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Self-diffusion of the Perchlorate Ion in Aqueous Electrolyte Solutions measured by ^{35}Cl NMR Spin–Echo Experiments

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We have described the first application of ^{35}Cl NMR in a pulsed field gradient spin–echo experiment which represents a promising new technique for determining the self-diffusion coefficient of perchlorate ions in solution. Specifically, we have been able to obtain the first experimental data for this diffusion coefficient in aqueous solutions of NaClO$_4$, LiClO$_4$ and Mg(ClO$_4$)$_2$ at 25 °C. We have also reported self-diffusion coefficients of water in these solutions obtained by ^{1}H NMR. Including recently published data for Ga(ClO$_4$)$_3$, at a given concentration the self-diffusion coefficient of ClO$_4^-$ was found to decrease in the sequence LiClO$_4$ > NaClO$_4$ > Mg(ClO$_4$)$_2$ > Ga(ClO$_4$)$_3$. This sequence is irregular for the sodium and lithium salts because, on the grounds of the lower structure-forming ability of the Na$^+$ ion, one would expect a higher mobility for ClO$_4^-$ in solutions containing Na$^+$ ions. The latter ('regular') behaviour is indeed found for the self-diffusion coefficients of water in these systems. These irregularities are discussed in relation to other anomalies in solutions of perchlorates and other structure-breaking anions, including the splitting of the vibrational bands of water, and the unusually strong concentration dependence of ^{23}Na$^+$ relaxation in such solutions. Moreover, it is pointed out that mutual diffusion coefficients and transference numbers reported in the literature also behave in a highly anomalous manner. The results support the hypothesis that in the presence of large structure-breaking anions there are distinct cation–anion–water configurations. These appear to be stronger with Na$^+$ as counter-ion than with Li$^+$.

The characterisation of dynamical processes in liquids and solutions by magnetic resonance techniques is of long-standing interest in this laboratory. In the course of this work we have recently demonstrated that a series of less-common nuclei can be successfully applied in self-diffusion measurements by the NMR spin–echo technique, *e.g.* the diffusion of noble gases in water[1,2] and non-aqueous solvents[3] observed *via* ^{129}Xe and ^{21}Ne NMR and the diffusion of ions such as ^{7}Li$^+$, ^{23}Na$^+$ and ^{133}Cs$^+$ in electrolyte solutions.[4] While, for a long time, tracer techniques have been the mainstay in this field,[5] spin–echo experiments are easier to handle and faster to perform, thus offering considerable advantages over tracer methods.

The applicability of the spin–echo technique in self-diffusion measurements is limited by an interplay between diffusion and transverse relaxation contributions to the attenuation of the spin–echo in static or pulsed field gradient (PFG) experiments.[6] High gyromagnetic ratios γ and long transverse relaxation times T_2, as found for spin-1/2 nuclei, favour spin–echo attenuation by self-diffusion. On the other hand, most nuclei have spin $I > 1/2$, and exhibit fast relaxation by interaction of the nuclear electric quadrupole moment with electric field gradients at the nucleus. Most of these quadrupolar nuclei are thus unsuitable for self-diffusion measurements. There are exceptions, however, whenever low nuclear quadrupole coupling constants (NQCC) of the nuclei cause comparatively long relaxation times. Such low NQCCs require both a low nuclear electric quadrupole moment and a small electric field gradient due to a high electronic symmetry around the nucleus. The latter condition is achieved in ionic nuclei such as ^{7}Li$^+$, ^{23}Na$^+$ and ^{133}Cs$^+$,[4] where the charge distribution inside the ion is of spherical symmetry. Then, relaxation is caused by intermolecular interactions with field gradients of solvent dipoles and counter-ions,[7] so that conditions may become correct for enabling self-diffusion measurements.

In the present study we report on self-diffusion coefficients of the perchlorate ion in aqueous solutions measured by ^{35}Cl NMR. In this case the nucleus lies in the centre of a molecular ion with T_d symmetry. At 25 °C and infinite dilution in water we have $T_1 = T_2 = 0.22$ s (T_1 is the longitudinal relaxation time to which this value refers).[8] Estimates show that, in spite of the comparatively low γ of ^{35}Cl, self-diffusion measurements should be possible. Similar experiments with the chloride ion would be much more difficult, as T_2 for chlorides in water is almost an order of magnitude shorter than for perchlorates.

