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TRANSFERENCE NUMBERS, POLYION MOBILITIES, AND CHARGE FRACTIONS IN AQUEOUS SOLUTIONS OF LITHIUM, SODIUM, AND POTASSIUM DEXTRANSULFATE

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Results of Hittorf type transference number measurements are reported for aqueous solutions of lithium, sodium, and potassium dextransulfate (DS) in the concentration range 0.008–0.09 moles of sulfate groups per liter. The results for the polyion transference number are combined with equivalent conductance measurements reported earlier to calculate the polyion equivalent conductance, and the polyion charge fraction based on Wall's method. Our results show that the transference number of this high charge density polyion is larger than unity over the entire concentration range studied, and decreases monotonously with increasing concentration. The calculated charge fraction f of the polyion increases with increasing concentration, and at any concentration f decreases in the order LiDS > NaDS > KDS. A comparison between the conclusions derived from these transport experiments and from both mean and single ion activity measurements in dextransulfate solutions shows the considerable uncertainties involved in either of these methods, and emphasizes the need for the application of a variety of techniques, including spectroscopic techniques, to determine differential ion binding by polyions.

1. Introduction

Reports on differential binding of alkalimetal ions by polyions are often contradictory, with different experimental methods leading to different conclusions. In many cases this may well be caused by the fact that the quantities measured do not reflect binding alone, but may also contain contributions from differences in e.g. hydration, mobility, etc. Polyions with sulfate or sulfonate ions as the fixed charges are thought to be only weakly dehydrating, yet even with these polymers the evidence for differential binding of alkali ions depends on the technique used. Ultrasonic absorption should be an excellent qualitative tool for detecting the dehydration which would accompany the polyion-counterion binding process. Using this technique, Tondre and Zana [1] do not find any specificity in alkalimetal ion binding to the polystyrene sulfonate anion. However, for the polyvinylsulfonate anion these authors find the unusual binding squence $K^+ > Na^+ > Rb^+ > Cs^+ > Li^+$. Hen and Strauss [2], from dialysis and dilatometry measurements come to a binding sequence $K^+ > Na^+ > H^+ \simeq Li^+$ for the same polyvinylsulfonate anion. For heparin, a highly charged polysaccharide with both sulfate and carboxyl groups in approximately a 3 : 1 ratio on the glucoside units, Salminen and Luomanmaki's ultrafiltration experiments [3] show a preference of heparin for K^+ over Na^+, similar to the results of ion exchange experiments of Dunstone [4]. For carrageenan, also a sulfate polysaccharide, Ashton et al. [5] using a dye binding method arrive at a binding sequence $Cs^+ > K^+ > Na^+ > Li^+$. For the same polyion, Pass et al. [6] from single ion activity measurements also find a sequence $K^+ > Na^+$. However, difficulties arise in the interpretation of activity measurements. In principle activity measurements should be able to show differences in binding quantitatively. Podlas and Ander [7], using the same carrageenan fraction as Ashton et al. and Pass et al., measured single ion activities and report a binding sequence $Na^+ > K^+$. For dextransulfate Sataki et al. [8] and Noguchi et al. [9] both conclude that the binding sequence is $K^+ > Na^+$, but there is a wide discrepancy between the actual

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activity coefficients reported by these groups, even when one takes into account the differences in the degrees of substitution of the polyions used. The measurement of the mean ionic activity coefficient of the added salt in polyelectrolyte- simple electrolyte mixtures should show the same difference in counterion binding as may be inferred from single ion activity measurements, especially when the polyion to coion ratio is high. For polystyrenesulfonate no significant differences in mean activity coefficients of added NaCl or KCl were detected [10], in agreement with the observations of Tondre and Zana mentioned earlier. But in mixtures of alkalimetal salts of dextransulfate and the corresponding alkalimetal chloride, using Li, Na, K and Cs salts, again no differences were found at low polymer concentrations and high polymer to salt ratios [11]. This finding contradicts the reports of differential binding based on single ion activity measurements [8,9].

