

# An Experimental Study of the Effect of Temperature on Effective Charge Numbers and Diffusion Coefficients of Lignosulfonate

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A study of the loss of the charge of lignosulfonate at ca. 40 °C has been carried out while varying the counterion and the ionic strength of the solution as a function of temperature. The effect of external field was studied at 43 °C. Also, the possibility of aggregation was investigated by measuring the surface tension and by gel chromatography. The results showed that the loss of charge at ca. 40 °C is independent of the choice of counterion (except in the case of Mg<sup>2+</sup>) but is dependent on the ionic strength: the greater the Debye length, the higher is the temperature at which the molecule undergoes complete ion-pairing. No evidence of the aggregation of lignosulfonate molecules could be found.

Resorting to the results measured in an external electric field it is concluded that the loss of charge at ca. 40 °C takes place only when the molecule is a compact sphere, and it is proposed to be due to changes in structured water near the surface of the macromolecule.

The effect of temperature on the effective charge numbers and diffusion coefficients of polyelectrolytes has not been subject to many studies. Most measurements have been carried out at room temperature.<sup>1</sup> This is surprising, since many important polyelectrolytes, such as proteins, operate at elevated temperatures, i.e. at ca. 40 °C. A recent study<sup>2</sup> showed that lignosulfonate, a polydisperse polyelectrolyte, lost its charge at about 40 °C when the supporting electrolyte was 0.1 M NaCl in water. It has been shown that lignosulfonate molecules are compact spheres in aqueous solutions,<sup>3</sup> except under an external electric field, when they appear to be exposed to conformational changes.<sup>4</sup>

When studying another spherical polyelectrolyte, viz. cytochrome-c in 0.1 M NaCl solution, the same behaviour was observed: cytochrome-c lost its charge.<sup>5</sup> The resemblance between these two polyelectrolytes is not very remarkable, except that their conformational structure is similar. This experimental observation encouraged us to carry out a more extensive study of the effect of temperature on effective charge numbers. We chose the model substance to be lignosulfonate because of its polydisperse nature, which enables us to consider the conformational structure through the Mark–Houwink equation. To elucidate the loss of charge on lignosulfonate at elevated temperatures the effect of the following parameters of the system were studied while varying the temperature: the counterions lithium, sodium and potassium were investigated to see if hydration energy has an impact on this phenomenon; also, the effect of the bivalent counterions magnesium and barium was measured; in order to see if the phenomenon is dependent on

the Debye length, the concentration of the base electrolyte (NaCl) was changed from 0.01 to 1.0 M in the solution; finally, an external electric field was applied to the homogeneous 0.1 M NaCl solution to determine whether the expected conformational changes give rise to dissociation.

The method employed here to measure the effective charge numbers and diffusion coefficients is described in detail elsewhere,<sup>3,6,7</sup> and is based on a convective diffusion process in a porous membrane.

## Experimental

**Apparatus.** Two different types of cell arrangement were employed. In order to measure the diffusion coefficients and effective charge numbers, a cell without ion-exchange membranes was used, i.e. in the cell in Fig. 1 the cation-exchange membranes were replaced by perspex plates. The arrangement just as in Fig. 1 was used to measure the effect of external electric field on transport properties. Both cells have been described in detail in previous papers.<sup>4,5</sup>

**Materials and analysis.** The sodium chloride, sodium bromide, lithium chloride, potassium fluoride, potassium chloride, magnesium chloride, barium chloride and sodium sulphate used were *pro analysis* grade. The sodium lignosulfonate was obtained from Borregaard (Norway) and contained ca. 99% lignosulfonates and ca. 1% carbohydrates. Its molar mass distribution differed slightly from that used earlier,<sup>3</sup> and was determined by gel filtration as presented elsewhere.<sup>3</sup>

The metal ion concentrations were analysed by atomic absorption spectroscopy (AAS). The total concentration of

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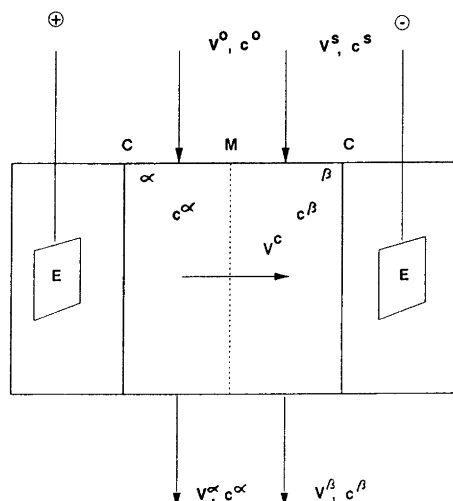