The characterisation of thermodynamic and transport properties of aqueous perchlorates is of considerable importance, as such salts are often used as supporting electrolytes in electrochemical measurements and in determinations of association constants for counter-ion- and ligand-binding processes. Unfortunately, self-diffusion measurements by conventional radioactive tracer techniques are difficult to perform since there is no commercial supply of ^{36}Cl-labelled ClO$_4^-$. Therefore, ^{36}ClO$_4^-$ has to be prepared from ^{36}Cl$^-$ by elaborate electrosyntheses and up to now only one system, namely aqueous solutions of Ga(ClO$_4$)$_3$, could be investigated.[9] Thus, ^{35}Cl NMR may provide an interesting alternative to tracer measurements opening the possibility of extensive ClO$_4^-$ (and Cl$^-$) self-diffusion studies.

When examining the use of ^{35}Cl NMR, we were, in the first instance, interested in aqueous solutions of the alkali-metal perchlorates LiClO$_4$ and NaClO$_4$. Solutions of NaClO$_4$ as well as sodium salts of some other large anions show a number of peculiarities, including a splitting of the vibrational bands of water in the fundamental and overtone regions[20] and an unusually strong concentration dependence of the ^{23}Na$^+$ relaxation time.[11] Many studies have dealt with these peculiarities. The main aspects have been discussed by Contreras and Hertz,[8,12] who have also compiled a large array of further studies. With lithium salts these anomalous

Table 1 Self-diffusion coefficients of the ClO_4^- ion in aqueous solutions of $LiClO_4$, $NaClO_4$ and $Mg(ClO_4)_2$ at 25 °C as a function of molality

m/mol kg^{-1}	$10^9 D$/m^2 s^{-1}		
	$LiClO_4$	$NaClO_4$	$Mg(ClO_4)_2$
0	1.792	1.792	1.792
0.25		1.65	1.62
0.5	1.65	1.58	1.44
0.8	1.59		
1	1.53	1.44	1.26
1.5	1.46		
2		1.29	0.95
2.5	1.32		
3	1.23	1.21	0.68
4	1.13	1.06	0.49
5	1.02	0.91	
7		0.79	
10		0.47	

effects appear to be smaller: vibrational band splitting is also observed, but $^7Li^+$ relaxation strengthening is absent.[8] There is agreement that this peculiar behaviour results from distinct anion–cation–water encounter configurations, associated with the peculiar hydration characteristics of the large 'structure-breaking' ClO_4^- anion.[8] If the formation of these configurations is more pronounced for $NaClO_4$ than for $LiClO_4$, it should be reflected by the self-diffusion coefficient of the perchlorate ion.

Solutions were prepared by weight from deionised and doubly distilled water using $LiClO_4$ (anhydrous, Alfa, Karlsruhe), $NaClO_4$ and $Mg(ClO_4)_2$ (both A.C.S. reagents, Aldrich). Solution compositions are given as molalities, m, referring to mol of salt per kg of water. In the case of $NaClO_4$ and $LiClO_4$ the compositions of the samples were checked by comparing their densities and electrical conductances with literature data.[13–15] Results agreed within the combined experimental accuracies.

Self-diffusion coefficients of ClO_4^- ions were measured by ^{35}Cl PFG spin–echo experiments using a Bruker pulsed FT–NMR spectrometer in the Fourier-transform mode and a wide-bore (89 mm) supercon magnet. The method is described in very fine detail in ref. 6. Details of the experimental set-up used in our laboratory and the general experimental procedures are described elsewhere.[16,17] With regard to the use of ^{35}Cl NMR, we have performed experiments at a resonance of 29.4 MHz. Depending on the perchlorate concentration, 10–40 accumulations were applied. For calibration of the gradient-coil factor the ^2D resonance of D_2O

at 46.1 MHz was used with $D = 1.872 \times 10^{-9}$ m^2 s^{-1} at 25 °C.[18] Details of this calibration procedure are described elsewhere.[17] The temperature of the samples was controlled to 25 °C by liquid thermostatting. Self-diffusion coefficients of water were measured by ^1H spin–echo experiments using a home-built apparatus working at 25 MHz. All data refer to normal water as a calibration fluid with $D = 2.30 \times 10^{-9}$ m^2 s^{-1} at 25 °C.[17,18]
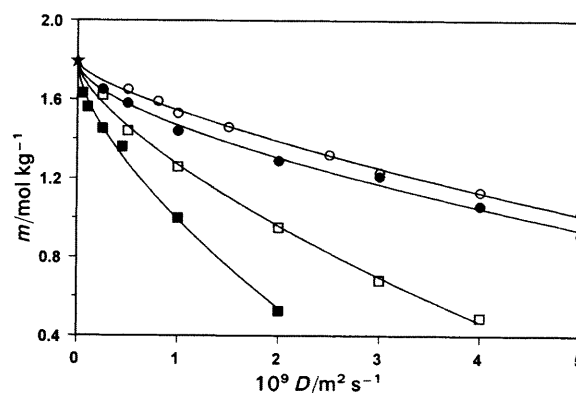
Self-diffusion coefficients, $D(ClO_4^-)$ of the perchlorate ion in aqueous solutions of $LiClO_4$, $NaClO_4$ and $MgClO_4$ at 25 °C are compiled in Table 1. The infinite dilution value calculated from the limiting ionic conductance using the Nernst–Einstein relation is 1.792×10^{-9} m^2 s^{-1}.[19] We estimate the accuracy of our data to be ca. $\pm 3\%$. For comparison, we have also determined self-diffusion coefficients of water, D_w, in these systems using ^1H NMR. These results are summarised in Table 2. We estimate the experimental precision to be ± 1–2%. Within the combined limits of experimental error they are in agreement with data for $LiClO_4$ extracted from a graph by Contreras and Hertz.[8]

