

The glass electrodes were preconditioned for 1 week in a 0.1 *m* NaCl or KCl solution. All emf measurements were made with a Beckman 101900 research pH meter utilizing a 0.2 mV scale. In the activity range of 0.0005–0.1, the response of the electrode was in excellent agreement with the Nernstian slope of a 59.1 mV. In the case of the Beckman 39278 electrode, the slope deviates from

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(2) (a) R. E. Mock and C. A. Marshall, *J. Polym. Sci.*, **13**, 263 (1954); (b) M. Nagasawa and I. Kagawa, *J. Polym. Sci.*, **25**, 61 (1959).

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Table I
Properties of Dextran Derivatives

Preparation	Sulfur Content (%)	Degree of Substitution	Mean Mol Wt of Derivative (Acid Form)
Dextran sulfate, DS-1	19.3	2.54	11.2×10^4
Dextran sulfate, DS-2	15.0	1.46	8.6×10^4
Dextran sulfate, DS-3	8.7	0.61	6.5×10^4
Carboxymethyldextran, CMD-1		2.50	9.4×10^4
Carboxymethyldextran, CMD-2		1.10	6.9×10^4
Sulfopropyldextran, SPD-1	14.6	2.20	13.2×10^4
Sulfopropyldextran, SPD-2	12.3	1.41	10.3×10^4
Sulfopropyldextran, SPD-3	10.0	0.92	8.4×10^4

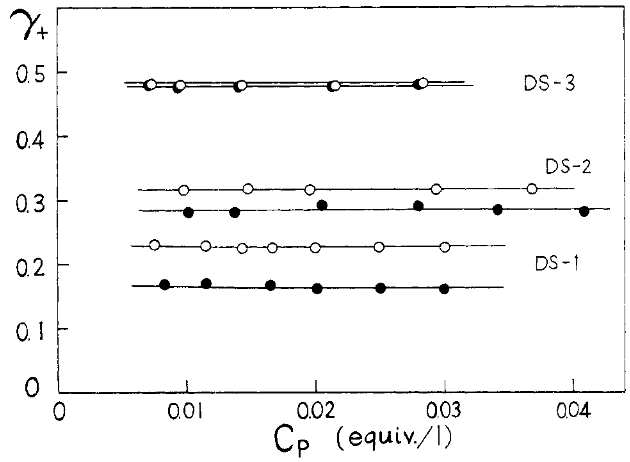

Figure 1. Counterion activity coefficients as a function of sodium and potassium dextran sulfate concentration in aqueous solution at 25°: (○) γ_{Na^+}; (●) γ_{K^+}.

the theoretical value by about 8% in the low activity range of 0.0005–0.005.

The value of emf for 0.1 *m* NaCl and KCl solutions was constant within 0.1 mV over 20 hr. Before and after emf measurement on a series of measured solutions, which takes 2 or 3 hr, calibration of the electrode was undertaken using two salt solutions of appropriate concentration. Readings were considered reliable if they were reproducible within ±0.1 mV. All measurements were made in a thermostat at 25 ± 0.02°.

Conductivity Measurement. The conductivity of the solutions was determined by means of an usual Wheatstone bridge circuit. The alternating current (1000 Hz) applied to the bridge was supplied by a Hewlett Packard 204C oscillator and the balance point of the bridge was detected by an audio detector, Yokogawa-Hewlett Packard 4402A, and an oscilloscope. A decade box, Yokogawa T-2786, served for readings to 111,111 ohms. The sensitivity of this apparatus was one part in 10^5. Measurements were also made in a thermostat at 25 ± 0.02°.

Sound Velocity Measurement. The sound velocity in solution was measured by the "sing-around pulse method" of high stability and precision developed by Greenspan and Tschiegg.[15] In our case, a 3-MHz blocking pulse oscillator was used and the sound velocity accurate to 1 cm/sec was measured.[16] This accuracy corresponds to the sensitivity of one part in 10^6, and to keep the sensitivity the measurements were carried in an accurate constant temperature bath at 25 ± 0.001°.