Fig. 1. A schematic drawing of the cell, which is divided into two compartments  $\alpha$  and  $\beta$  with a porous membrane (M). Cation exchange membranes (C) separate the electrode compartments from compartments  $\alpha$  and  $\beta$ . The supporting electrolyte solution is pumped into compartments  $\alpha$  and  $\beta$  at constant rates  $V^\alpha$  and  $V^\beta$  and at constant concentrations  $c^\alpha$  and  $c^\beta$ . The polyelectrolyte is fed into the system in the flow  $V^s$ . A flow  $V^\alpha$  is pumped out from compartment  $\alpha$  while  $V^\beta$  is a free outlet flow. The convective flow  $V^c$  is then the difference  $V^\alpha - V^\beta$ .  $c^\alpha$  and  $c^\beta$  are the stationary-state concentrations in compartments  $\alpha$  and  $\beta$ . Compartments  $\alpha$  and  $\beta$  are stirred with the aid of magnetic fleas.

lignosulfonate was determined by UV-VIS spectrophotometry, and the bromide concentration was analyzed by ion-exchange chromatography (Millipore, Waters).

**Measurements.** Four sets of experiments were performed. In the first set the influence of monovalent counterions ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) was studied using 0.1 M supporting electrolyte solutions of LiCl, NaCl and KF, while varying the temperature from ca. 10 to 50°C. It must be realized that the use of KCl as a supporting electrolyte when determining the effective charge numbers is unreasonable because of the negligible difference in mobilities of  $\text{K}^+$  and  $\text{Cl}^-$  ions.<sup>6</sup>  $\text{K}^+$  ion in the case of LiCl and NaCl and  $\text{Na}^+$  ion in the case of KF were used as internal standards to determine the membrane constant  $A/l$ .

In the second set of experiments the effect of divalent counterions ( $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ) was investigated using 0.1 M supporting electrolyte solutions of  $\text{MgCl}_2$  and  $\text{BaCl}_2$  while varying the temperature from ca. 10 to 50°C.  $\text{K}^+$  ion was used as the internal standard. In the third set of experiments it was studied how ionic strength affects the diffusion coefficients and charge numbers of lignosulfonate. These experiments were carried out at supporting electrolyte concentrations of 0.01, 0.1 and 1.0 M of sodium chloride and at temperatures from 30 to 45°C.  $\text{K}^+$  ion was again used as the internal standard.

In the fourth set of experiments the influence of a weak external electric field (ca. 10  $\text{V m}^{-1}$ ) was studied at 40°C when the supporting electrolyte was 0.1 M sodium chlo-

ride. This was done in order to find out if the electric field changes the conformation of the lignosulfonate molecules in a similar manner to that which occurs at 20°C.<sup>4</sup>  $\text{Br}^-$  ion was used as an internal standard because of the cation-exchange membranes used in the cell (Fig. 1).

In the first three sets of experiments the measurements of the diffusion coefficients of lignosulfonate were carried out with the concentration of the supporting electrolyte kept constant throughout the system. This was achieved by having the same concentration of the supporting electrolyte in the feeds  $V^\alpha$  and  $V^\beta$ . With the feed  $V^s$  the internal standard and lignosulfonate were introduced into the system at the concentrations  $2 \times 10^{-4} \text{ mol dm}^{-3}$  and  $1 \text{ g dm}^{-3}$ , respectively. The concentration ratios  $c^\beta/c^\alpha$  for lignosulfonates of different molar masses were determined as presented earlier.<sup>3</sup> Measurements of the effective charge numbers of the lignosulfonates were performed by using supporting electrolyte concentrations  $c_+^o = 0.5 c_+^{\text{H}}$  and  $c_+^s = 1.5 c_+^{\text{H}}$  in the feeds  $V^\alpha$  and  $V^\beta$ , respectively.  $c_+^{\text{H}}$  is the concentration of the supporting electrolyte system used in the corresponding  $D_i$  measurement. The concentrations of the internal standard and lignosulfonate were the same as in the diffusion coefficient measurements.

In the fourth set of experiments the electric currents were 3.64, 2.84, 1.83, 0.46, 0.131 and 0.066 mA, corresponding to an electric field strength from 25 to 0.05  $\text{V m}^{-1}$ . The concentrations  $c^\alpha$  and  $c^\beta$  in feed solutions  $V^\alpha$  and  $V^\beta$  were calculated according to eqn. (T3) in Table 1, to obtain a homogeneous system with respect to the supporting electrolyte solution. For further details see Ref. 4. In all the above experiments the flow rates were very similar to those presented previously.<sup>8</sup>

With regard to the reproducibility of the measurements, every measurement was made several times and, without bacteria growth, results are the same with an accuracy of better than 5%.

An effort was made to find out if aggregation of lignosulfonate molecules occurs during the transport process and whether this phenomenon could cause the sudden loss of charge near 40°C. First, the molar mass distribution of lignosulfonate was analyzed as a function of temperature by performing the gel filtration described earlier in a thermostatted column at temperatures between 10 and 50°C, so that the lignosulfonate concentrations in the column were of the same order as the concentrations in the transport experiments.

