Table VII
NMR Coupling Parameter $\Delta J = \langle J_{\mathrm{anti}} \rangle - \langle J_{\mathrm{syn}} \rangle$

x	Stereo-configuration	T, °C	ΔJ, Hz Exptl	ΔJ, Hz Calcd	$10^2\, d\Delta J/dT$, Hz K^{-1} Exptl	$10^2\, d\Delta J/dT$, Hz K^{-1} Calcd
2	m	26	$1.0^{a,d}$	0.6 ± 0.5		
	r	20	$3.6^{a,e}$	4.2 ± 1.3	−2.8	−1.5 ± 0.4
3	mm^{h}	26	$1.6^{a,d}$	0.9 ± 0.6		
	$\mathrm{m^*r}^{h,i}$	26	$1.0^{a,d}$	0.8 ± 0.5		
	$\mathrm{r^*m}^{h,i}$	26	$5.0^{a,d}$	6.2 ± 1.0		
	rr^{h}	26	$3.8^{a,d}$	5.4 ± 0.8	−1.2	−0.9 ± 0.2
∞	$(\mathrm{m})_\infty$	25	$1.3^{b,e}$			
		25	$1.9^{b,f}$	1.9 ± 0.6		
		25	$2.5^{b,g}$			
		140	$1.2^{c,d}$	2.2 ● 0.8		

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mental inaccuracies and the simplifications employed above.

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Electric Transport for Aqueous Solutions of Sodium Alginate and Sodium Polygalacturonate

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ABSTRACT: The electrical conductances and transport numbers were determined in aqueous solutions at 25° for sodium alginate and sodium polygalacturonate at several concentrations. The measurements indicated that the sodium polygalacturonate has a greater degree of dissociation than does the sodium alginate even though the latter has a smaller charge density. Measurements of the conductances of aqueous sodium chloride solutions of these polyelectrolytes at several concentrations of simple salt and of polyelectrolyte resulted in higher conductances for the sodium polygalacturonate solutions over the whole concentration range. A comparison of the electrophoretic mobilities at 0°C for both polyelectrolytes resulted in higher values obtained with the sodium polygalacturonate. The data were correlated with Manning's theory of polyelectrolyte solutions.

Ionic polysaccharides of both plant and animal origin appear to be of lesser interest for study than proteins and nucleic acids, yet they are of importance in all living matter. With our interest in the interaction of small ions with polyelectrolytes, we report the results of electric transport at 25° obtained using the sodium salts of alginic acid and polygalacturonic acid in aqueous solution with and without NaCl present and the electrophoretic mobilities at 0°C of both polyelectrolytes in NaCl. It was of interest to compare the solution properties of sodium alginate (NaAlg) and sodium polygalacturonate (NaPGal) because they are stereoisomers with different spacings of their pendant carboxyl groups.[1-5] Alginic acids are linear copolymers of D-mannuronic acid and L-guluronic acid[6-9] and their x-ray patterns have been studied.[10,11] Polygalacturonic acid is a linear homopolymer of D-galacturonic acid derived from pectins.[12] It has been shown that pectic acid and sodium pectates of different origin have the same distance per pyranose unit.[1,2]

Experimental Section

Materials. The sodium alginate sample used in this study was a gift of the Kelco Co. This material, KNLV-6573, although of high purity, was further purified by the method described by Haug and Smidsrod.[13,14] The purification process involved three successive ethanol (95%) precipitations. The amount of calcium or magnesium in the samples was determined using a Techtron AA4 Atomic Absorption Spectrophotometer. The purification reduced the concentration of Ca^{2+} and Mg^{2+} ions to less than 0.05%. The sodium alginate had a water content of 10.25 ± 0.03%, and an equivalent weight of 207 ± 1, which indicates that each unit contained one carboxyl group per monomer unit.

Polygalacturonic acid (Control No. 9501) of high purity was obtained from Nutritional Biochemical Corporation. This material was converted to the sodium form of the polyelectrolyte by titrating the slightly soluble acid with 0.1000 *M* NaOH. The sodium polygalacturonate was precipitated from solution using 95% ethanol. The purification steps mentioned above were used to ensure calcium and magnesium concentrations of less than 0.05%. The sodium polygalacturonate had a water content of 11.02 ± 0.02% and an equivalent weight of 207 ± 0.5, which indicates that each unit contained one carboxyl group per monomer unit.

