Biophysical Chemistry 7 (1978) 379–386
© North-Holland Publishing Company

THE EQUIVALENT CONDUCTIVITY OF AQUEOUS SOLUTIONS OF ALKALI METAL SALTS OF A NUMBER OF IONIC POLYSACCHARIDES

Jan C.T. KWAK, George F. MURPHY and Ester J. SPIRO
Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada

Received 14 April 1977
Revised manuscript received 3 October 1977

Measurements of the equivalent conductivity of aqueous solutions of alkalimetal salts of a number of ionic polysaccharides at 25°C are reported. The polysaccharides studied are: (1) three carboxymethylcelluloses of various degrees of substitution (Li^+, Na^+, K^+, Cs^+ salts) in the concentration range $4 \times 10^{-4} - 6 \times 10^{-2}$ equivalents alkali ion per liter, (2) Polypectate (Li^+, Na^+, K^+, Cs^+ salts) in the range $1.5 \times 10^{-4} - 2 \times 10^{-2}$ equivalent alkali ion per liter, and (3) Dextransulfate (Li^+, Na^+, K^+ salts) in the range $3 \times 10^{-4} - 10^{-1}$ equivalent alkali ion per liter. The results are compared to some earlier data and to a limiting law for conductance of rod-like polyions derived by Manning. It is concluded that although qualitative agreement is obtained between observed data and the limiting law when various polyions of different charge densities are compared at a given concentration, the concentration dependence predicted by the limiting law is in agreement with the observed curves only for polyions of a relatively low charge density. At higher charge densities appreciable deviations occur, and dextransulfate which does not have the rod-like polyion structure required by theory does not conform to the predicted concentration dependence at all.

1. Introduction

In spite of the success of conductance theory in describing the concentration dependence of the equivalent conductivity of simple ionophores, the development of a satisfactory theory for the conductivity of polyelectrolytes is still in its infancy. One reason for this may be the lack of a region which can be experimentally and theoretically identified as exhibiting a limiting behaviour. Consequently, no meaningful extrapolation can be made to obtain a mobility in the limit of zero concentration, to be used as a starting point for solutions of finite concentrations. Conductance theory of course shares the problems posed by the absence of an infinite dilution limit with equilibrium theory. However in the latter case theory has progressed to the point where, based on certain reasonable model assumptions, a variety of theoretical techniques can be employed to calculate total and partial molar free energies and their derived quantities [1–5], and in some cases similarities and discrepancies between different theories can be pointed out, predictions tested, etc. In the case of electrical transport however most attention has been paid to the calculation of the "fraction of free ions", f, obtained from conductivity and transport number measurements or from tracer diffusion measurements, and a relatively minor part of the research effort has been directed towards the property which has proven so useful in simple electrolytes the equivalent conductivity and its concentration dependence. From a theoretical point of view, the only effort so far to give an ab initio calculation of the conductivity of polyelectrolytes from the charge density of the polyion, the radius of the rod-like polyion and the limiting mobility of the counterion, without using adjustable parameters [6], clearly points at the special problem encountered in these systems. In his theory, Manning not only has to calculate the influence the polyion-small ion interactions have on the mobilities of both, a problem which can be seen as corresponding to the various effects ionic interactions have on the conductivity of simple electrolytes, but he also has to find an expression for the ionic conductivity of the polyion, λ_p, where in the case of simple electrolytes we always have the starting point of Λ^0 or λ_i^0 values even though of course the extrapolation procedure for Λ or t_i depends on the theoretical expression used. The model of a free draining rigid cylinder used by Manning to find an expression for the polyion mobility is obviously a very crude approximation at best, and it is for this reason that Manning's theory should be used more for its prediction of the concentration dependence of Λ and λ_p than for its calculation of the actual magnitude of Λ.