Secondly, the temperature behaviour of surface tension of the polyelectrolyte solutions was studied in order to detect signs of aggregation. The surface tension measurements were carried out by the pendant drop technique with the aid of a microcomputer. A video image of a drop hanging from the tip of a capillary was analyzed as follows: after a snapshot from a drop was taken it was digitized into  $512 \times 512$  pixels, each having an 8 bit integer value according to its brightness. The coordinates of the edge of the drop were then found by searching the maxima of the differences of the integer values between two parallel pix-

Table 1. The equations needed to evaluate diffusion coefficients and charge numbers of a polyelectrolyte and the membrane constant.

Diffusion coefficient ( $D_i$ ):

$$\frac{c_i^\alpha}{c_i^\beta} = \left(1 + \frac{V^\alpha}{V^c}\right) \exp\left(\frac{V^c}{A/l} D_i\right) - \left(\frac{V^\alpha}{V^c}\right) \quad (\text{T1})$$

Charge number ( $z_i$ ):

$$\frac{c_i^\alpha}{c_i^\beta} = \exp\left(\frac{V^c}{(A/l)D_i}\right) \left(\frac{c_+^\beta}{c_+^\alpha}\right)^{-\left[\frac{z_i}{z_+}\left(1 - \frac{D_\pm}{D_+}\right)\right]} \\ \times \left\{1 + \frac{V^\alpha}{D_i(A/l)} \int_0^1 \exp\left(\frac{V^c x}{D_i(A/l)}\right) \left(\frac{c_+}{c_+^\alpha}\right)^{-\left[\frac{z_i}{z_+}\left(1 - \frac{D_\pm}{D_+}\right)\right]} dx\right\} \quad (\text{T2})$$

where

$$\frac{c_+}{c_+^\alpha} = \left(1 + \frac{V^\alpha}{V^c} - \frac{c_+^o}{c_+^\alpha} \times \frac{V^o}{V^c}\right) \exp\left(\frac{V^c x}{D_\pm(A/l)}\right) + \frac{c_+^o}{c_+^\alpha} \times \frac{V^o}{V^c} - \frac{V^\alpha}{V^c}$$

 $D_i$  or  $z_i$  under external electric field for 1,1-supporting electrolyte:

$$\frac{c_i^\beta}{c_i^\alpha} = 1 + \frac{V^\alpha}{\left(V^c + \frac{z_i D_i j}{(D_+ + D_-) F c^{\alpha,\beta}}\right)} \\ \times \exp\left[\left(\frac{V^c}{D_i} - \frac{z_i j}{(D_+ + D_-) F c^{\alpha,\beta}}\right) \times \frac{1}{(A/l)}\right] - \frac{V^\alpha}{\left(V^c + \frac{z_i D_i j}{(D_+ + D_-) F c^{\alpha,\beta}}\right)} \quad (\text{T3})$$

where the supporting electrolyte has been made homogeneous with the aid of the relationship:

$$c^o = c^{\alpha,\beta} - \frac{t_i j}{F V^o}; \quad c^s = c^{\alpha,\beta} + \frac{t_i j}{F V^c}$$

Membrane constant ( $A/l$ ) from the supporting electrolyte:

$$\frac{c_+^\beta}{c_+^\alpha} = \left(1 + \frac{V^\alpha}{V^c} - \frac{c_+^o}{c_+^\alpha} \times \frac{V^o}{V^c}\right) \exp\left(\frac{V^c}{D_\pm(A/l)}\right) + \frac{c_+^o}{c_+^\alpha} \times \frac{V^o}{V^c} - \frac{V^\alpha}{V^c} \quad (\text{T4})$$

Definitions of the parameters in eqns. (T1)–(T4):  $V^o$ ,  $V^s$ ,  $V^\alpha$ ,  $V^c$  ( $= V^o - V^\alpha$ ) and  $V^\beta$  ( $= V^s + V^o$ ) are the flow rates described in Fig. 1;  $c^o$ ,  $c^s$ ,  $c^\alpha$  and  $c^\beta$  are the concentrations of the supporting electrolyte in the flows, respectively;  $c_+^\alpha$  and  $c_+^\beta$  are the polyelectrolyte or the internal standard concentrations in the flows  $V^\alpha$  and  $V^\beta$ , respectively;  $A/l$  is the membrane constant;  $D_\pm$ ,  $D_+$  and  $D_-$  are the diffusion coefficients of the salt, cation and anion of the supporting electrolyte, respectively;  $D_i$  is the diffusion coefficient of the polyelectrolyte or the internal standard;  $i$  is the electric current;  $c^{\alpha,\beta}$  is the homogeneous concentration of the supporting electrolyte;  $z_i$  is the effective charge number of the polyelectrolyte or the internal standard; and  $z_+$  is the charge number of the cation of the supporting electrolyte.

els. Illumination produced an extremely sharp contrast between the drop and the background, and no problems in the detection of the edge occurred.