The equivalent weights of the polysaccharides were determined gravimetrically by ignition to sodium carbonate. The equivalent weight of the polygalacturonate was also checked by titrating the acid from which the salt was made with standardized NaOH. All equivalent weight values are an average of at least four determinations.

The moisture content of each polysaccharide was determined by drying to constant weight in a vacuum oven at 40°C. An average of four determinations of the moisture content were used.

All inorganic chemicals used were reagent grade and were dried prior to use. Conductivity water was used to prepare all solutions.

Solution Preparation. Polyelectrolyte solutions were prepared by dissolving a weighed amount of polymer in water or in the appropriate aqueous salt solution. All experimentation was completed on each solution within 48 hr. This procedure eliminated the possibility of biological contamination and ensured the complete dissolution of the polyelectrolytes.

Conductance. Modified Shedlovsky type conductance cells[15] were used for all conductance measurements. Platinized electrodes were employed. The cell constants for the cells used were found to be 0.6261 ± 0.0002 and 1.1627 ± 0.0003 cm^{-1}, using standard KCl solutions. Conductance measurements were performed at 25 ± 0.001°C in an oil bath using an Industrial Instruments Model RC 18 conductance bridge, which has an accuracy of ±0.01%. All conductance measurements were performed at a frequency of 1000 Hz. Nelson[16] has shown that readings extrapolated to infinite frequency are approximately 0.1% lower than those obtained at 1000 Hz, thus indicating negligible errors due to polarization. The cells were allowed to equilibrate in the bath for 10 min before a reading was taken. Nelson[16] has also shown, and it was verified in this work, that during thermal equilibrium adsorption of the polymer onto the electrode is negligible. The reproducibility of the conductance measurements was approximately less than 1%.

Transference. Transference experiments were performed on salt-free polyelectrolyte solutions at 25 ± 0.01°C using a standard three-compartment Hittorf type cell with platinum electrodes. Darkus et al.[17] showed that a conventional three-compartment Hittorf cell gave identical results when compared to a two-compartment horizontal cell in which the compartments are separated by a sintered glass disk. Constant current was supplied from Electronic Research Associates' Model CC-200 power supply. This unit had an accuracy of ±0.01 mA. The transference number of the polyion constituent T_p was calculated from

$$T_p = (Q_p/n)/(1 - \kappa_0/\kappa) \quad (1)$$

where n Faradays transported Q_p equivalents of polyion constituent and the term $(1 - \kappa_0/\kappa)^{-1}$ is a correction for the current carried by the solvent in the solution in which κ_0 and κ are the specific conductivities of the solvent and the polyelectrolyte solution, respectively. The values of Q_p were determined gravimetrically by drying to constant weight. The reproducibility of the transference measurements was approximately ±2%.

Electrophoresis. Electrophoretic mobility measurements were conducted at 0°C using a Perkin-Elmer Apparatus Model 238.[16] All mobility values were extrapolated to zero polyelectrolyte concentration from the ascending and descending boundaries.

Results and Discussion

Table I
Electric Transport Parameters for Aqueous Solutions of the Sodium Salts of Algin and Polygalacturonic Acid at 25°C

	$N_p \times 10^3$, equiv dm^{-3}	Λ_p, Ω^{-1} cm^2 equiv^{-1}	T_p	f	$\Lambda_{p(\text{theo})}$, Ω^{-1} cm^2 equiv^{-1}
NaAlg	1.0	51.3	0.75	0.58	67.8
	5.0	45.8	0.65	0.57	60.2
	10.0	44.3	0.63	0.57	56.8
	15.0	44.0	0.62	0.57	54.6
NaPGal	1.0	60.3	0.83	0.60	59.4
	5.0	53.8	0.72	0.60	52.9
	10.0	50.4	0.65	0.61	49.9
	15.0	49.4	0.62	0.61	48.1

