CRYPTATE $^{13}$C AND $^{23}$Na NUCLEAR MAGNETIC RELAXATION AS A PROBE OF COUNTERION DYNAMICS IN AQUEOUS POLYACRYLATE SOLUTIONS

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In a series of fully alkali neutralized polyacrylate solutions the counterions are included by a macrobicyclic ligand (cryptand) to form a well-defined coordination shell. Vapor pressure experiments show the polyacrylate–cryptate system to behave osmotically as an ordinary polyelectrolyte solution. Cryptate $^{13}$C and $^{23}$Na relaxation show that the influence of polyions on the counterion reorientational mobility is moderate. The main $^{23}$Na relaxation mechanism is found to be the fluctuating electric field gradient caused by the surrounding ligand.

1. Introduction

Due to the high linear charge density on the polyion in polyelectrolyte solutions, the oppositely charged counterions are strongly attracted by the chain. Various descriptions exist of the resulting distribution of counterions about cylindrical polyelectrolytes [1]. A common feature is the accumulation of ions around the chain when the linear charge density parameter $\xi$ exceeds unity. The charge density parameter is defined as the ratio of the electrostatic energy of neighboring charges on the chain to the thermal energy:

$$\xi = \frac{2}{4\pi \varepsilon_0 \varepsilon A kT}. \quad (1)$$

Here, $A$ denotes the distance between neighboring charged beads and the other symbols have their usual meaning. In this report, the effect of this accumulation on the reorientational mobility of counterions will be investigated by cryptate $^{13}$C and $^{23}$Na NMR.

The $^{23}$Na quadrupolar relaxation is determined by the interaction of the nuclear electric quadrupole moment with fluctuating electric field gradients at the nucleus [2]. Especially in polyelectrolyte solutions, the separation of electric field gradients caused by the surrounding water molecules and the charged polyions is difficult. Therefore, in this contribution, the counterions are included by a macrobicyclic ligand to form a well-defined coordination shell. An equivalent amount of cryptand [2.2.2] (see fig. 1) is added to a fully neutralized polyacrylate solution to form stable counterion inclusion complexes, in which the ligand entirely surrounds the cation.

The polyion–cryptate interaction is studied by vapor pressure experiments. The derived osmotic coefficient $\Phi$ is the ratio of real to ideal osmotic pressures and represents the fraction of osmotically active counterions [3].

The reorientational mobility of the complexed counterions has been investigated by $^{13}$C relaxation. The $^{13}$C relaxation is mainly determined by dipolar coupling to the CH$_3$ protons, which is modulated by reorientational motion. The carbon spectrum of [2.2.2] yields three peaks. Because the principal axes of the $^{13}$C dipolar interaction tensors do not coin-
cide, the symmetry of the motion can be evaluated. Comparison of reorientational correlation times in polyacrylate and low molecular weight chloride solutions characterizes the polyion–cryptate interaction. Electric field gradients experienced by the included counterions can be estimated from $^{23}\text{Na}$ relaxation. The quadrupolar interaction with the electric field gradient due to the enclosing ligand is an important relaxation mechanism. Under the assumption that this is the only significant contribution to the observed relaxation rate and that the correlation time as obtained from $^{13}\text{C}$ relaxation represents the motion which modulates the interaction, the quadrupolar coupling constant can be determined [41]. Electric field gradients caused by the charged polyions can also be an effective relaxation mechanism of enclosed counterions. Information on a possible contribution of the polyion gradients has been obtained by comparison of the estimated quadrupolar coupling constants of sodium cryptates in polyacrylate and low molecular weight chloride solutions.

2. Experimental

All solutions are made by weight. PAA, degree of polymerization DP = 4270, was synthesized and fractionated as described before [5]. DP was determined by low-angle laser light scattering (KMX-6, Chromatix). Distilled water was deionized and filtered by a Millipore water purification system (Millipore Co.). The conductance did not exceed $1 \times 10^{-6}$ cm$^{-1}$ Ω$^{-1}$. To remove gaseous oxygen and to avoid degradation of the ligand due to peroxide, all solutions were degassed with argon. No additional low molecular weight salt is present in solution.