Wall [12] introduced the use of transference and conductance measurements to calculate the "fraction of free counterions", f, in salt-free polyelectrolytes from the equation:

$$\Lambda = f(t_p \Lambda + \lambda_c) \,. \qquad (1)$$

Λ is the equivalent conductance of the salt-free polyelectrolyte, t_p the polyion transference number and λ_c the equivalent ionic conductance of the counterions. In Wall's and in most subsequent calculations λ_c was assumed to be equal to the equivalent ionic conductance of the counterion in a simple electrolyte solution of a concentration equal to that of free counterions in the polyelectrolyte solution. Kurucsev et al. [13,14] and Ander et al. [15,16] use λ_c^0, the infinite dilution value instead of λ_c in their calculation of f. The choice of λ_c^0 or λ_c seems rather arbitrary, and neither approach is strictly valid [13]. The use of λ_c^0 neglects the mutual interactions of the free counterions, whereas the use of λ_c assumes that the interactions between small ions in a salt free polyelectrolyte solution are identical to those in a simple electrolyte solution. In this paper we adopt the procedure of Kurucsev and Ander and use λ_c^0. From the assumptions used in deriving eq. (1) it is clear that the quantity f calculated from Λ and t_p measurements is far from being an unambiguous representation of the fraction of free counterions. Manning [17] reasoning from condensation theory, arrives at the same form of eq. (1) but finds:

$$f = 0.87\,\xi^{-1} \,, \qquad (2)$$

where ξ is the charge density parameter of the polyion. In condensation theory of course ξ^{-1} is the fraction of free counterions in salt-free polyelectrolytes, not f. Among the most critical conditions for f to represent the fraction of free ions in Wall's formulation, or for Manning's form of eq. (1) to be valid, is the assumption that the bound or condensed counterion moves with the polyion. Indeed it will be very difficult if not impossible to distinguish between a real difference in the degree of binding and various degrees of mobility of bound or condensed counterions. Thus the interpretation of measured f values may suffer from considerable uncertainty just like the interpretation of activity coefficients, or the variety of other techniques referred to earlier. In view of these uncertainties, it is surprising that so few studies exist where the degree of binding as determined by a variety of methods is compared for the same polyion-counterion combination. The synthetic biopolymer dextransulfate is a stable sulfated polymer, important in medical applications both for direct use and as an analog of heparin. Thermodynamic properties of solutions of alkalimetal salts of dextransulfate have been reported.

The excellent agreement between the values of NaCl mean activity coefficients in solution containing NaCl and Na dextransulfate, as reported by different groups using different dextransulfate samples and purification procedures [11,25] attests to the stability and purity of this material. As was mentioned above, mean activity measurements of the added alkalimetal salt did not reveal any differences in the degree of binding of the alkalimetal ions, but reported single ion activity coefficients have been interpreted in terms of preferential binding of K^+ over Na^+. As was stated above the quantitative interpretation of transport number measurements in terms of the determination of the fraction of free ions suffers from a number of uncertainties, but there is no question concerning the qualitative interpretation of transport numbers or ion mobilities in relation to the degree with which counterions move together with the polyion. In this paper we will report t_p measurements in salt-free Li, Na and K dextransulfate solutions, and we will report the calculated values of f using eq. (1). We will compare our findings to the conclusions based on activity measurements.

2. Experimental

Na dextransulfate was obtained from Pharmacia, Uppsala, Sweden. The preparation of Li, Na and K dextransulfate, purification, concentration and equivalent weight determination all were the same as described in an earlier communication [11]. All solutions were made in deionized water with a specific conductance less than 10^{-6} Ohm^{-1} cm^{-1}. All solutions were made up by weight, and all concentrations were initially determined as moles/kg solution. Densities accurate to 0.02% were determined with a simple pycnometer method, and these results were used to calculate concentrations in mole/ℓ. These last units are used throughout in the presentation of our results.