Salt-Free Solutions. The equivalent conductance Λ_p of the polyelectrolyte was calculated from

$$\Lambda_p = 10^3(\kappa - \kappa_0)/N_p \quad (2)$$

where N_p is the equivalent concentration of the polyelectrolyte. The values of Λ_p and T_p for NaAlg and NaPGal in the concentration range 1.0 to 15.0 × 10^{-3} *N* were calculated from eq 2 and 1, respectively, and are listed in Table I. The charge fraction parameter f of unassociated free counterions is given by[17–19]

$$f = \Lambda_p/(\lambda_p + \lambda_c) \quad (3)$$

where λ_p and λ_c are the equivalent conductances of the polyion and the unassociated counterions, respectively, and

$$\lambda_p = T_p\Lambda_p \quad (4)$$

Since λ_c is an unknown quantity in this study, we employed the commonly used assumption[17] that λ_c is approximately equal to the ionic conductance at infinite dilution λ_c^0 for a polyelectrolyte-free salt solution. This is discussed by Kurucsev and Steel,[18] who also noted that the values of f are relatively insensitive to the polyelectrolyte concentration for several polyelectrolytes. The calculated values of f here, which are listed in Table I, were found to be independent of concentration. Similar results have been reported for sodium alginate, with the values of f in close agreement with results reported here.[20,21] Jordan et al.[19] found f to be independent of concentration for aqueous solutions of polystyrenesulfonic acid and sodium polystyrenesulfonate for both the isotactic and atactic forms. However, Dolar et al.[22] found increasing f values for sodium polystyrenesulfonate in aqueous solution with increasing polymer concentration for higher concentrations than those reported by Jordan. Shavit[23] reported that the mobility of K$^+$ ions increased with increasing concentration of potassium polyacrylate for salt-free aqueous solutions at concentrations greater than 0.025 monomol/l. This may be of help in explaining the results found by Dolar et al.,[22] where polyelectrolyte–polyelectrolyte interaction may increase the mobility of counterions at higher polyelectrolyte concentrations. For the concentration range where f is independent of concentration, the value of f is due principally to the linear charge density of the polyion. Experimentally this is manifest in the f values found for other polyelectrolytes.[24]

Since ionic polysaccharides are fairly stiff molecules, a theoretical model of cylindrical symmetry for the polyion would be expected to describe its behavior in solution. Schmitt and Varoqui[25] showed that the rod-like model at high degrees of neutralization fits the experimental data best. The line charge model of Manning[26] was found to be a good representation for synthetic[24,27–29] and biological polyelectrolytes of high charge density.[30–33] Recently, Manning[34] extended his line charge model to calculate the equivalent conductance of the polyion λ_p in salt-free solution. Some success between the theory and experiment was achieved with alkali metal ion salts of polystyrenesulfonic acid in aqueous solution.[35,36] Recently, Kwak and Johnson[37] reported that the equivalent conductivity of aqueous solutions of salts of carboxymethylcellulose were in excellent agreement with the predicted values from Manning's theory, especially in the lower concentration range.

For NaAlg and NaPGal in water at 25°C Manning's equation for λ_p is

$$\lambda_p = \frac{22.32|\ln Ka|}{1 + 0.0690|\ln Ka|} \tag{5}$$

where K is Debye screening constant and a is the radius of the polyion, reported[4] to be 5.6×10^{-8} cm. The theoretical equivalent conductance $\Lambda_{p(\text{theo})}$ is calculated from eq 3 and 5 with $\lambda_c^0 = 50.1$,[38] $f = 0.866\xi^{-1}$, and ξ, the charge density parameter, given by $7.135b^{-1}$ for water at 25°C, where b is the distance between charges, taken to be 5.0 and 4.37 Å for NaAlg[1] and NaPGal,[1] respectively. This gives $\xi = 1.43$ and $f = 0.61$ for NaAlg and $\xi = 1.63$ and $f = 0.53$ for NaPGal. The theoretical values for f are close to the average experimental values of 0.57 and 0.61 for NaAlg and NaPGal, respectively, which were found to be independent of concentration in agreement with the theory. From Table I, it is noted that lower Λ_p values were obtained for NaAlg when compared to those found for NaPGal. The values for NaAlg are in reasonable agreement with those reported by others.[20] It is seen from Table I that the Λ_p values decrease with increasing concentration, this trend predicted correctly from Manning's model. Excellent agreement between the theoretical and experimental values for NaPGal is seen in Table I. The poorer correlation obtained for the NaAlg was probably due to the low equivalent conductivity for this ionic polysaccharide. The carefully performed conductivity study reported for a similar ionic polysaccharide, the lithium, sodium, potassium, and cesium salts of carboxymethylcellulose, showed very close agreement with the values predicted from Manning's theory up to 0.01 N; good agreement was obtained in this concentration range for other polyelectrolytes of varying charge density.[37] It would be of interest to perform these experiments using ionic polysaccharides which have a distance between charges such that the charge density is lower than its critical value and *no* condensation is predicted.