Fig. 1 shows the composition dependence of $D(ClO_4^-)$. We have also included results for $Ga(ClO_4)_3$ reported by Price and Woolf.[9] No other literature data are known to us. The principal result is that at a given concentration the self-diffusion coefficients of the ClO_4^- ion follow the sequence $LiClO_4 > NaClO_4 > Mg(ClO_4)_2 > Ga(ClO_4)_3$. With respect to Li^+ and Na^+, this sequence is the reverse of what is intuitively expected because of the lower structure-forming ability of the Na^+ ion, and is generally observed with other anions. Taking recommended data from the compilation of Mills and Lobo,[5] chloride ion diffusion obeys the sequence $NaCl > LiCl > MgCl_2 > LaCl_3$, where it could be expected that $LaCl_3$ mimics the behaviour of $GaCl_3$. Also, for iodide ions which are closer in size to the perchlorates the sequence $NaI > LiI$ is found. Only data for self-diffusion of the tetrafluoroborate ion[8] might indicate the trend observed with the perchlorates, in that the self-diffusion coefficients of BF_4^- in aqueous solutions of $NaBF_4$ and $LiBF_4$ have been found to be equal within experimental resolution. In general, tetrafluoroborates behave very similarly to perchlorates.[8] Note that the data for $Mg(ClO_4)_2$ and $Ga(ClO_4)_3$ correspond approximately to what could be expected for solutions containing di- and tri-valent cations, as also emphasised by Price and Woolf.[9]

Interestingly, neither the self-diffusion coefficients of water shown in Fig. 2 nor viscosities in solutions of $LiClO_4$ and $NaClO_4$[15] show this inverse behaviour. Rather, the sequence corresponds to the general experience that for a given anion

Table 2 Self-diffusion coefficients of water in aqueous solutions of $LiClO_4$, $NaClO_4$ and $Mg(ClO_4)_2$ at 25 °C as a function of molality

m/mol kg^{-1}	$10^9 D$/m^2 s^{-1}		
	$LiClO_4$	$NaClO_4$	$Mg(ClO_4)_2$
0.1		2.29	
0.2	2.25	2.29	2.18
0.5	2.20	2.25	2.08
1	2.12	2.20	1.88
2	1.98	2.11	1.43
3	1.85	1.97	1.06
4	1.73	1.82	0.75
5	1.58	1.67	

Fig. 1 Self-diffusion coefficients of ClO_4^- in aqueous solutions of $LiClO_4$ (O), $NaClO_4$ (●), $Mg(ClO_4)_2$ (□) and $Ga(ClO_4)_3$ (■) at 25 °C. Data for $Ga(ClO_4)_3$ are taken from ref. 9.

the self-diffusion of water is faster for sodium than for lithium salts. Moreover, one may note that the results for NaClO$_4$ show that at low concentrations this salt leaves the self-diffusion coefficient of water almost unaffected. In conventional notions NaClO$_4$ is just borderline between a 'structure-breaker' and 'structure-former'. In contrast, owing to the larger structure-forming ability of Li$^+$, LiClO$_4$ is a structure-former.

The observation that LiClO$_4$ and NaClO$_4$ behave differently is reinforced when considering the Onsager limiting law for ionic self-diffusion coefficients[19] which also predicts D(NaClO$_4$) > D(LiClO$_4$) for the self-diffusion coefficient of ClO$_4^-$. Moreover, as a rule of thumb one expects for a solution with $m = 0.5$ mol kg^{-1} that the self-diffusion coefficient of univalent anions should be $ca.$ 10–15% above the limiting-law prediction, as can be exemplified by analysis of the data for many alkali-metal halides[5] ($e.g.$ 12% for I$^-$ diffusion in LiI). The value observed by us for the self-diffusion coefficient of ClO$_4^-$ in LiClO$_4$ corresponds well with this rule in that an increase of 13% over the limiting-law predictions is found (neglecting a small difference between molar and molal concentrations). For ClO$_4^-$ diffusion in NaClO$_4$ the corresponding factor is only 7%.