The transference numbers were determined by the Hittorf method. The Hittorf cell is made of 1.3 cm internal diameter pyrex tubing. A number of turns introduced between anode and cathode departments provide horizontal and vertical sections intended to break up convection currents, and keep the cell compact to ensure temperature uniformity. The anode and cathod compartments contain approximately 45 ml each, and the middle compartment contains about 22 ml. By introducing stopcocks in suitable locations the middle compartment can be drained first, followed by draining of the electrode compartments. In initial experiments colored indicators were used to verify that H^+ or OH^- migration does not reach the middle compartment during regular runs. Platinum wire electrodes were used. In order to achieve a relatively constant current across the high cell resistance, a resistance of up to 200 kOhm was placed in series with the cell, and current was supplied by a high voltage power supply (IP-17 or IP-32, Heath Co., Benton Harbour, Mich.). Even so the cell resistance changed enough so that for the low concentration solutions a sufficiently constant current could not be maintained during the electrolysis. For this reason, the voltage drop across a calibrated 100 Ohm resistor in series with the cell was recorded during all experiments. In most transport experiments between 8–20 coulombs were passed through the cell in 60 to 90 minutes (currents ranged from 2 to 4 mA). The accuracy of the charge passed through the cell is estimated at ±0.2%. After electrolysis the three compartments are drained, rinsed, and the contents weighed. Concentrations and total number of moles of alkali ions were determined by ion exchange using a small column with strongly acidic cation exchange resin in the H^+ form. Reproducibility of the concentration determinations is ±0.2% for the higher concentrations and ±0.4% for the lowest concentrations used (0.008–0.01 moles/kg solution). In all experiments concentrations and total number of moles in all three compartments were determined. Experiments in which the concentration of the middle compartment changed by more than 0.5% were discarded. Concentration changes in the electrode compartments varied between 5 and 15%. The reported transference numbers in the concentration range 0.008–0.09 M are reproducible within respectively 2 to 4%. Most of the transference numbers recorded are the average values calculated from the data for both anode and cathode compartments. The uncertainty in the concentration determination is the main cause of error in the reported t_p values.

3. Results and discussion

In fig. 1 measured polyion transference numbers (t_p) are plotted as a function of the LiDS, NaDS or KDS concentrations (moles M^+/ℓ). The observed t_p values for all three salts of dextransulfate are larger than unity over the entire concentration range investigated in this work. It is well known that t_p is strongly dependent on ξ, the charge density of the polyion, i.e. the larger ξ the larger t_p. Thus it is not at all unusual to find t_p values larger than unity [12,14,16,18], indicating that a major fraction of the counterions moves in the same direction as the polyions. No prior measurements on dextransulfate have been reported, but we can compare our results to transference measurements on Na polystyrenesulfonate, a polyion with about the same charge density. Jordan et al. [4] report t_p values between 1.7 and 1.6 for an atactic polymer with a degree of substitution of 1.1, i.e. a charge density ξ of approximately 3.1, in the concentration range 4×10^{-4}–1.4×10^{-3} equiv/ℓ. Dolar et al. [18] find t_p values decreasing from about 1.6 to about 1.0 between 2.5×10^{-3} and 8×10^{-2} equiv/ℓ for a high molecular weight polystyrenesulfonate sample with a degree of substitution of 1.0. These authors also find only a slight dependence of t_p on the molecular weight of the polymer. The values reported here for NaDS show a very similar concentration dependence as was reported by Dolar et al. for Na polystyrenesulfonate.

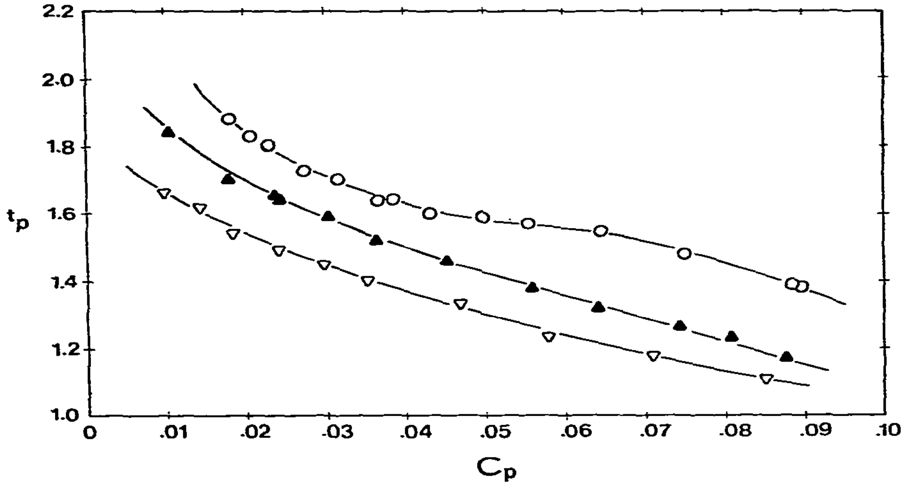

Fig. 1. The concentration dependence of the polyion transference number (t_p) to LiDS (▲), NaDS (○), and KDS (▽). C_p is in moles counterion/ℓ.