Results and Discussion

Single Ion Activity Coefficients in Pure Polyelectrolyte Solution. Figures 1, 2, and 3 represent the results of the measurements on the counterion activity coefficients in the pure polyelectrolyte solution without added salts. Sodium and potassium ion activity coefficients showed no polymer concentration dependence over the concentration range of 0.007–0.04 equiv/l. for all dextran derivatives. The average activity coefficients of counterions, $\langle\gamma_+\rangle$, are given in Table II.

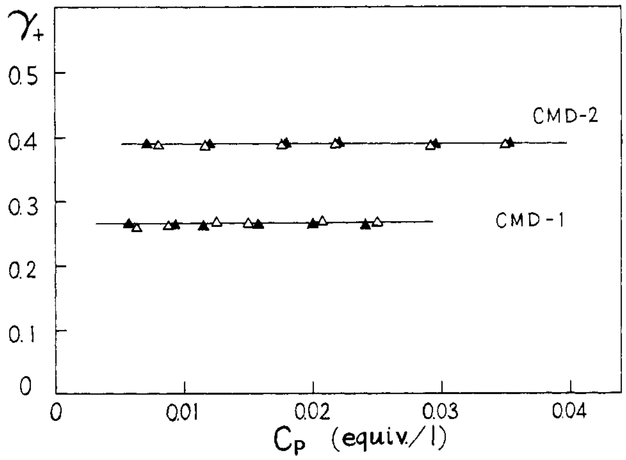

Figure 2. Counterion activity coefficients as a function of sodium and potassium carboxymethyldextran concentration in aqueous solution at 25°: (△) γ_{Na^+}; (▲) γ_{K^+}.

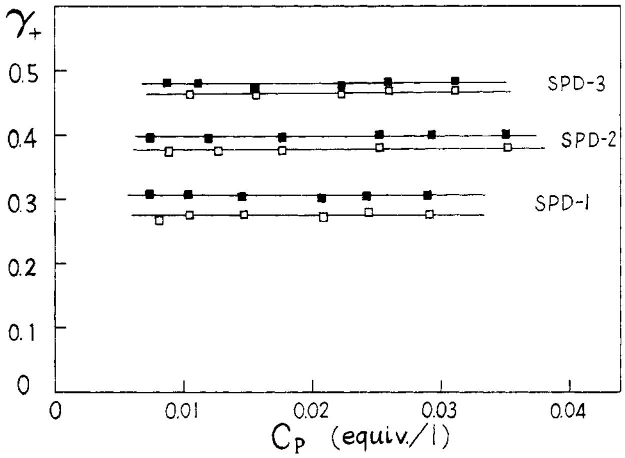

Figure 3. Counterion activity coefficients as a function of sodium and potassium sulfopropyldextran concentration in aqueous solution at 25°: (□) γ_{Na^+}; (■) γ_{K^+}.

It was found that $\langle\gamma_{Na^+}\rangle$ and $\langle\gamma_{K^+}\rangle$ were the same for carboxy derivatives of dextran at the same degree of substitution, but those for sulfate and sulfonate derivatives showed significant differences depending on the degree of substitution (Figure 4). The values of $\langle\gamma_{Na^+}\rangle$ and $\langle\gamma_{K^+}\rangle$ for both dextran sulfate and sulfopropyldextran decrease with an increasing degree of substitution. The result indicates that with a greater charge density on the polymer chain there is a greater degree of binding of the counterions as already reported by Hardisty and Neale[4] for sodium carboxymethylcellulose with degrees of substitution from 0.43 to 0.83. It is interesting that $\langle\gamma_{Na^+}\rangle$ is larger than $\langle\gamma_{K^+}\rangle$ for dextran sulfate and the situation is reversed for sulfopropyldextran, and that the differences between $\langle\gamma_{Na^+}\rangle$ and $\langle\gamma_{K^+}\rangle$ for these derivatives are larger the greater the degree of substitution. It is noteworthy that $\langle\gamma_{K^+}\rangle$ for dextran sulfate with a degree of substitution 2.54 is only 0.16 suggesting some specificity in the interaction of the polysulfate with potassium ions.