A number of studies on the concentration dependence of Λ of saltfree polyelectrolytes and biopolymers have been published [7–19], and many other conductivities at a single concentration have been reported in papers dealing with transportnumber, activity, or diffusion coefficient determinations, or in studies of the conductivity of polyelectrolyte – simple electrolyte mixtures. In some of the early studies attempts were made to find extrapolation procedures which yield infinite dilution values of Λ, however this approach did not prove very useful and it has been pointed out that such extrapolations may lead to ambiguities [13]. Manning's conductance theory [6] predicts that the charge density and the radius of the polyion, assumed to be rod-like, are the only factors influencing the conductivity and its concentration dependence of a given polyelectrolyte, apart of course from the limiting equivalent conductivity of the counterion with which the polyion is combined. Possibly this prediction, and its counterpart in Debye-Hückel type approximations for equilibrium properties, including condensation theory, has led to a relative neglect of the study of differences observed in the conductivity curves of different polyelectrolytes. In this paper we will attempt to make such a comparison by presenting conductance curves of the Li^+, Na^+, K^+ and Cs^+ salts of a number of polysaccharides, including carboxymethylcelluloses (CMC) which varying degrees of substitution, pectic acid (PA), and dextransulfate (DS). Previous studies comparing Manning's limiting law for the conductivity of polyelectrolytes to observed conductance curves have shown significant variations from one polyelectrolyte to another [15–19]. Polysaccharides are often assumed to have considerably stiffer polymer "backbones" than vinylic type polymers, and a good qualitative agreement between the limiting law and alkalimetal salts of a low charge density carboxymethylcellulose [17] and Na-poly-galacturonate (Na-pectate) [18] has been reported. On the other hand, the agreement for Na-alginate was not very satisfactory [18]. The polysaccharides studie in this paper vary with respect to polymer structure, charge separation, and functional groups. Although w will compare our results to Manning's conductance equation, simply because this is the only theoretical equation available, it will become clear that this equation cannot adequately explain the variety of conductance curves observed.

2. Experimental

2.1. Materials

Three different carboxymethylcellulose samples, kindly supplied as sodium salts by Dr. M. Rinaudo of the Centre de Recherches sur les Macromolecules Vegetales (C.N.R.S.), Grenoble, France, were used. The degrees of substitution of the three samples were given by Dr. Rinaudo as 0.95, 1.35 and 1.82. The respective degrees of polymerization as determined by viscometry were 26, 170 and 80. The degree of substitution of each sample was redetermined in our laboratory, the results agreed within measurement error (2% with the numbers cited above. Each sample was purified once more by ion-exchange and the final stock solutions of each alkalimetal salt were prepared as described earlier [17].

Polypectate was obtained as the sodium salt from Nutritional Biochemicals Corporation, Cleveland, Ohi The salt was further purified by repeated cation- and anion exchange. The final stock solutions of the alkali metal salts were prepared from the pectic acid stock s lution as described above for CMC. The degree of este ification of the carboxylic groups, determined using a standard ester hydrolysis method [21], was found to be 2(± 2)%, indicating that within experimental error essentially all carboxylic groups in the pectate sample employed are not esterified. The equivalent weight of the Na-pectate, determined by drying a preweighed known Na-pectate stock solution to dryness under vacuum at 60°C, was found to be 259 ± 3, which leads to an estimated neutral sugar content of 7(± 2)% base on a molecular weight of 242 for the Na-galacturonat repeating unit. This value compares well to the 10% neutral saccharide content of carefully analyzed pectinates used by Kohn [22].

Dextransulfate was obtained from Pharmacia Fine Chemicals as the sodium salt. Purification and conversion to other ionic forms of this polysaccharide cannot be done by ion-exchange, since the acid form rapidly hydrolyzes. This acid hydrolysis effect is especially noticeable in conductance. Sodium salts prepared by neutralization of the acid form of dextransulfate, even if it had been in the acid form for less than two hours, showed conductance curves similar to those of strong low molecular weight electrolytes, with Λ decreasing from 140 to 100 $\text{ohm}^{-1}\ \text{cm}^{-1}\ \text{equiv}^{-1}$ between 10^{-3} and 10^{-1} equiv ℓ^{-1}, in strong contrast to the curves reported here. For this reason the dextransulfate obtained from the distributor was purified by repeated diafiltration while adding deionized water to keep the concentration constant. An "Amicon" 65 ml stirred cell and PM 10 ultrafiltration membranes (molecular weight cut-off 10 000) were used (Amicon Inc, Stamford, Conn., USA). The purified sodium salt was converted to other alkalimetal salts by exhaustive exchange dialysis against the required alkali chloride. The extraneous salt in the resulting dextransulfate was removed by dialysis followed by diafiltration, until no salt could be detected in the filtrate (by conductance) and no Cl^- could be detected in the final stock solution. The last step was an ultrafiltration step to bring the stock solution to the required concentration. Concentrations of the resulting lithium, sodium and potassium dextransulfate solutions were determined by standard methods [23]. Certain ambiguities arise in considering the degree of substitution of the dextransulfate polyion. Pharmacia, in its product information bulletin, quotes a sulfur content of 17%. This would correspond to a degree of sulfonation of 1.9 (i.e. 1.9 sulfonate groups per glycosyl unit) and not 2.3 as reported in the bulletin. Wells [24] working with the same product, gives a sulfur content of 17.5%, corresponding to a degree of sulfonation of 2.0. Unfortunately relatively small errors in the %S determination result in large differences in the calculated degree of substitution. On the other hand, equivalent weight determinations attempted in our laboratory by drying a weighed quantity of solution of known concentration to constant weight also result in considerable uncertainties, more so then is the case with the other polysaccharides studied. Our best value for the degree of substitution, based on drying a large number of both NaDS and KDS samples to constant weight is 2.2 ± 0.3, and we will use this value in our calculation of ξ.