Two PAA solutions were fully neutralized with KOH (Titrisol, Merck). To one of them an equivalent amount of cryptand (Kryptofix [2.2.2], Merck, used without further purification) was added to complex the counterions. A series with an increasing fraction of complexed counterions was obtained by mixing these two solutions. The polymer monomobility ($n\phi$) was $2 \times 10^{-2}$.

The osmotic activity was determined by a Hitachi vapor pressure osmometer, operating at a temperature of 335.5 ± 0.2 K. Infrared absorbance measurements on solutions in D$_2$O (Aldrich) and neutralized with KOD (Merck) were performed on a double-beam Perkin–Elmer 325 spectrometer, at a temperature of 333 ± 1 K.

For NMR a stock solution of PAA was fully neutralized with NaOH (Titrisol, Merck). After adding an equivalent amount of cryptand, samples were prepared by dilution. The cryptate chloride solution was prepared by adding cryptand to a NaCl (Suprapur quality, Merck) solution. NMR sample tubes (Wilmad, 5 mm) were thoroughly cleaned with NaHCO$_3$ and heated with EDTA to remove paramagnetic impurities.

$^{23}$Na magnetic resonance experiments were performed on a home modified Bruker SXP spectrometer, operating at a magnetic field strength of 6.3 T. Longitudinal relaxation rates were determined by the inversion recovery method. FID were accumulated, while the relative phase of the $\pi$ and the $\pi/2$ pulses was alternated [6]. A hundred data points were collected and fitted to a single exponential. The estimated accuracy is better than 2%.

Carbon-13 relaxation rates were obtained with a Bruker WM-300 spectrometer, equipped with a 7 T magnet, and were determined by the inversion recovery method. The MLEV-16 proton decoupling pulse sequence was applied to minimize radiofrequency power dissipation within the sample [7]. After Fourier transforming the FID, the peak intensities were fitted to single exponentials. The estimated accuracy is 5%. For both spectrometers the temperature was maintained at 298 ± 1 K by gas thermostating.

3. Results and discussion

Cryptands are diamines, which means that if excess acid is added to a cryptate solution the overall reaction is [8,9]

$$[2.2.2.\text{M}]^+ + 2\text{H}^+ = [2.2.2.2\text{H}]^{2+} + \text{M}^+.$$  

Thus, if a polyelectrolyte solution is not completely neutralized with alkali, the remaining polyacid causes the complexed counterions to dissociate. This is confirmed by the infrared polyacrylate asymmetric carboxylate absorbance, which shows nearly complete dissociation of the polyion due to protonation of cryptate. Another indication of the dissociation of
complexed counterions due to excess polyanion is the 
$^{23}$Na magnetic resonance spectrum. In a partly alkali
neutralized polycryliculate solution with an amount of
cryptand equal to the number of counterions, two
$^{23}$Na resonances are observed. These resonances are
separated by a chemical shift of 8.2 ppm and belong
to free and enclosed counterions respectively. However,
in the present contribution, polycrylic acid was
fully neutralized to obtain the salt. After adding an
equivalent amount of cryptand a single sodium NMR
resonance was observed, definitely belonging to
enclosed counterions. Hence, it is concluded that the
counterions are complexed by the ligand and the
amount of free cryptand present in solution is
degregate.

The influence of complexation of the counterions
on the polyion-counterion interaction was investi-
gated by vapor pressure experiments. The potassium
salt was chosen, because of the high stability of the
$[2.2.2.X]^+$ complex [10]. For a general description
of polyelectrolyte osmotic properties ref. [3] may be
consulted.

3.1. The effect of complexation on the osmotic
activity

Fig. 2 displays the osmotic coefficient of a $2 \times 10^{-2}$
monomolar potassium polycryliculate solution as a
function of the fraction of complexed counterions.
This fraction has been calculated as the ratio of added
cryptand to the total amount of potassium counter-
ions. The osmotic coefficient is calculated as the ratio
of the vapor pressure of a polycryliculate solution with
respect to the pressure of a low molecular weight salt
solution with an equivalent molality of small ions.

The osmotic coefficient of a $[2.2.2.Na]Cl$ and a NaCl
solution was checked to be equal. Because the degree
of polymerization is high, the influence of the poly-
mer on the solvent vapor pressure is negligible [3].
Therefore, the data displayed in fig. 2 reflect the
osmotic activity of the counterions.