The determination is based on the inflexion point method,<sup>9</sup> which has become accessible via the use of com-

puters; from a photograph it is impossible to determine the inflexion point accurately enough. In the inflexion point method the complicated nonlinear differential equation is reduced to an algebraic equation from which the surface tension can be solved in a simple way.<sup>10</sup>

The inflexion point of the edge curve was found by fitting the curvature between the tip of the capillary and the widest plane of the drop into a fifth-degree polynomial, differentiating it twice (analytically), and determining the zero of the third-degree polynomial thus obtained. All the software was self-made, but in the fitting procedure library subroutines from Ref. 11 were utilized.

After setting, a new drop at the tip of the capillary surface tension tends to decrease until a steady value is reached. Therefore, 150 snapshots were taken from each drop, and the time of each snapshot was also registered. From these surface tension versus time curves 10 successive values after reaching steady state were selected to calculate an average value. Standard deviations were ca.  $0.2 \text{ mN}^{-1}$ .

*Evaluation of diffusion coefficients and effective charge numbers from the measured data.* The equations from which the diffusion coefficients and charge numbers were evaluated are presented in Table 1. Eqn. (T1) was used to calculate diffusion coefficients,<sup>3</sup> eqn. (T2) to calculate charge numbers,<sup>7</sup> eqn. (T3) to obtain either the diffusion coefficient or the charge number<sup>4</sup> when the other one is given, under an external electric field, and eqn. (T4) was used to obtain the membrane constant when the supporting electrolyte system is inhomogeneous.<sup>6,8</sup> When the membrane constant was evaluated with the aid of an internal standard, eqn. (T1) was used in the case of a homogeneous supporting electrolyte and eqn. (T2) was used for an inhomogeneous supporting electrolyte.

As can be seen in eqns. (T1)–(T4), the concentrations of supporting electrolyte in the feed solutions as well as in the compartments  $\alpha$  and  $\beta$  must be known, and the concentration ratios of lignosulfonate and the internal standard are needed in the calculations. Also, all the flow rates must be measured.

Eqns. (T2)–(T4) are derived assuming that ion–ion interactions are negligible, i.e. the Nernst–Planck equation is used in the conventional form,<sup>12</sup> in which the ionic diffusion coefficients due only to the solvent–ion interaction are considered. As has been shown earlier,<sup>13</sup> this simplification can be avoided provided that data for diffusion coefficients, activity coefficients and transport numbers for the supporting electrolyte are available. Unfortunately, this is not the case here, because no pertinent data have been presented over the concentration and temperature ranges studied. That is why we have to resort to the use of the equations in Table 1. However, in the case of a univalent supporting electrolyte at concentrations 0.1 M or lower, the correction due to the ion–ion interaction is not very meaningful, although in the case of 2,1-electrolytes the effect is of such a magnitude that no reasonable results for the diffusion coefficients and charge numbers could be obtained. This fact was deduced when studying the behaviour of the internal standard. It gave unrealistic values for the membrane constant, indicating that the tracer-diffusion coefficient obtained from a very dilute solution of this ion, has

the wrong value. This is evidently due to the unsymmetrical base electrolyte; for further details see Ref. 14.

The crucial point of evaluating the charge numbers is the ‘choice’ of the diffusion coefficient  $D_{\pm}$  and the ionic diffusion coefficient of the cation  $D_{+}$  of the supporting electrolyte. For the electrolytes used, no data over the studied concentration and temperature ranges were found from the literature. Therefore, the following procedure to estimate the values of these quantities was used. For univalent supporting electrolytes at a concentration of 0.1 M or less we utilized the Nernst–Hartley equation  $D_{\pm} = |z_{+}z_{-}|D_{+}D_{-}/(|z_{-}|D_{-} + z_{+}D_{+})$ , where the ionic diffusion coefficients ( $D_{+}, D_{-}$ ) were obtained from Ref. 15. The values given by Dobos<sup>15</sup> are probably based on conductivity data, and are given as a function of concentration and temperature. Reasonable agreement with the measured and calculated diffusion coefficients was obtained in the cases where a comparison could be made. For 1 M NaCl solutions this approach did not work sufficiently well, and therefore Walden’s rule ( $\eta D/T = \text{constant}$ , where  $\eta$  is the viscosity) was applied, one reason being the availability of the viscosity data.<sup>16</sup> Thus, using the measured diffusion coefficients and transport numbers ( $t_{+}$ ) at 25 °C a relationship for  $D$  in the form of  $D(T) = T(\eta_{25}D_{25}/T_{25})/\eta(T)$  and for  $D_{+}$  in the form of  $D_{+} = D(T)/2(1-t_{+})$  was derived;  $\eta_{25}$ ,  $D_{25}$  and  $T_{25}$  denote the values of viscosity, diffusion coefficients and thermodynamic temperature at 25 °C, respectively.