All solutions were made from double distilled equilibrium water with a specific conductance between 0.8 and $1 \times 10^{-6}\ \text{ohm}^{-1}\ \text{cm}^{-1}$.

The conductance bridge and cells were the same as used in earlier work [15, 17]. The conductance cells used had lightly platinized electrodes. All reported conductivities are as measured at 2000 cycles. The frequency dependence of the conductivity in the $5 \times 10^2 - 10^4\ \text{s}^{-1}$ frequency range is small.

Densities of the more concentrated solutions were determined to ± 0.02% with a simple pycknometer. For our purposes (i.e. within the accuracy necessary to obtain conductivity values with an estimated error less than 0.1%) densities vary linearly with the concentration in the concentration range employed.

Reproducibilities of conductance values of solutions made from the same stock solution is ± 0.1%, the estimated error in the weight dilution. A number of times comparisons were made between solutions of the same salt made from different stock solutions. In such cases the agreement was always within the error in the concentration determination of the stock solution which is ± 0.7%. The four CMC salts were made by neutralization of the same HCMC stock solution, and the four PA salts were made by neutralization of the same pectic acid stock solution. Thus in comparing the four CMC salts or the 3 PA salts the estimated error in the difference in equivalent conductance is not more than 0.2%. However, in comparing the salt of one polyion with that of another, or in the case of the dextransulfates the error in the difference may be up to 1.5%.

3. Results and discussion

Results for the equivalent conductivity Λ of lithium, sodium, potassium and cesium salts of three different carboxymethylcellulose samples with degrees of substitution of 0.95, 1.35 and 1.82 are given in figs. 1–3. The equivalent conductivities of lithium, sodium, potassium and cesium pectate are given in fig. 4, together with data by Tuffile and Ander [18] for a Na-polygalacturonate from a different source. Finally, the equivalent conductivities of lithium, sodium and potassium dextransulfate are presented in fig. 5. All reported conductivities were measured at 25°C, and have been corrected for the background conductivity of the water.

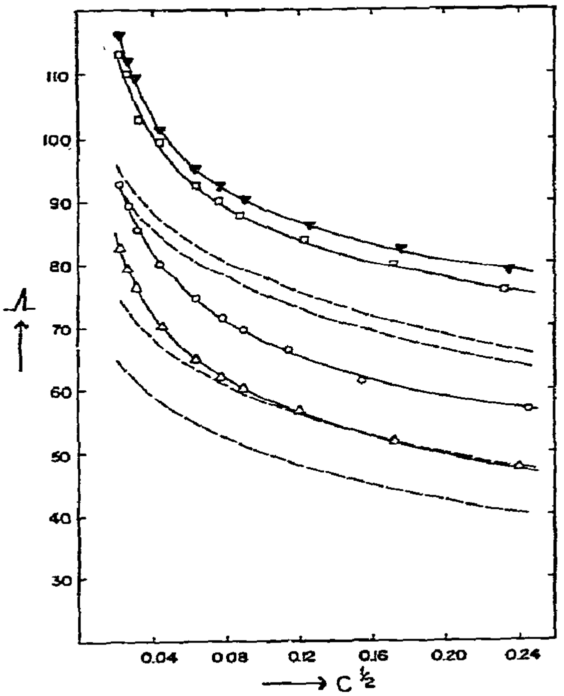

Fig. 1. Equivalent conductivities Λ (ohm^{-1} cm^{2} equiv^{-1}) of alkali metal salts of carboxymethylcellulose (ξ = 1.32) as a function of $C^{1/2}$ (equiv$^{1/2}$ ℓ$^{-1/2}$), at 25°C. Counterions: △ = Li^{+}, ○ = Na^{+}, □ = K^{+}, ▼ = Cs^{+}.