As judged from the osmotic activity, the com-
plexed counterions can certainly not be regarded as
osmotically free. The effect of enclosing the counter-
ions by a macrobicyclic ligand on the vapor pressure
is moderate. Accordingly, the polycryliculate-cryptate
solution can osmotically be regarded as an ordinary
polyelectrolyte system. The small increase of the
osmotic coefficient as a function of the fraction of
complexed counterions is in qualitative accord with
the analytical solution of the Poisson-Boltzmann
equation for the cell model with two species of

After this discussion of the polyion-cryptate inter-
action from osmotic activity experiments, attention
will be directed to the reorientational mobility of
complexed counterions as studied by $^{13}$C relaxation.

3.2. Reorientational mobility of complexed
counterions

The cryptate $^{13}$C relaxation is mainly determined
by dipolar coupling to the CH$_2$ protons. No field
dependence of longitudinal $^{13}$C relaxation rates was
observed. Under extreme narrowing conditions the
longitudinal relaxation rate is given by

$$R_C = 2 \left( \frac{\gamma_H^2 \gamma_C^2 \mu^2}{\rho_{CH}^6} \right) \tau_{\text{com}},$$

with $r_{CH} = 1.085 \pm 0.005$ Å [4]. Intermolecular dipoi-
lar coupling to water protons is negligible. Longitu-
dinal cryptate carbon relaxation rates are presented
in table 1. To all samples an equivalent amount of
cryptand was added to include all the sodium coun-
terions. The spectrum of $^{13}$C shows three peaks.
Within experimental error (5%), the relaxation rates
for cryptate carbon atoms in each sample are equal.
Hence, a possible anisotropy in reorientational
motion of cryptates could not be detected. Reorien-
tational correlation times $\tau_{\text{com}}$, as obtained from
averaging the $^{13}$C relaxation rates of the three sepa-
rated peaks, are also presented in table 1. The values
for the 0.010 molal $[2.2.2.Na]PAA$ and 0.014 molal
$[2.2.2.Na]Cl$ solutions have been obtained by $^{23}$Na

Fig. 2. The osmotic coefficient of a fully neutralized potassium
 polysacrylate solution ($c_p = 2 \times 10^{-2}$ monomolal) as a function of
 the fraction of complexed counterions. The line is drawn as a guide
 to the eye. $T = 335.5 \pm 0.2$ K, DP = 4270.
Table 1
Longitudinal relaxation rates and some derived quantities. The indexes a, b, c refer to the $^{13}$C positions indicated in fig. 1

<table>
<thead>
<tr>
<th>Solute</th>
<th>Molality (f)</th>
<th>$R_{Na}$ (s$^{-1}$) (± 2%)</th>
<th>$R_{C}$ (s$^{-1}$) (± 5%)</th>
<th>$\tau_{com}$ (ps)</th>
<th>$\chi$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[2.2.2.Na]Cl</td>
<td>0.100</td>
<td>221</td>
<td>1.8</td>
<td>42 ± 3</td>
<td>1.15 ± 0.03</td>
</tr>
<tr>
<td>[2.2.2.Na]Cl</td>
<td>0.014</td>
<td>191</td>
<td>1.9</td>
<td>37 ± 3</td>
<td>-</td>
</tr>
<tr>
<td>[2.2.2.Na]PAA</td>
<td>0.349</td>
<td>343</td>
<td>2.8</td>
<td>64 ± 4</td>
<td>1.16 ± 0.03</td>
</tr>
<tr>
<td>[2.2.2.Na]PAA</td>
<td>0.100</td>
<td>266</td>
<td>2.3</td>
<td>52 ± 3</td>
<td>1.13 ± 0.03</td>
</tr>
<tr>
<td>[2.2.2.Na]PAA</td>
<td>0.024</td>
<td>235</td>
<td>2.1</td>
<td>48 ± 5</td>
<td>1.11 ± 0.05</td>
</tr>
<tr>
<td>[2.2.2.Na]PAA</td>
<td>0.010</td>
<td>215</td>
<td>-</td>
<td>-</td>
<td>43 ± 5</td>
</tr>
</tbody>
</table>

relaxation and quadrupolar coupling constants of 1.11 ± 0.05 and 1.15 ± 0.03 MHz respectively (see below). Correlation times are understood to be averaged over the distribution with respect to the polyion, no specific correlation times of, e.g., associated and free counterions are defined.