In the case of  $\text{MgCl}_2$  and  $\text{BaCl}_2$  as supporting electrolyte the approach used for univalent electrolytes did not work at all, at least when using data given by Dobos,<sup>15</sup> showing values which deviated considerably from the measured values for  $\text{MgCl}_2$ <sup>17</sup> and  $\text{BaCl}_2$ <sup>18</sup> at 25 °C (ca. 20 %). Furthermore, a possible ion association of these bivalent cations needs to be considered because of its great impact on the mathematical modelling.<sup>13</sup> The major handbooks of stability constants<sup>19</sup> do not give evidence of ion pairing for  $\text{MgCl}_2$  and  $\text{BaCl}_2$ , but in a monograph<sup>20</sup> evidence is presented which refers to a considerable ion pairing of  $\text{MgCl}_2$ . Taking into account the abovementioned reasons, we feel unable to present quantitative results for the diffusion coefficients and charge numbers of lignosulfonate when the counterions are  $\text{Mg}^{2+}$  and  $\text{Ba}^{2+}$ . However, we are able to say when the charge number goes to zero. This is due to the fact that when the charge number is zero there is no difference in the concentration ratios ( $c^{\beta}/c^{\alpha}$ ) of lignosulfonates when the supporting electrolyte is homogeneous or inhomogeneous, provided that the flow rates are the same in both measurements. This gives a good diagnostic criterion for the complete ion pairing of the polyelectrolyte, even though exact numerical values for the diffusion coefficients cannot be obtained owing to a poor knowledge of the transport data.

A separate problem is the use of an internal standard when the supporting electrolyte is homogeneous throughout the whole system, because the only way to determine the membrane constant is the use of a trace ion added in small amounts into the system. In this case the diffusion coefficient of this tracer ion must be known, and again

Table 2. Diffusion coefficients  $D$  (in  $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ) of the supporting electrolyte at various temperatures.

Supporting electrolyte	$c/M$	$t = 10^\circ\text{C}$		$t = 20^\circ\text{C}$		$t = 30^\circ\text{C}$		$t = 40^\circ\text{C}$		$t = 50^\circ\text{C}$	
		$D_{\pm}$	$D_+$	$D_{\pm}$	$D_+$	$D_{\pm}$	$D_+$	$D_{\pm}$	$D_+$	$D_{\pm}$	$D_+$
LiCl	0.1	0.75	0.55	1.01	0.76	1.29	0.98	1.59	1.22	1.91	1.47
NaCl	0.01	1.00	0.82	1.33	1.11	1.68	1.42	2.04	1.74	2.43	2.08
	0.1	0.91	0.74	1.21	1.00	1.52	1.27	1.86	1.56	2.22	1.87
	1.0	1.01	0.82	1.33	1.11	1.69	1.42	2.12	1.75	2.57	2.14
KF	0.1	1.05	1.29	1.23	1.50	1.55	1.88	1.89	2.28	2.25	2.69

reasonable data are available only for a univalent base electrolyte. For further details see, e.g., Ref. 14. However, for bivalent cations problems arise, obviously due to the unsymmetrical concentration field in which the trace-ion has to travel. As discussed by Erdey-Gruz,<sup>14</sup> there are more or less suitable theoretical approaches to estimate the tracer-diffusion coefficients, but in the present case we do not have to resort to these theoretical calculations. This is due to the possibility of measuring them, because in the inhomogeneous supporting electrolyte system when we know  $D$  for the salt we can calculate the membrane constant ( $A/l$ ) from eqn. (T4), and use the value thus obtained in eqn. (T2) to compute the diffusion coefficient for the tracer ion. In the case where an external electric field is applied we proceeded as described elsewhere.<sup>4</sup> We have presented the diffusion coefficients used in Table 2. The values are obtained as described above.

## Results

The diffusion coefficients and effective charge numbers of lignosulfonate with different monovalent counterions ( $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ) are presented in Table 3 for various temperatures (10–50°C). The diffusion coefficients of these different counter-ion systems do not differ very much from each other and increase slightly with increasing temperature. In the earlier paper<sup>2</sup> it has been reported that the conformation of the lignosulfonate molecules in 0.1 M NaCl solution does not change in the temperature range 10–50°C. This is also the case in 0.1 M LiCl and KF solutions. The exponent  $b$  in the Mark-Houwink equation ( $D = KM^b$ ) varies from  $-0.24$  to  $-0.38$ , indicating that the molecules are compact spheres. Also, the effective charge numbers of lignosulfonate molecules in 0.1 M LiCl or KF solution behave like those in 0.1 M NaCl solution,<sup>2</sup> i.e. they decrease slightly with increasing temperature from 10 to 30°C, and then at 40°C molecules become completely ion-paired.