An examination of the experimental f values given in Table I indicates that NaPGal is dissociated to a slightly greater extent than is NaAlg. The similarity of the experimental f values for NaAlg and NaPGal and the better agreement of the theoretical and experimental f values for NaAlg might indicate that the distance between the charged groups on the NaPGal chain in solution is slightly larger than the reported crystallographic distance. This is also borne out when a comparison is made between the theoretical values of the sodium ion activity coefficient γ_{Na^+} with the experimental values of 0.48 and 0.50 for NaAlg and NaPGal, respectively,[39] at 1.0×10^{-3} N polyelectrolyte concentration. From Manning's theory[26] $\gamma_{Na^+} = e^{-1/2\xi^{-1}}$, giving γ_{Na^+} values of 0.42 and 0.37 for NaAlg and NaPGal, respectively, as compared to their respective experimental values of 0.48 and 0.50, indicating that the value of b for NaAlg is more in accord with the rod-like model and also that the charge spacing in NaPGal is probably slightly larger in solution. If b for NaPGal is slightly larger than 4.37 Å in solution, experimental Λ_p values lower than those theoretically predicted would be expected, but, nevertheless, the concentration dependence of Λ_p would still be much more in accord with theory than those obtained for NaAlg.

Salt-Containing Solutions. The specific conductances of aqueous NaCl solutions of NaAlg and NaPGal were determined at 25°C at the same polyelectrolyte concentrations as for the salt-free solutions. They are given in Table II.[40] An apparent equivalent conductance of the polyelectrolyte can be calculated from eq 1, where κ_0 is taken to be the specific conductance of the aqueous NaCl solution at the concentration used. It should be clearly understood that this procedure does *not* give the equivalent conductance of the polyelectrolyte because the simple salt–polyelectrolyte interactions have not been taken into account.[41] Strauss[42] used a simple model to correct conductance data for the effect of the polyelectrolyte on the conductance of the simple salt.

Table III

A Comparison of the Experimental and Theoretical Values of A_p in Several Aqueous NaCl Solutions at 25°C[a]

N_s, equiv dm^{-3}	λ_p, Ω^{-1} cm^2 equiv^{-1}	NaAlg		NaPGal	
		$A_{p,\text{theo}}$	A_p	$A_{p,\text{theo}}$	A_p
0.001	64.0	70.8	43.6 ± 1.5	62.1	56.7 ± 2.1
0.005	43.3	55.7	37.5 ± 0.7	48.9	41.5 ± 1.1
0.010	34.4	49.1	34.7 ± 0.4	43.1	40.6 ± 0.2
0.025	22.6	40.1	32.1 ± 0.1	35.1	36.0 ± 0.1
0.050	13.6	33.2	30.0 ± 0.0	29.1	33.2 ± 0.2
0.100	4.72	26.0	28.2 ± 0.6	22.8	

[a] A_p has units of Ω^{-1} cm^2 equiv^{-1}.

An extension of Manning's theory by Devore and Manning[43] to calculate the equivalent conductances of counterions and coions in polyelectrolyte solutions led to some success when correlated with the experimental transport results of Nagasawa et al.,[44] especially for the highest charge density of the polyelectrolyte. More recently, Ross, Scruggs, and Manning[45] found qualitative agreement with Manning's theory for the conductance of DNA in aqueous simple salt solution. A similar correlation with Manning's theory will be made with the conductance results presented in Table II.