Addition of simple salts leads to the well-known decrease in the viscosity of polyelectrolyte solutions. We

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Table II
Counterion Activity Coefficients in Pure Dextran Derivative Solutions at 25°

Dextran Derivative	Degree of Substitution	$\langle\gamma_{Na^+}\rangle$	$\langle\gamma_{K^+}\rangle$
Dextran sulfate	2.54	0.22_8	0.16_4
	1.46	0.31_6	0.28_4
	0.61	0.48_1	0.47_7
Carboxymethyldextran	2.50	0.26_6	0.26_4
	1.10	0.38_9	0.39_3
Sulfopropyldextran	2.20	0.27_3	0.30_5
	1.41	0.37_7	0.39_6
	0.92	0.46_6	0.48_1

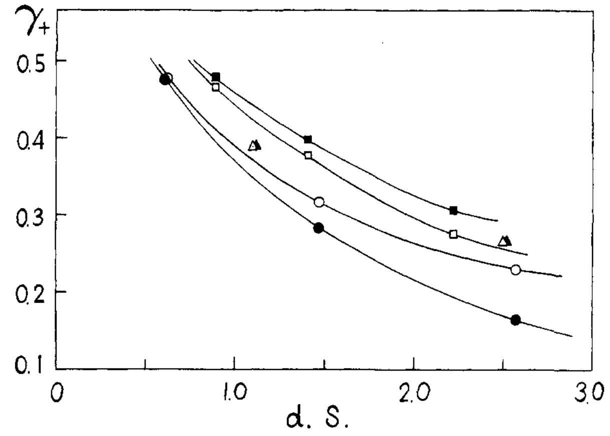

Figure 4. The relation between counterion activity coefficients and degree of substitution of dextran derivatives at 25°: (○) γ_{Na^+} for sodium dextran sulfate; (●) γ_{K^+} for potassium dextran sulfate; (△) γ_{Na^+} for sodium carboxymethyldextran; (▲) γ_{K^+} for potassium carboxymethyldextran; (□) γ_{Na^+} for sodium sulfopropyldextran; (■) γ_{K^+} for potassium sulfopropyldextran.

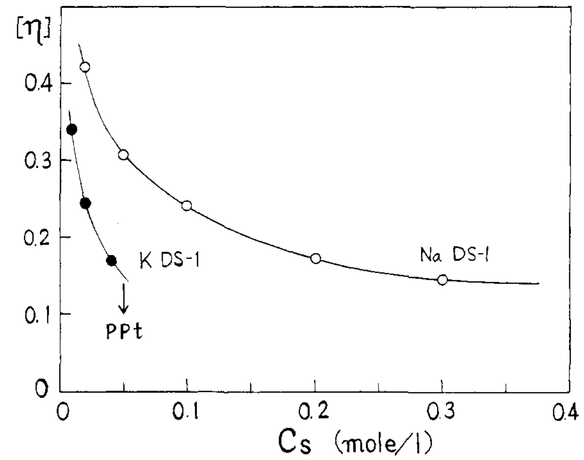

Figure 5. Intrinsic viscosity of dextran sulfate in salt solution at 25°: (○) in NaCl solution; (●) in KCl solution.