From the reorientational correlation time and the Stokes–Einstein relation

$$\tau_{com} = \frac{4}{3} \pi \eta r^3 / kT$$

a value of the hydrodynamic radius of cryptate can be derived. Using the viscosity of pure water ($\eta = 0.8937$ cP) and the correlation time of [2.2.2.Na]$^+$ in a 0.014 molal chloride solution, a value of 3.4 Å is obtained. This value agrees with the crystallographic result of Metz et al., in which the metal–water distance was found to be 3.5 Å [12].

In polyacrylate solutions, the cryptate reorientational correlation times are of the same order as the value in a 0.1 molal low molecular weight chloride solution. A small increase of the correlation time with increasing concentration is observed. In this first experimental determination, the effect of the electrostatic polyion–counterion interaction on the cryptate reorientational mobility is found to be moderate. Site-binding is not very likely to occur, because this would cause a much more pronounced decrease in reorientational mobility. These results are in contrast to the reorientational behavior of the double-charged Mn$^{2+}$ ion in polyelectrolyte solutions, which shows a dramatic decrease of reorientational mobility [13].

To evaluate the electric field gradients experienced by the enclosed counterions, sodium relaxation will be discussed and combined with the dynamical information obtained from $^{13}$C relaxation.

### 3.3. $^{23}$Na relaxation behavior

As a first approximation, it is assumed that $^{23}$Na relaxation is completely determined by the electric field gradient caused by the enclosing ligand. No field dependence of longitudinal $^{23}$Na relaxation rates was observed. Under extreme narrowing conditions the longitudinal relaxation rate is given by

$$R_{Na} = \frac{3}{8} (\pi \eta^2)^2 (1 + \frac{1}{\eta^2}) \tau_{com}.$$

The asymmetry parameter $\eta$ of the field gradient is unknown, therefore an effective coupling constant will be defined:

$$\chi^* = \chi (1 + \frac{1}{\eta^2})^{1/2}.$$

Now, under the assumption that the reorientational correlation time as obtained from $^{13}$C relaxation represents the motion which modulates the quadrupolar interaction, the effective quadrupolar coupling constant can be estimated. For all samples studied, the $^{23}$Na longitudinal relaxation was observed to be exponential. The corresponding rates are presented in table 1. Effective quadrupolar coupling constants, calculated according to eqs. (5) and (6) and by inserting the $^{13}$C correlation times and $^{23}$Na relaxation rates, are also presented in table 1. Kintzinger and Lehn [4] obtained a value of 1.01 ± 0.10 MHz for [2.2.2.Na]Cl in methanol/D$_2$O 95/5, which is in reasonable agreement.

Within experimental error, the values of the effective $^{23}$Na quadrupolar coupling constants of cryptates in polyacrylate solutions are equal to the corresponding value in the low molecular weight chloride solution. However, if electric field gradients caused by the polyions provide an effective relaxa-
tion mechanism, the estimated effective coupling constants are expected to be higher than the value of sodium cryptate in the chloride solution. Hence, within present experimental accuracy, it is concluded that the $^{23}$Na relaxation process is determined by the electric field gradient due to the surrounding ligand.

The present results contrast sharply with the relaxation behavior of "bare" $^{23}$Na$^+$ in polyelectrolyte solutions at comparable concentrations [14]. There, the relaxation was observed to be clearly out of the extreme narrowing limit. The results on the cryptate counterions indicate the importance of fluctuations in close proximity to the ion for the interpretation of ion magnetic relaxation. Especially in macromolecular solutions, the altered adjacent water dynamics and fluctuations of the charged beads may provide an important contribution. Finally, it should be noted that complexation of the counterions may obscure the presence of long-range field gradients as an effective relaxation mechanism. One possibility could be a difference in the Sternheimer antishielding factor for included and free ions. However, calculations show the Na$^+$ antishielding factor to decrease only by 3.6% in going from the free ion to the solid state [15].

References