The observed anomaly extends an array of other anomalous properties already noted in the Introduction. The most spectacular of these is certainly the splitting of vibrational bands of water by perchlorates, tetrafluoroborates and some other large ions. According to Dryanski and Kecki[10] the newly appearing high-frequency band may originate from water molecules located between cations and anions, which are sufficiently separated from the hydrogen-bonded network of the remaining bulk water to vibrate in a limited high-frequency range. Such splittings are observed both with lithium and sodium salts. In the second place there is an unusually large concentration dependence of the ^{23}Na$^+$ quadrupolar relaxation rates in the presence of ClO$_4^-$ and other large anions such as BF$_4^-$, as first observed by Eisenstadt and Friedman.[11] The relaxation enhancement is accompanied by upfield ^{23}Na chemical shifts.[20] Contreras and Hertz[8] have reviewed a series of other studies reporting similar observations. In contrast, ^{7}Li$^+$ does not show a similar relaxation strengthening.[8] There is no doubt that these effects originate from the presence of distinct cation–anion encounter configurations leading to high electric-field gradients at the ^{23}Na$^+$ nucleus. We conclude that these configurations are also responsible for the slowing down of ClO$_4^-$ self-diffusion in the presence of Na$^+$.
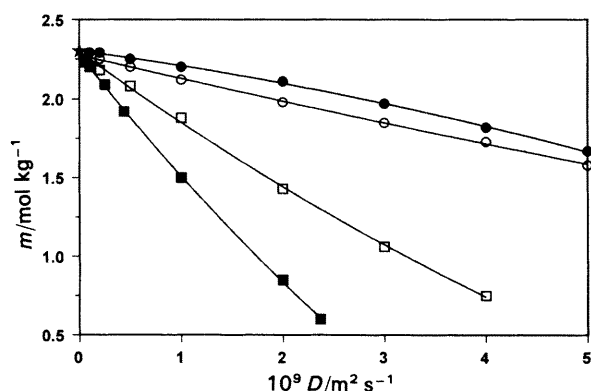
While these peculiarities are well known, two other striking anomalies have remained rather unnoticed. First, the concentration dependence of the experimental mutual diffusion coefficient, D_v, of aqueous NaClO$_4$[21] does not exhibit the typical features obtained for the mutual diffusion of other sodium salts.[15] Second, according to literature data[13,22] the transference numbers of the ClO$_4^-$ ion, t^-, show a highly anomalous behaviour. Although no accurate data are available at low concentrations, it appears that initially t^- decreases with concentration. At $ca.$ 3 mol kg^{-1} a minimum occurs, followed by a rapid increase. The existence of such a minimum as well as the initial decrease are exceptional. Debye–Hückel–Onsager theory implies a positive limiting slope, whenever the tranference number t_X of a cation or anion X of a 1:1 electrolyte at infinite dilution is larger than 1/2 (and $vice$ $versa$).[19] For NaClO$_4$ at infinite dilution we have $t^- = 0.573$.[13,19] In other cases this anomalous behaviour in the low-concentration regime has been attributed to ion association,[19] but this cannot explain the existence of a pronounced minimum and the subsequent increase.

In summary, there is little doubt that in solutions of perchlorates there must be very distinct cation–anion–water configurations which are stronger with Na$^+$ than with Li$^+$ salts. Presumably, this effect is directly related to the weak hydration of the perchlorate ion which allows a close approach of the cation which is then stabilised by peculiar water structures in the neighbourhood of the anion. It is intriguing to expect that such a process is more favoured by weaker cation hydration, so that the necessary reorganisation of the cationic hydration sphere is facilitated. We note that this model has some similarity to that used for explaining the high quadrupolar relaxation rates of anionic nuclei such as ^{81}Br$^-$ in the presence of hydrophobically hydrated species[23,24] in water and for explaining the unusual anion effects on transport and thermodynamic properties in solutions of tetra-alkylammonium salts in water.[25,26] In the latter case the role of anions and cations appears to be the reverse to that observed here.

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Fig. 2 Self-diffusion coefficients of water in aqueous solutions of LiClO$_4$ (○), NaClO$_4$ (●), Mg(ClO$_4$)$_2$ (□) and Ga(ClO$_4$)$_3$ (■) at 25 °C. Data for Ga(ClO$_4$)$_3$ are taken from ref. 9.

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