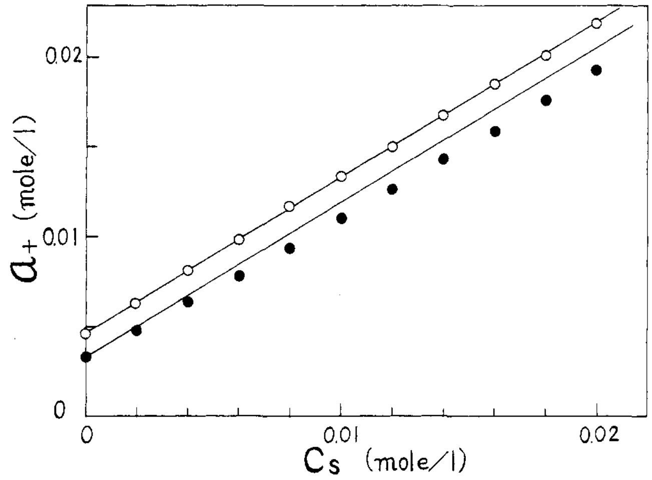

Figure 6. Counterion activities in solutions containing a constant amount of DS-1 and varying amounts of added salt at 25°; DS-1 concentration, 0.0200 equiv/l.: (○) a_{Na^+} (observed); (●) a_{K^+} (observed); solid line, calculated value, $a_+^{\mathrm{p}} + a_+^{\mathrm{s}}$.

measured the intrinsic viscosity of solutions containing dextran sulfate and salt (see Figure 5) and found that potassium dextran sulfate precipitated in 0.05 *M* KCl solution, while sodium dextran sulfate is soluble in NaCl solutions of concentrations above 1 *M*. This also indicates some specific interaction between potassium ion and dextran sulfate.

Single Ion Activity Coefficients in Polyelectrolyte Solution with Added Salt. The empirical rule of additivity of counterion activities in solutions of polyelectrolyte has been investigated extensively.[2,4-7,9,11] It can be written as

$$a_+^{\mathrm{obsd}} = a_+^{\mathrm{p}} + a_+^{\mathrm{s}} \qquad (1)$$

where a_+^{p} is the counterion activity of cations from the polyelectrolyte in pure polyelectrolyte solution, and a_+^{s} is the counterion activity of the salt cations in pure salt solution. The value of a_+^{s} is calculated from the known molal concentration of added salt using an extrathermodynamic assumption.[6]

We measured the counterion activities, a_+^{obsd}, in solutions containing a constant amount of dextran sulfate and varying amounts of added salt. The results are shown in Figure 6. Deviations from the additivity rule are usually characterized by

$$\Delta a_+ = \frac{a^{\mathrm{calcd}} - a^{\mathrm{obsd}}}{a^{\mathrm{obsd}}} 100 \qquad (2)$$

The additivity rule holds for sodium dextran sulfate plus NaCl system within 1.5%, but the deviation reaches 8.8% for potassium dextran sulfate with KCl. There have been other reports of deviations from the additivity rule, *e.g.*, in solutions of sodium poly(vinyl sulfate) + NaCl, magnesium poly(vinyl sulfate) + $MgCl_2$, sodium DNA + NaCl,[6] and sodium λ-carrageenan + NaCl, potassium λ-carrageenan + KCl systems,[10] in which cases the deviations from the additivity rule may exceed 10%.

We also examined the additivity rule for sodium carboxymethyldextran + NaCl and potassium carboxymethyldextran + KCl. The polymer concentrations of these systems were 0.0150 and 0.0147 equiv per l., respectively, and the maximum concentration of added salt was 0.02 *M*. It was found that deviations from the additivity rule for both cases were within 1.5%. Taking account of these results it is considered that there exists a different mode of binding between K+ ion and dextran sulfate, in addition to the usual electrostatic diffuse binding.