For salt-containing polyelectrolyte solutions,

$$\kappa - \kappa_s = 10^{-3} A_p N_p \tag{6}$$

where κ and κ_s are the specific conductances of the polyelectrolyte–simple salt solution and simple salt solutions, respectively, and A_p is an empirical coefficient obtained from linear regression plots of κ vs. N_p, for the concentration range studied. The resulting values of A_p and its standard error are shown in Table III; correlation coefficients of better than 0.992 were obtained for all linear regression fits of the experimental data. To calculate the theoretical value of A_p, the expressions derived by Manning employed are

$$A_p = \xi^{-1}[(t_{Na^+}{}^{(s)} - 1/6) + \lambda_p] \tag{7}$$

where $t_{Na^+}{}^{(s)}$ is the transference number of Na$^+$ in NaCl solution and the equivalent conductance of the polyion λ_p is given by

$$\lambda_p = (F/300)(\epsilon kT/3\pi\eta e)|\ln Ka| \tag{8}$$

where F is the Faraday, ϵ is the dielectric constant, η is the viscosity of bulk solvent, e is the proton charge, k is Boltzmann's constant, T is the temperature, K is the Debye screening parameter for the salt solution in the absence of polyelectrolyte, and a is the radius of the cylindrical polyelectrolyte, taken to be 5.6×10^{-8} cm.[4] Using reported transport data for aqueous NaCl solutions,[38] eq 7 and 8 were used to calculate theoretical values for λ_p and A_p, which are listed in Table III. It should be first noted from Table III that the experimental A_p values for NaPGal are in good agreement with the theoretical values, while those for NaAlg are only in fair agreement. (Better agreement with theory for the salt-free values of Λ_p was also obtained for NaPGal, as is evident from Table I.) Also, better correlation between the theoretical and experimental values is obtained as the simple salt concentration increases. As reported for DNA,[45] the value of A_p decreases

Table IV
A Comparison of the Experimental and Theoretical Electrophoretic Mobility Values in Several Aqueous NaCl Solutions at 0°C

N_s	$\lambda_{p,theo}$, Ω^{-1} cm^2 equiv	$U_{p,theo}$ $\times 10^4$, cm^2 sec^{-1} v^{-1}	U_{NaAlg} $\times 10^4$, cm^2 sec^{-1} v^{-1}	U_{NaPGal} $\times 10^4$, cm^2 sec^{-1} v^{-1}
0.010	19.4	2.01	2.66	2.97
0.025	14.0	1.45	2.08	2.24
0.050	9.9	1.02	1.79	1.90

as the simple salt concentration increases. However, unlike the results obtained for DNA, the calculated A_p values do *not* consistantly underestimate those measured. In light of the promising correlation between the theoretical and experimental values, conductance results for other systems should be analyzed in this manner.

Since the theoretical values of the conductance parameter A_p for DNA at 5°C consistently underestimates the measured values,[45] it would be worthwhile to compare measured and calculated electric transport values obtained at 0°C. Electrophoretic mobilities U_p of NaAlg and NaPGal in aqueous NaCl solutions were determined at 0°C. The U_p values listed in Table IV were determined at infinite dilution of polyelectrolyte by extrapolating the values obtained from the ascending and descending boundaries. At each simple salt concentration the experimental U_p value for NaPGal is greater than that for NaAlg, in accord with their conductances at 25°C. From eq 8 and the relation $U_p = \lambda_p F$, theoretical values for λ_p and U_p were calculated and are listed in Table IV. It is noted from this table that the theoretical values of U_p correctly predict a decrease in U_p with an increase in simple salt concentration, but the theoretical values underestimate the experimental ones. To test Manning's theory adequately, electric transport experiments should be performed not only varying the polyelectrolyte and simple salt concentration, but also varying simple salt valence type and the temperature.

Supplementary Material Available. The conductances of aqueous NaCl solutions of sodium alginate and sodium polygalucturonate at 25°C will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number MACRO-75-789.

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Moments and Transport Coefficients of Wormlike Rings

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ABSTRACT: The translational friction coefficient and intrinsic viscosity of ring stiff chains without excluded volume are evaluated by an application of the Oseen–Burgers procedure of hydrodynamics to ring wormlike cylinder models. The mean reciprocal distance and mean-square distance between two points on the cylinder axis, and the mean-square radius, which are required for the calculation of the transport coefficients, are evaluated in an approximate fashion. The results are applied to estimation of the molecular parameters of circular DNA.

In previous papers,[1,2] the translational friction coefficient and intrinsic viscosity of linear stiff chains without excluded volume have been evaluated by an application of the Oseen–Burgers procedure of hydrodynamics to linear wormlike cylinder models. The light-scattering form factor of linear wormlike chains without excluded volume has also