As discussed above, we are not able to present numerical data for the diffusion coefficients and effective charge numbers of lignosulfonate in the case of bivalent counterions ( $\text{Mg}^{2+}$  and  $\text{Ba}^{2+}$ ). However, from the measured data we can determine that the charge numbers when  $\text{Ba}^{2+}$  is used as a counterion drops to zero at 40°C. In the case of  $\text{Mg}^{2+}$  as counterion the charge numbers decrease but do not reach zero.

The effect of the ionic strength of the supporting electrolyte was studied near the temperature at which charge is lost in 0.1 M solutions. The results are listed in Table 4. As can be seen, the ionic strength has a clear effect on the temperature at which the charge number goes to zero. In 1 M NaCl solutions the zero charge is reached at 35°C, whereas in 0.01 M solution the charge does not go to zero even at 45°C.

The effect of an external electric field at 43°C in 0.1 M NaCl solution was studied. Because the contribution of migration is always present when carrying out experiments under an external electric field, the diffusion coefficients and charge numbers cannot be measured separately. Therefore either  $D_i$  or  $z_i$  must be given in order to obtain the other. As presented previously,<sup>4</sup> the conformation of lignosulfonate molecules changes from a compact sphere to a non-free-draining coil when the external electric field strength exceeds  $10 \text{ V m}^{-1}$  at 20°C. That is why it is assumed that this is also the case at 43°C. The measurement at 43°C clearly showed that the transport of lignosulfonate molecules is affected by an electric field, indicating the charged nature of these molecules. Thus it was deduced that the change in conformation changes the ion-pairing equilibrium. In Table 5 the diffusion coefficients of lignosulfonate are presented on varying the electric field strength from 0.5 to 25  $\text{V m}^{-1}$  and using  $z_i$ -values at 30°C.<sup>2</sup> This approach, in which we assume that the charge goes to zero at elevated temperatures only when the molecules are compact spheres, gives reasonable results. For instance, when evaluating the exponent  $b$  in the Mark-Houwink equation from the diffusion coefficients presented in Table 5, the values characteristic of a non-free-draining coil were obtained, i.e.  $-b = 0.5-0.6$ .

The molar mass distribution of lignosulfonate was unaltered by temperature, indicating that no aggregation takes place. Also, no aggregation can be detected in the surface tension data presented in Table 6.

## Discussion

The results for the diffusion coefficients of lignosulfonate show that no structural changes which could reflect to the diffusion coefficient take place under the conditions studied, except under an external electric field. This is also the case when the effective charge number goes to zero. There-

**Table 3.** The diffusion coefficients,  $D_i$ , and effective charge numbers,  $z_i$ , of lignosulfonate when supporting electrolyte is 0.1 M LiCl, NaCl or KF and the temperatures are 10, 20, 30, 40 or 50°C.  $M$  is the molar mass of lignosulfonate,  $T$  is the temperature and  $[D] = 10^{-6} \text{ cm}^{-2} \text{ s}^{-1}$ .

$M/10^3$	0.1 M LiCl		0.1 M NaCl		0.1 M KF	
	$D_i$	$z_i$	$D_i$	$z_i$	$D_i$	$z_i$
<b><math>T = 10^\circ\text{C}</math></b>						
50	0.79	-19.9	0.46	-26.7	0.59	-22.5
45	0.80	-19.5	0.48	-24.7	0.62	-21.1
40	0.81	-18.3	0.51	-24.5	0.65	-20.1
35	0.82	-17.8	0.53	-23.5	0.68	-18.7
30	0.84	-17.0	0.54	-22.0	0.71	-16.9
25	0.87	-15.9	0.57	-18.6	0.75	-16.1
20	0.92	-14.8	0.62	-18.0	0.82	-14.8
15	1.00	-13.6	0.71	-16.5	0.92	-12.5
10	1.12	-12.1	0.83	-10.5	1.07	-11.9
5	1.37	-8.9	0.97	-5.5	1.29	-7.8
<b><math>T = 20^\circ\text{C}</math></b>						
50	0.89	-20.2	0.84	-21.9	0.84	-19.2
45	0.91	-19.3	0.87	-20.1	0.86	-18.4
40	0.95	-18.6	0.91	-18.8	0.90	-17.2
35	0.98	-18.2	0.94	-18.2	0.92	-16.8
30	1.00	-17.5	0.97	-17.0	0.96	-15.7
25	1.05	-15.9	1.05	-15.8	1.02	-14.1
20	1.12	-14.8	1.09	-14.5	1.12	-12.0
15	1.25	-13.2	1.16	-12.4	1.26	-9.7
10	1.45	-11.9	1.31	-9.1	1.49	-7.1
5	1.65	-8.6	1.58	-6.1	1.77	-5.0
<b><math>T = 30^\circ\text{C}</math></b>						
50	1.16	-17.0	0.98	-21.2	1.41	-19.5
45	1.20	-16.2	1.03	-19.0	1.45	-17.0
40	1.24	-15.2	1.09	-17.9	1.54	-15.2
35	1.27	-14.1	1.11	-17.0	1.57	-13.1
30	1.31	-13.6	1.15	-15.5	1.62	-12.2
25	1.38	-12.5	1.23	-13.3	1.68	-11.5
20	1.50	-12.0	1.31	-12.3	1.82	-10.0
15	1.66	-10.9	1.44	-10.5	2.02	-9.2
10	1.94	-9.2	1.58	-9.0	2.35	-6.1
5	2.32	-6.9	1.88	-6.5	2.81	-2.9
<b><math>T = 40^\circ\text{C}</math></b>						
50	1.41	-2.5	1.24	0.2	1.67	-1.5
45	1.51	-2.7	1.29	0.1	1.78	-1.6
40	1.60	-2.6	1.34	0.2	1.86	-0.9
35	1.64	-2.4	1.41	0.0	1.92	-0.8
30	1.75	-2.6	1.46	-0.1	2.00	-0.5
25	1.86	-2.3	1.53	0.0	2.15	0.3
20	2.04	-1.8	1.58	-0.2	2.35	0.5
15	2.31	-1.7	1.69	-0.2	2.65	0.6
10	2.75	-1.4	1.91	-0.3	3.09	0.1
5	3.43	-1.7	2.31	-0.5	3.58	0.4
<b><math>T = 50^\circ\text{C}</math></b>						
50	1.70	-1.9	1.54	0.1	1.94	-1.0
45	1.77	-1.2	1.58	0.2	1.96	-0.2
40	1.86	-0.7	1.67	0.0	2.03	0.6
35	1.93	-0.6	1.68	0.0	2.06	0.7
30	1.99	0.4	1.77	-0.1	2.16	0.6
25	2.13	0.2	1.89	0.0	2.38	0.6
20	2.30	0.7	1.97	-0.3	2.67	0.4
15	2.55	0.8	2.21	0.2	3.12	0.3
10	3.10	0.5	2.64	0.0	3.68	0.1
5	3.72	0.6	3.28	-0.3	3.92	-0.3