No hydrolysis correction was applied, pH determinations of all solutions showed this correction to be negligible.

The broken lines in all figures indicate the theoretical curves for Λ as calculated from Manning's equations [6]:

$$\Lambda = f(\lambda_{+}^{0} + \lambda_{\mathrm{p}}), \qquad (1)$$

$$\lambda_{\mathrm{p}} = 22.29|\ln \kappa a|[1 + 3.454(\lambda_{+}^{0})^{-1}|\ln \kappa a|]^{-1}. \qquad (2)$$

For a univalent counterion, f is equal to 0.87 ξ^{-1}, with ξ the charge density parameter, $\xi = e^2(DbkT)^{-1}$, e is the proton charge, D the bulk dielectric constant, k Boltzmann's constant, and b is the average spacing of charged groups on the polymer. λ_{+}^{0} is the limiting equivalent conductivity of the free counterion, i.e. 38.7 for Li^{+}, 50.1 for Na^{+}, 73.5 for K^{+}, and 77.3 for Cs^{+} [25]. The polyion equivalent conductivity λ_{p} depends on κa where $\kappa^2 = \lambda\Sigma_i c_i z_i^2$, with $\lambda = e^2(DkT)^{-1}$, c_i is the con-

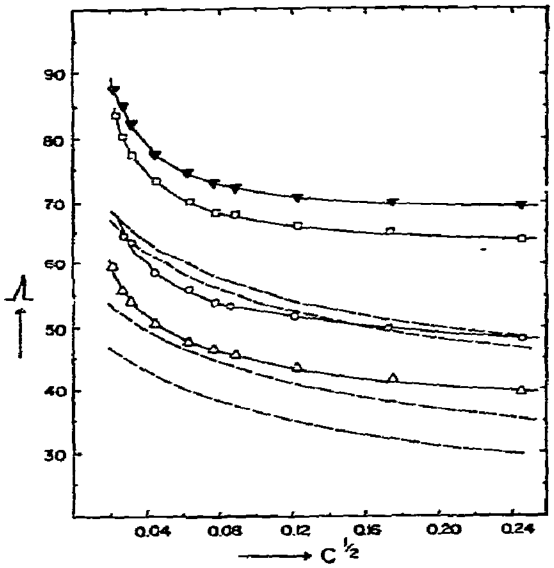

Fig. 2. Equivalent conductivities Λ (ohm^{-1} cm^{2} equiv^{-1}) of alkali metal salts of carboxymethylcellulose (ξ = 1.88) as a function of $C^{1/2}$ (equiv$^{1/2}$ ℓ$^{-1/2}$), at 25°C. Counterions: △ = Li^{+}, ○ = Na^{+}, □ = K^{+}, ▼ = Cs^{+}.

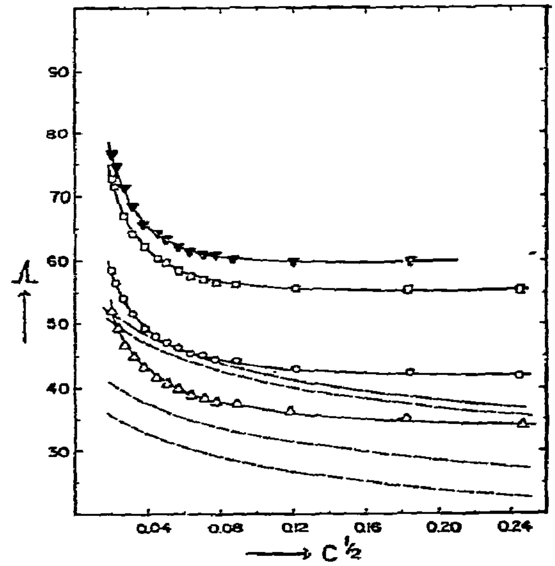

Fig. 3. Equivalent conductivities Λ (ohm^{-1} cm^{2} equiv^{-1}) of alkali metal salts of carboxymethylcellulose (ξ = 2.53) as a function of $C^{1/2}$ (equiv$^{1/2}$ ℓ$^{-1/2}$), at 25°C. Counterions: △ = Li^{+}, ○ = Na^{+}, □ = K^{+}, ▼ = Cs^{+}.