In fig. 2 the polyion equivalent conductance, λ_p, is plotted as a function of the polyelectrolyte concentration. These λ_p values are calculated from the transference numbers reported in fig. 1 and equivalent conductance values for the respective alkalimetal dextran sulfates reported earlier [19]. Also shown in fig. 2 are

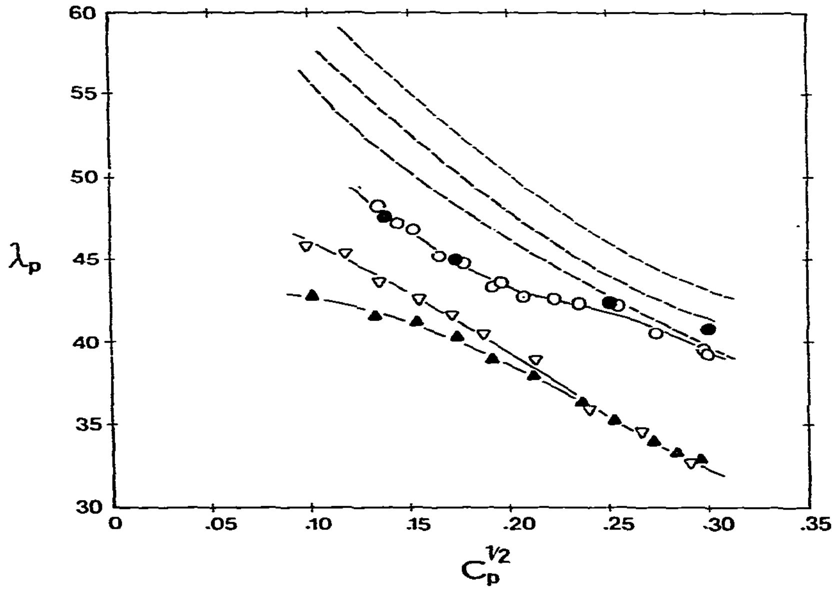

Fig. 2. The concentration dependence of the polyion equivalent conductance (λ_p, Ohm^{-1} cm^2 equiv^{-1}) in LiDS (▲), NaDS (○), and KDS (▽). ●: data for Na-poly(styrenesulfonate) from ref. [18]. Broken lines: Theoretical values (refs. [17,21]).

the limiting law values for λ_p calculated from Manning's theory [17,21], λ_c^0 values of 38.6 for Li^+, 50.1 for Na^+, and 73.5 for K^+ are used [20]. A value of 0.7 nm is used for a, the radius of the hypothetical cyclindrical polyion. The λ_p values calculated from Manning's equation depend on the choice of a. For instance, calculated values as plotted decrease by 8 to 12 units when a is changed from 0.7 to 1.2 nm. On the other hand the nature of the concentration dependence remains practically the same. Because of rather severe assumptions in the polyion model used, Manning's relation for λ_p will only give very approximate values for λ_p, and Λ has been found to be well represented by the theoretical expressions. The choice of 0.7 nm for a, though approximate, is probably appropriate, and it would be not in accordance with the nature of the theory to use a as an adjustable parameter in fitting the theoretical predictions to the data. Although the equivalent conductance data for dextransulfates do not correspond at all to Manning's limiting law for conductance [19,22], the theoretical λ_p values have a concentration dependence very similar to what is observed. But theory of course predicts a regular decrease of λ_p in the order KDS > NaDS > LiDS whereas the observed trend is NaDS > KDS > LiDS. Ross and Scruggs [24] found that the electrophoretic mobility of NDA was highest in KCl and lowest in LiCl, with an intermediate value in NaCl. The authors interpreted these data by assuming preferential binding of DNA in the order Li > Na > K, but Manning [23] has interpreted these differences as partly due to differences in the local viscosity around the polymer, with Li ions increasing the viscosity more than sodium and potassium ions. Following this argument our λ_p values for KDS are clearly abnormally low. In fig. 2 we have also plotted some λ_p values for Na polystyrenesulfonate calculated from the data of Dolar et al. [18]. Interestingly enough the λ_p values for the dextransulfate polyion and the polystyrenesulfonate polyion, both with Na^+ as the counterion, are in very close agreement.