**Table 4.** The diffusion coefficients  $D_i$  and effective charge numbers  $z_i$  of lignosulfonate when the supporting electrolyte is 0.01 M NaCl or 1.0 M NaCl and the temperature is 30, 35 or 45°C.  $M$ ,  $T$  and  $[D_i]$  are as in Table 3.

$M/10^3$	0.01 M NaCl		1.0 M NaCl	
	$D_i$	$z_i$	$D_i$	$z_i$
<b><math>T = 30^\circ\text{C}</math></b>				
50	0.95	-20.2	1.57	-5.5
45	1.02	-17.3	1.67	-5.8
40	1.10	-18.3	1.74	-4.3
35	1.14	-17.6	1.82	-4.0
30	1.19	-16.1	1.91	-3.6
25	1.25	-15.4	2.00	-2.7
20	1.32	-13.5	2.14	-2.6
15	1.48	-11.4	2.43	-2.3
10	1.70	-8.8	2.94	-2.6
5	2.21	-7.6	3.48	2.0
<b><math>T = 35^\circ\text{C}</math></b>				
50	1.10	-12.0	1.72	-0.1
45	1.18	-8.5	1.83	0.0
40	1.28	-8.0	1.93	0.2
35	1.33	-8.2	1.98	0.5
30	1.39	-6.2	2.06	0.8
25	1.47	-6.0	2.13	0.9
20	1.58	-5.1	2.29	1.5
15	1.82	-4.6	2.55	2.0
10	2.01	-2.5	2.96	1.3
5	2.34	-1.2	3.55	-1.5
<b><math>T = 45^\circ\text{C}</math></b>				
50	1.55	-6.5	2.17	0.0
45	1.59	-6.8	2.29	0.2
40	1.69	-6.6	2.36	0.3
35	1.72	-7.0	2.44	0.1
30	1.79	-7.1	2.52	0.6
25	1.89	-7.2	2.64	0.9
20	2.01	-7.0	2.80	1.5
15	2.22	-6.8	3.14	1.8
10	2.63	-5.7	3.56	1.2
5	3.22	-4.8	4.40	0.8

**Table 5.** Diffusion coefficients  $D_i$  of lignosulfonate when the supporting electrolyte is 0.1 M NaCl, the temperature is 43°C and the electric field strength (in  $\text{V m}^{-1}$ ) is (a) 25.1, (b) 19.5, (c) 12.6, (d) 0.32, (e) 0.09, (f) 0.05 and (g) 0.