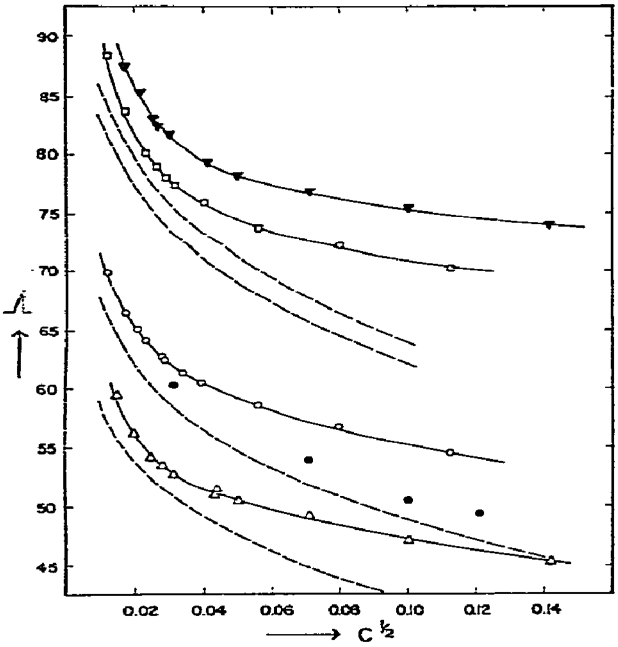

Fig. 4. Equivalent conductivities Λ (ohm^{-1} cm^2 equiv^{-1}) of alkali metal salts of pectic acid as a function of $C^{1/2}$ (equiv$^{1/2}$ ℓ$^{-1/2}$), at 25°C. Counterions: △ = Li$^+$, ○ = Na$^+$, □ = K$^+$, ▼ = Cs$^+$, ● Na galacturonate data of Tuffile and Ander [18].

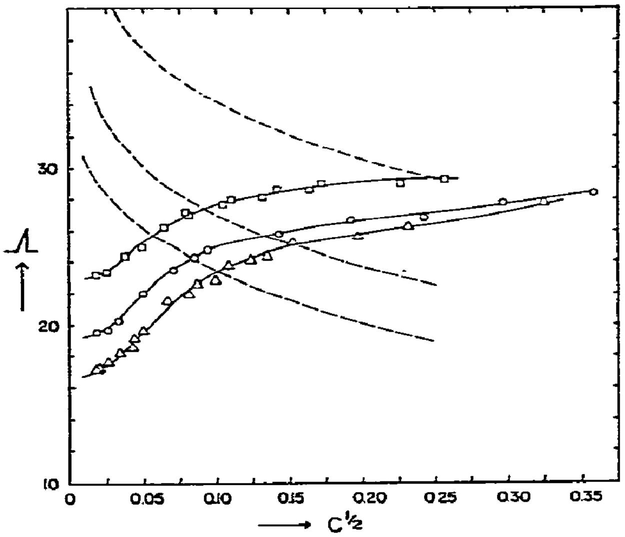

Fig. 5. Equivalent conductivities Λ (ohm^{-1} cm^2 equiv^{-1}) of alkali metal salts of dextransulfate as a function of $C^{1/2}$ (equiv$^{1/2}$ ℓ$^{-1/2}$), at 25°C. Counterions: △ = Li$^+$, ○ = Na$^+$, □ = K$^+$.