The "polyion charge fraction", f, calculated from eq. (1) using the present t_p data and our earlier data for Λ [19] is plotted as a function of the dextransulfate concentration in fig. 3. f values decrease in the order LiDS > NaDS > KDS at all concentrations investigated. For all three salts f increases with increasing polyion

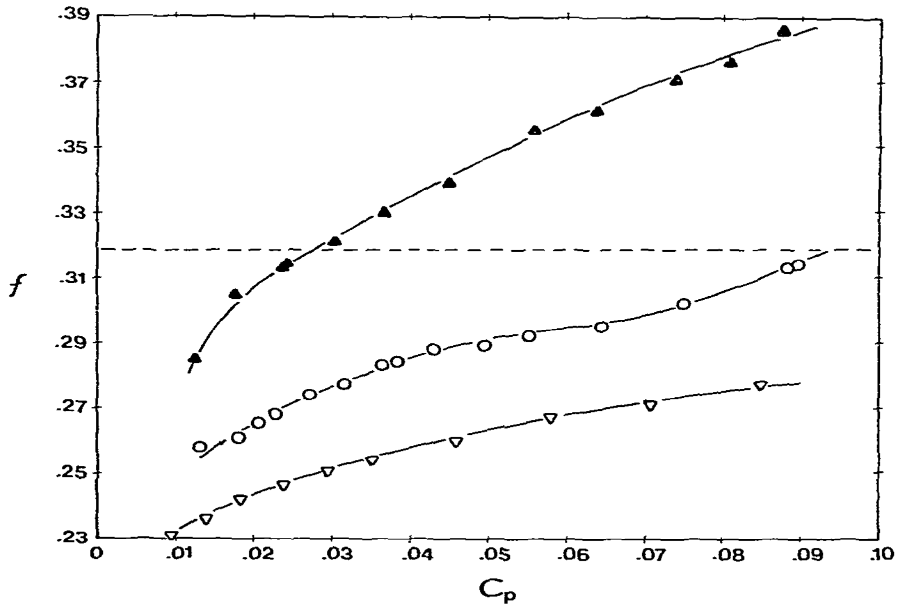

Fig. 3. The concentration dependence of f in LiDS (▲), NaDS (○), and KDS ( ). Broken line: eq. (2).

concentration. Reports on the variation of f with concentration are now available for various polyelectrolytes [12,14–16]. For sodium polystyrenesulfonate both Dolar et al. [18] and Kowblanski and Ander in solutions containing added NaCl [16] observe a large increase in f with an increase in concentration. If the data for Na-polysytrenesulfonate and NaDS are compared in a similar concentration range, the changes reported in f for the former polyion are almost twice the magnitude of the changes in f reported for the latter. On the other hand the data of Jordan et al. [14] at lower concentrations show a much smaller concentration dependence of f for Na polystyrenesulfonate. For various other polyelectrolytes, e.g. Na polyacrylate [12], Na alginate [15], Na pectate [15] and poly (4-vinyl-N-n butyl pyridinium bromide) [14] f was found to be practically concentration independent.

The reported f values for NaDS and KDS are lower than the Manning limiting law value of $0.87\,\xi^{-1}$, i.e. 0.314, in the entire concentration range. For LiDS f becomes larger than the limiting law value above 0.03 M. At this point it is of interest to recall our results for the mean activity coefficient of the added salt in LiCl-LiDS, NaCl-NaDS, KCl-KDS, and CsCl-CsDS mixtures [11]. We observed very similar values for the activity coefficients of the alkalimetal chlorides at the lowest polyion concentration used (0.009 m). As the polyion concentration was increased the activity coefficient at constant coion/polyion concentration ratio increased more for LiCl than for NaCl, and remained practically constant for KCl and CsCl. These results however were not thought to be indicative of differential binding. The anomalous position of the K^+ λ_p data in fig. 2 and the significant differences found in f values for the three alkalimetal salts indicate that transport properties are affected differently. Manning [21] already indicated that f can be considered to represent the fraction of free ions only if the free counterions do not interact with the polyion of reduced charge, or with other counterions. Moreover, there is uncertainty over the choice of value to be used for λ_c in eq. (1). Thus, the f values as reported in fig. 3 may not necessarily indicate a specific binding sequence in the order $K^+ > Na^+ > Li^+$. The actual situation is quite complex. All ions defined as "bound" or "condensed" from measurements of equilibrium properties may still not be moving with the polyion in transport processes, or may do so to different degrees, leading to different f values. In addition, effects like e.g. the influence of the counterions on the local viscosity around the polyion may cause different λ_p and f values as well.

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