Sound Velocity Increment in Polyelectrolyte Solution with Added Salt. In order to obtain additional evidence on the behavior of counterions around polyion in the solution, the sound velocity increment, $\delta u = u_{\mathrm{s}} - u_{\mathrm{w}}$, in polyelectrolyte–salt mixtures was measured. Here u_{s} and u_{w} are the sound velocities in the solution and in pure water, respectively. We found u_{w} = 149,678 cm/sec at 25°. The results for δu in solutions containing a constant amount of dextran sulfate and varying amounts of added salt are

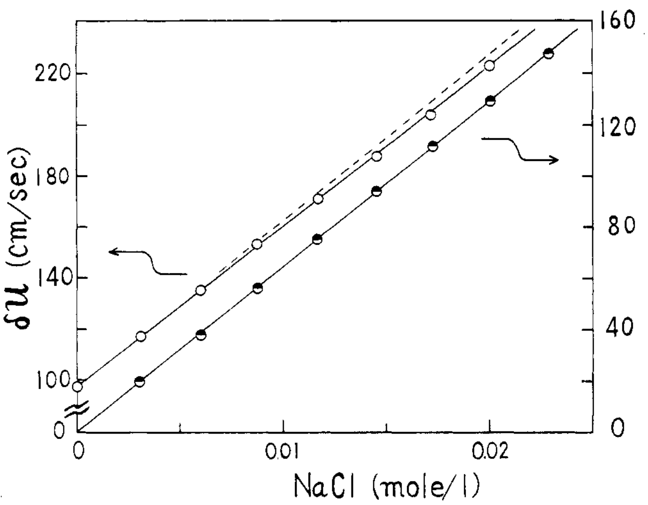

Figure 7. Sound velocity increment in sodium DS-1 and NaCl mixture and NaCl solution at 25°, DS-1 concentration, 0.0140 equiv/l.: (○) sodium DS-1 + NaCl; (◒) NaCl; broken line, calculated value.

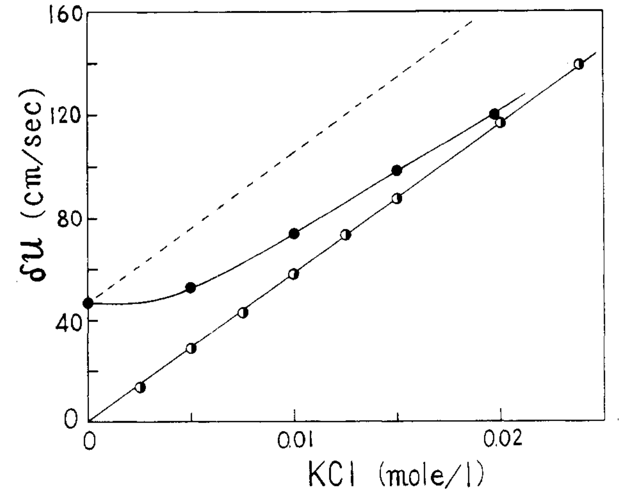

Figure 8. Sound velocity increment in potassium DS-1 and KCl mixture and KCl solution at 25°; DS-1 concentration, 0.0160 equiv/l.: (●) potassium DS-1 + KCl; (◑) KCl; broken line, calculated value.

shown in Figures 7 and 8. In a series of separate experiments we measured the sound velocity increment in aqueous solutions of HCl, NaCl, and KCl at various concentrations less than 0.03 *M* and also in mixtures of NaCl and HCl and of NaCl and KCl. It was found that the sound velocity is additive for dilute electrolyte solutions where no specific interaction exists between the component ions.

In the case of sodium dextran sulfate + NaCl, the additivity of sound velocity increment in the mixtures holds almost completely (see Figure 7), but in the system containing potassium dextran sulfate and KCl the observed values of the increment deviated significantly from the calculated values as shown in Figure 8. From this it is concluded that there is no specific interaction between dextran sulfate and Na^+ ion, but that in the case of K^+ ion the situation is different.