centration of mobile ion i with charge z_i, a is the radius of the rod-like polyion. λ_p also depends on the nature of the counterion through the λ_+^0 term. It should be noted that although in our experiments the term $3.454(\lambda_+^0)^{-1}|\ln \kappa a|$ is always smaller than 1, it is not negligible under any of our experimental conditions and can reach values as high as 0.4. Thus Manning's equation does not predict a simple $C^{1/2}$ type limiting concentration dependence for λ_p or for Λ in the normally accessible concentration range. For a, the radius of the assumedly rod-like polymer cylinder we used a value of 7 Å for all polymers. Fortunately, λ_p does not depend strongly on a, and although in some cases we could have obtained better quantitative agreement between theoretical and experimental curves by varying a, we felt it would not be realistic to do so. Certainly, the arbitraryness in the choice of a is one of the factors contributing to the appreciable uncertainty in the absolute magnitude of the theoretical Λ values at any given concentration. For the charge density parameters ξ we used the degrees of substitution of each sample reported in the previous section. For the three CMC samples, using a 5.15 Å length of the cellulose repeating unit [20], we find average charge separations of 5.42, 3.81 and 2.83 Å, resulting in ξ values of 1.32, 1.88 and 2.53 respectively. For the pectate we assume a charge separation of 4.35 Å, equal to the unit length of the polygalacturonate chain, giving $\xi = 1.61$. Finally, for the dextransulfate the average linear charge separation is 2.3 Å, based on a repeating unit length equal to the 5.15 Å length of the D-glycopyranose unit [20], from which we calculate $\xi = 3.1$. Again, appreciable uncertainties maybe introduced in the theoretical Λ values through uncertainties in ξ for each given polymer, but this or the uncertainty in a should not influence the concentration dependence in a major way.

Manning [6] rearranged eq. (1) and (2) to arrive at an expression for the concentration dependence of Λ which does not depend on a. This relation has been used [15–17] to check the validity of the concentration dependence predicted by Manning's expression for Λ. However, the same can be done by carefully analyzing the curves given in figs. 1–5, and in this paper we will limit ourselves to this approach. In considering the experimental data we will focus on the following four characteristics: (1) the dependence of Λ

Table 1
Comparison of calculated and experimental values for the equivalent conductivities of the sodium salts of some selected polyelectrolytes

Polyelectrolyte	ξ	C (equiv ℓ^{-1})	$a \times 10^8$ (cm)	Λ_{calc}	Λ_{exp}	ref.	remarks
carboxymethylcellulose	1.15	0.005	7	70.5	64.3	[29]	
	1.20	0.005	7	68.3	66.8	[17]	
	1.32	0.005	7	62.3	72.9	this work	*
	1.88	0.005	7	45.1	54.7	this work	*
	2.53	0.005	7	34.4	44.9	this work	*
	3.46	0.005	7	25.5	33.6	[27]	*
alginate	1.43	0.005	7	60.2	45.8	[18]	
	1.43	0.0058	7	57.1	48	[28]	
pectate	1.61	0.005	7	51.9	57.4	this work	
	1.61	0.005	7	51.9	53.8	[18]	
polyacrylate (68% neutralized)	1.90	0.0044	5	47.7	42.0	[10]	
polystyrenesulfonate	2.84	0.005	8	31.8	36.3	[15]	mol. wt. 500,000
	2.84	0.005	8	31.8	40.8	[16]	mol. wt. 570,000
	2.84	0.005	8	31.8	37.2	[14]	mol. wt. 500,000
dextransulfate	3.06	0.005	7	28.6	23.5	this work	

* These 4 CMC samples were all prepared in Dr. Rinaudo's laboratory [27]. They have a relatively low molecular weight, appreciably lower than the commercial CMC used in refs. [17] and [29].

at a given concentration on the polyion charge density ξ, (2) the concentration dependence of Λ as compared to the limiting law predictions, (3) the influence of the specific counterion, and (4) the influence of the specific polyion structure.

In table 1 we list equivalent conductivities at 25°C of sodium salts of a wide variety of poly-anions. The choice of concentrations and counterions made in table 1 was made in order to accomodate the largest number of available data at a concentration where the limiting laws might reasonably be expected to hold. The table is not meant to be an exhaustive compilation of existing data, but rather uses selected data to cover a range of charge densities and types of polyions. In comparing the results from different investigations, some allowance should be made for the uncertainty in the concentration determination which is often 1–2%. Although for the higher molecular weight polyions the molecular weight dependence of Λ is relatively small, differences in sample molecular weight especially of the CMC used in this work and ref. [27] as compared to the CMC used in refs. [17] and [29] may well be the cause of the differences observed. In the light of the work by Oman [30], reexamination of the molecular weight dependence of the equivalent conductance and of many other properties may well be in order.