$M/10^3$	(a)	(b)	(c)	(d)	(e)	(f)	(g)
50	0.36	0.44	0.52	0.78	1.19	1.40	1.35
45	0.45	0.50	0.60	0.87	1.32	1.57	1.40
40	0.48	0.54	0.66	0.97	1.47	1.70	1.45
35	0.52	0.58	0.70	1.01	1.50	1.76	1.52
30	0.57	0.64	0.78	1.13	1.61	1.86	1.57
25	0.69	0.75	0.91	1.26	1.79	2.03	1.65
20	0.75	0.84	1.01	1.39	1.99	2.18	1.69
15	0.91	1.01	1.22	1.66	2.28	2.45	1.81
10	1.01	1.22	1.47	2.00	2.90	2.95	2.12
5	1.61	1.72	2.06	2.66	3.63	3.55	2.43

Table 6. Surface tensions ( $\gamma$  in  $\text{mN m}^{-1}$ ) at different temperatures, ionic strengths and lignosulfonate (LS) concentrations.

$t/^\circ\text{C}$	$\text{H}_2\text{O}$	0.01 M NaCl, $1 \text{ g l}^{-1}$ LS	0.1 M NaCl		1 M NaCl, $1 \text{ g l}^{-1}$ LS
			$1 \text{ g l}^{-1}$ LS	$10 \text{ g l}^{-1}$ LS	
25	70.8	61.9	61.6	42.2	40.1
30	70.5	62.4	61.6	40.2	38.7
35	70.0	60.4	59.1	39.3	38.7
40	69.6	57.4	58.3	40.9	38.0
42	69.3	58.6	58.3	41.1	37.8

fore, an explanation based on structural changes to the lignosulfonate molecule when the charge is lost is in doubt.

The free energies of hydration of the monovalent counterions used are 480, 375 and  $310 \text{ kJ mol}^{-1}$  for the  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  ions, respectively.<sup>21</sup> In spite of the above values, no differences could be measured in the loss of charge at ca.  $40^\circ\text{C}$  with different counterions. Also, the divalent counterion  $\text{Ba}^{2+}$  supported this result, but  $\text{Mg}^{2+}$  did not, probably owing to the high charge density of this ion and the discrete nature of the ionizing groups at the surface of the lignosulfonate molecule. Thus it can be concluded that the counterion is not responsible for this phenomenon.

The ionic strength has a clear effect on the temperatures at which the loss of charge takes place. The results give evidence that the smaller the Debye length, i.e. the greater the ionic strength, the lower is the temperature at which the molecule becomes neutral. This behaviour refers to the importance of the diffuse double layer adjacent to the surface of the macromolecule. However, quantitative studies are not reasonable because the available model for the diffuse double layer (Gouy–Chapman) is so rudimentary, and can be used only in very dilute solutions.<sup>22</sup>

The measurements under an external electric field showed that lignosulfonate is also migrating when the temperature exceeds  $40^\circ\text{C}$ . In other words, it behaves as if it were charged. This result contradicts our results that the charge numbers go to zero at ca.  $40^\circ\text{C}$ . However, as has been presented recently, the conformation of the lignosulfonate molecule is changing, when an external electric field of  $10 \text{ V cm}^{-1}$  or more is applied, from a compact sphere to a non-free-draining coil.<sup>4</sup> That is why we conclude that the loss of charge takes place only when the molecule behaves like a compact sphere. This conclusion is supported by quite recent results with polystyrene sulfonate and cytochrome-c. The conformation of the former corresponds to a non-free-draining coil, and it did not lose its charge under the conditions for which lignosulfonate did.<sup>23</sup> The conformation of cytochrome-c is a compact sphere, and it did lose its charge similarly to lignosulfonate.<sup>5</sup>

One possibility of explaining the loss of charge at ca.  $40^\circ\text{C}$  is aggregation. It is clear that the aggregation of lignosulfonate molecules changes the whole interpretation procedure of the measured parameters. A detailed study shows that the calculation of the diffusion coefficients

would lead to completely unrealistic values of the diffusion coefficients of lignosulfonate, even in an aggregated form. Therefore, the possibility of aggregation must be rejected. Furthermore, in an early study<sup>24</sup> the possibility of aggregation of lignosulfonate was ruled out. Also, our measurements of surface tension and gel chromatography while changing the temperature gave strong evidence against aggregation. As a result, the possibility of aggregation as an explanation of the loss of the charge at  $40^\circ\text{C}$  can be ruled out.

Therefore, the following conclusion is drawn. The change of structured water around an organic polyelectrolyte molecule, which is a compact sphere, provides a simple rationalization of the obtained results. At a certain temperature the coordination water is lost, and a 'naked' surface of the macromolecule is 'seen' by the counterions, and since this kind of surface has a very low relative permittivity ion pairing takes place. This reasoning becomes clear when the simple electrostatics of electrolyte solutions<sup>20</sup> is considered. Preliminary calculations show that if the charged groups are attached to a surface having a low relative permittivity, the groups are ion-paired owing to the strong electric field created by the charges and their images. However, if the relative permittivity of the dielectric media, i.e. the body of the macromolecule, is increased either by the penetration of the solvent inside the polymer matrix of the macromolecule or by the shielding of the structured water, the electric field is so low that ion pairing does not take place. A quantification of this thinking is in progress.

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