When counterions are bound to polyions, the release of the water of hydration decreases the sound velocity, since the adiabatic compressibility of water molecules bound by electrostriction to cations is negligibly small compared to water in bulk.[17,18] The decrease of δu in the mixture with

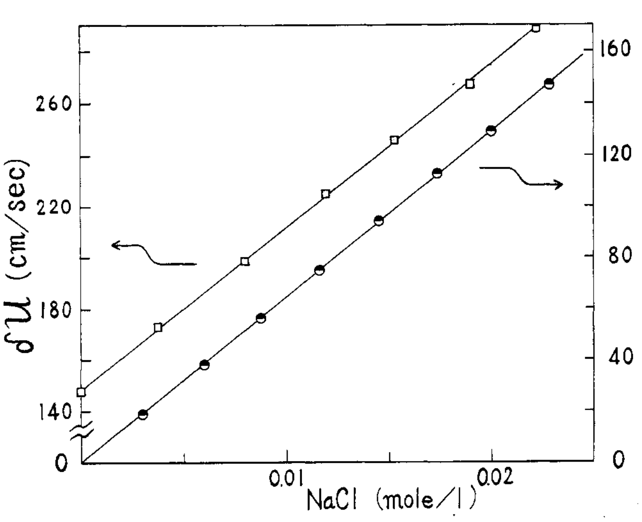

Figure 9. Sound velocity increment in sodium SPD-1 and NaCl mixture and NaCl solution at 25°; SPD-1 concentration, 0.0182 equiv/l.: (□) sodium SPD-1 + NaCl; (◒) NaCl.

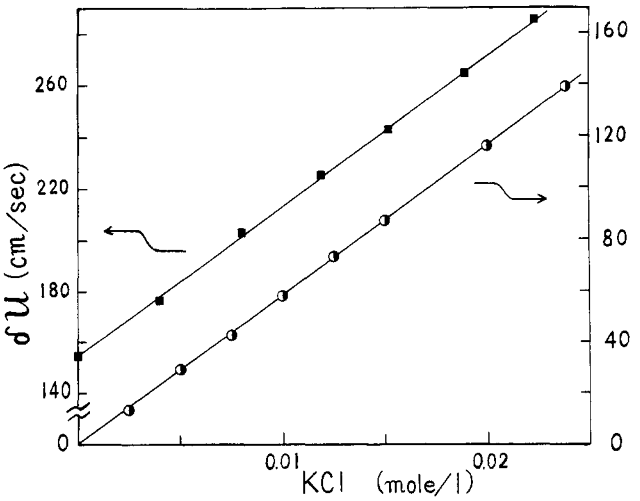

Figure 10. Sound velocity increment in potassium SPD-1 and KCl mixture and KCl solution at 25°; SPD-1 concentration, 0.0197 equiv/l.: (■) potassium SPD-1 + KCl; (◑) KCl.

the addition of KCl is therefore considered to be the result of complex formation between potassium ions and sulfate groups, leading to a release of water of hydration. In the case of sulfopropyldextran + salt, the observed sound velocity increments in the mixture are very close to the calculated increments (see Figures 9 and 10) as well as in the sodium dextran sulfate + NaCl system. Therefore, there seems to be no specific interaction of Na^+ and K^+ ions with sulfopropyldextran. The same results were also obtained for carboxymethyldextran + salt.

Specific Conductivity in Polyelectrolyte Solution with Added Salt. Specific conductivities, κ, of mixtures containing a constant amount of dextran sulfate and varying amounts of KCl or NaCl (see Figure 11) provided additional information. The per cent deviation of the observed value from those expected by simple additivity is characterized by

$$\Delta\kappa = \frac{\kappa^{\text{calcd}} - \kappa^{\text{obsd}}}{\kappa^{\text{obsd}}} 100 \qquad (3)$$

Table III gives the average, $\langle\Delta\kappa\rangle$, over the added salt concentration from 0.0025 to 0.02 *M*. In the case of specific conductivity additivity does not exactly hold for every system, but it is recognized that the deviation in the case