In spite of these uncertainties, the data clearly indicate the overriding effect ξ has on the measured equivalent conductivity, in accordance with our earlier compilation of available data on this effect [17]. However, it is also becoming clear that individual deviation do occur not only from one polyion to another at a given concentration, but also from taking the data at different concentrations. Related to this is the mounting experimental evidence that the "degree of binding parameter f as determined from conductivity and transport number data is not independent of concentrations, as can be seen from the work of Dolar et al. [14] and of Shavit [26] on such "standard" polyelectrolytes as polystyrenesulfonate and polyacrylate. Indeed, a careful examination of existing data for tracer diffusion coefficients and single ion activity coefficients of counterions of polysaccharides of the type studied in this paper in many cases reveals a definite concentration dependence, a dependence which is of course not predicted by condensation theory and the limiting laws. Still, table 1 shows that the single parameter strongly influencing the equivalent conductivity, regardless of the particular polyion involved and regardless of the counterions involved as long as we take into account their different limiting mobilities, is the polyion charge density parameter ξ, and thus the average linear charge separation on the polyion. Therefore the surprising conclusion reached in our previous communication [17], stating that the limiting law for conductance enables us to predict at least qualitatively the conductivity of any polyelectrolyte at a given concentration, still stands even though in what follows we will point out a number of obvious deviations from the detailed predictions of these limiting laws. It is our opinion that in those cases where gross deviations of Λ from the predicted values occur a close scrutiny of the experimental data and of the appropriateness of the ξ parameter used is in order.

In turning to the remaining three points, i.e. the observed concentration dependence, the influence of the counterion, and the differences observed between various polyions, we can see that deviations from the predicted behaviour become more obvious at higher polyion charge densities. With respect to the concentration dependence, the observed conductivity curve of dextransulfate, the polyion with the highest charge density studied in this investigation, has no correspondence whatsoever to the predicted curve (fig. 5). The conductivity curves of polystyrenesulfonates of only slightly lower charge densities [14–16] showed at least reasonable agreement with the limiting law at the lowest concentrations studied, but at higher concentrations equivalent conductivities of salts of this polymer also increase with concentration [14, 15]. Counter- and coion activities in dextransulfate solutions are very well described by the limiting laws for activities [24]. Dextran is a highly branched polysaccharide, and contains 1–6 glycoside linkages rather than the 1–4 linkages in the other polysaccharides studied, imparting a far higher flexibility to this polyion. Possibly transport properties are very sensitive to deviations from the rod-like model, whereas equilibrium properties are not very sensitive to such deviations, at least not in relatively dilute solutions. Still, the correct order of magnitude prediction of Λ given by the limiting law, which is based largely on the prediction of the fraction of condensed ions, is not unexpected. Similarly, it is not unreasonable to attribute the deviations observed at higher concentrations for Λ of polystyrenesulfonates, which have a flexible vinylic backbone, to polymer-polymer interactions caused by extensive coiling. However, it is clear that also in the case of the linear carboxymethylcelluloses the observed conductances are higher than the predicted values, and the concentration dependence of Λ can also deviate appreciably from the predicted dependence. This becomes more pronounced at higher ξ values, and is also more pronounced for Cs^+ than it is for Li^+ counterions, to the point where above 0.01 N the equivalent conductivity of cesium- and potassium salts of the highest charge density CMC becomes independent of concentration. Our data also show a stronger than predicted decrease of Λ with increasing concentrations at the low concentration side. This effect also becomes more pronounced as ξ increases, but in contrast to the high concentration effect it is independent of the counterion. For polysaccharides with low ξ values the deviations from the limiting law at a given concentration are independent of the counterion, however for the high charge density CMC we notice that the Li^+ and Na^+ salts deviate less from the limiting law values than the K^+ and Cs^+ salts. One could relate this to the binding sequence reported for high charge density CMC's [27], but in view of the uncertainties in the application of the limiting law such a conclusion seems not yet warranted.

Finally, we will discuss the influence of the specific polyion structure on the conductance. As the dextransulfate example shows, model criteria for the applicability of the limiting laws for conductance and for equilibrium properties must be different, and polyions which are known not to conform to the model assumptions will not satisfy the limiting laws. If we consider the three linear polysaccharides of comparable charge density reported in table 1, i.e. alginate, CMC and pectate, it is clear that deviations from the calculated values occur between different polyions, and even between the same polyion of different preparation and molecular weight. Although partially obscured by unavoidable but actually surprisingly small differences between the reported conductivities of the same polysaccharide prepared from widely different sources in different laboratories, the trend seems to be that pectates and CMC's have conductivities slightly higher than the predicted values, whereas alginate has a conductivity which is considerably lower than predicted. Tuffile and Ander [18] noted that pectate (polygalacturonate) conforms closer to the limiting law for conductance than alginate, but that the charge fraction parameter and counterion activity coefficient of alginate are in better agreement with the limiting law for these properties. The general trend observed in table 1 would lead us to conclude that alginate has the larger deviation, but additional work on both transport and equilibrium properties is necessary to clarify the situation. In this respect it is important to know the source and actual mannuronic to guluronic acid residue ratios of the alginate used, which may vary considerably from source to source. In general, the ξ parameter for any given polysaccharide may be subject to considerable uncertainty, due to e.g. the presence of neutral sugars or to the unknown proportions of different glycosyl units. This uncertainty is of considerable importance in the comparison of thermodynamic and transport properties of different ionic polysaccharides.

Acknowledgement

The authors express their gratitude to Dr. M. Rinaudo of the Centre de Recherches sur les Macromolecules Vegetales (C.N.R.S.), Grenoble, France, for preparing and characterizing the CMC samples. This work was supported by the National Research Council of Canada.

References

[1] F. Oosawa, Polyelectrolytes (Marcel Dekker, New York, 1971).
[2] G.S. Manning, Ann. Rev. Phys. Chem. 23 (1972) 117.
[3] D. Dolar, in: Polyelectrolytes, ed. E. Selegny (D. Reidel, Publishing Co., Dordrecht, Holland, 1974) p. 97.
[4] K. Iwasa, J. Chem. Phys. 64 (1976) 3679.
[5] K. Iwasa and J.C.T. Kwak, J. Phys. Chem. 81 (1977) 408.
[6] G.S. Manning, J. Phys. Chem. 79 (1975) 262.
[7] D.R. Briggs, J. Phys. Chem. 38 (1934) 867.
[8] A. Oth and P. Doty, J. Phys. Chem. 56 (1952) 43.
[9] H.P. Gregor and D.H. Gold, J. Phys. Chem. 61 (1957) 1347.
[10] H. Eisenberg, J. Polymer Sci. 30 (1958) 47.
[11] H. Eisenberg, G. Mohan Ram, J. Phys. Chem. 63 (1959) 671.
[12] D.O. Jordan, T. Kurucsev and M.L. Martin, Trans. Faraday Soc. 65 (1969) 606.
[13] R.E. Nelson and P. Ander, J. Phys. Chem. 75 (1971) 1691.
[14] D. Dolar, J. Span and S. Isakovic, Biophys. Chem. 1 (1974) 312.
[15] J.C.T. Kwak and R.C. Hayes, J. Phys. Chem. 79 (1975) 265.
[16] J. Symczak, P. Holyk and P. Ander, J. Phys. Chem. 79 (1975) 270.
[17] J.C.T. Kwak and A.J. Johnston, Can. J. Chem. 53 (1975 792.
[18] F.M. Tuffile and P. Ander, Macromolecules 8 (1975) 78
[19] H. Kranck, C. Hesse-Bezot, M.A. Rix-Montel, H. Grassi and D. Vasilescu, Biopolymers 15 (1976) 599.
[20] K. Ward, Jr. and P.A. Seib, in: The carbohydrates, chemistry and biochemistry, Vol. IIA, eds. W. Pigman and D. Horton (Academic Press, New York, 1970) p. 420.
[21] T.H. Schulz, Methods Carbohyd. Chem. 5 (1965) 189.
[22] R. Kohn and O. Luknar, Coll. Czech. Chem. Commun. 40 (1975) 969.
[23] J.C.T. Kwak, J. Phys. Chem. 77 (1973) 2790.
[24] J.D. Wells, Proc. R. Soc. London Ser. B, 183 (1973) 399
[25] R.A. Robinson and R.H. Stokes, Electrolytes solutions (Butterworths, London, 1959).
[26] N. Shavit, Israel J. Chem. 11 (1973) 235.
[27] M. Rinaudo and M. Milas, J. Chim. Phys. Physicochim. Biol. 66 (1969) 1489.
[28] P. Buchner, R.E. Cooper and A. Wasserman, J. Chem. Soc. London (1961) 3974.
[29] D.R. Hardisty and S.M. Neale, J. Polym. Sci. 46 (1960) 195.
[30] S. Oman, Makromol. Chem. 178 (1977) 475.