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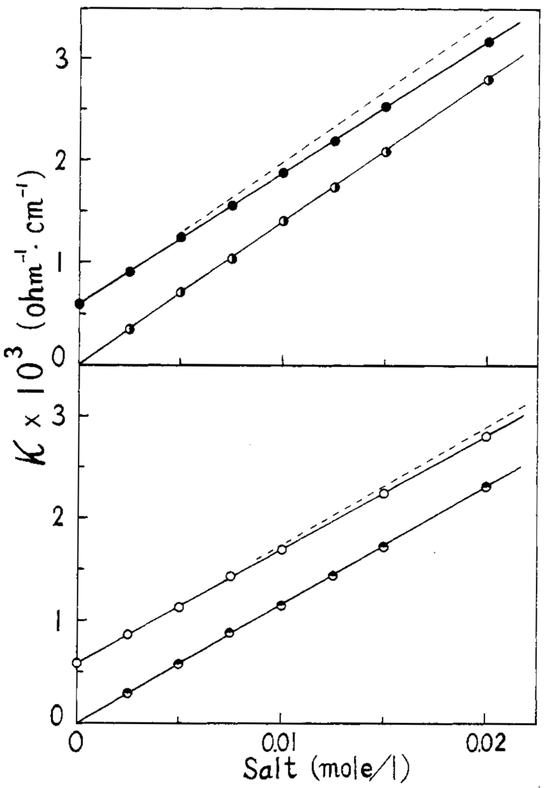

Figure 11. Specific conductivity in DS-1 and salt mixture and salt solution at 25°; sodium DS-1 concentration, 0.0242 equiv/l.: potassium DS-1 concentration, 0.0239 equiv/l.: (○) sodium DS-1 + NaCl; (◓) NaCl; (●) potassium DS-1 + KCl; (◑) KCl; broken line, calculated value.

of the potassium dextran sulfate + KCl system is clearly large compared with the other systems, and this is considered to be caused by a stronger association of K$^+$ ion to potassium dextran sulfate.

Podlas and Ander[10] found that γ_{K^+} values are higher than γ_{Na^+} for both κ- and λ-carrageenans but Schachat and Morawetz[19] found no difference in the carrageenan interaction with Na$^+$ and K$^+$. Both carrageenan molecules carry sulfate groups, so that these results contrast with our finding that γ_{Na^+} values are higher than γ_{K^+} for dextran sulfate with a high degree of substitution. We assume here that counterion activity coefficients depend only on the presence of sulfate groups and not on the side-chain structure or polymer conformation. It would be desirable to perform the measurements on the counterion activity for carrageenan molecules with a known density of sulfate groups, since our results indicate that the binding of Na$^+$ and K$^+$ ions to ionic dextran derivatives depends on the density of ionizable groups.

Table III
Average Deviation of Specific Conductivity, $\langle\Delta\kappa\rangle$, in the Mixing Solutions at 25°

System	C_p[a]	C_s[b]	$\langle\Delta\kappa\rangle$
Potassium dextran sulfate (DS-1) + KCl	0.239	0.0025–0.02	6.3
Sodium dextran sulfate (DS-1) + NaCl	0.0242	0.0025–0.02	3.0
Potassium carboxymethyl-dextran (CMD-1) + KCl	0.0251	0.0025–0.025	1.4
Sodium carboxymethyl-dextran (CMD-1) + NaCl	0.0248	0.0025–0.025	2.5
Potassium sulfopropyl-dextran (SPD-1) + KCl	0.0182	0.0025–0.02	1.4
Sodium sulfopropyl-dextran (SPD-1) + NaCl	0.0197	0.0025–0.02	2.1

[a] C_p, polymer concentration (equiv/l.). [b] C_s, salt concentration (mol/l.).

The most interesting result of our study is the finding that γ_{Na^+} is about 40% higher than γ_{K^+} for dextran sulfate with a high degree of substitution. If a system with a still higher density of sulfate groups could be made, the selectivity of the binding affinity for Na$^+$ and K$^+$ ions should be further enhanced, and a synthetic membrane containing condensed sulfate groups should be highly selective for the transport of K$^+$ over Na$^+$.

Acknowledgment. The authors thank Dr. T. Numasawa, Director of Research Institute of Meito Sangyo Co., Ltd., Nagoya, for supplying these materials.

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