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PAPER

The structure of hyperalkaline aqueous solutions containing high concentrations of gallium – a solution X-ray diffraction and computational study

T. Radnai,[a] S. Bálint,[a] I. Bakó,[a] T. Megyes,[a] T. Grósz,[a] A. Pallagi,[bc] G. Peintler,[cd] I. Pálinkó[ce] and P. Sipos*[bc]

Highly concentrated alkaline NaOH–Ga(OH)$_3$ solutions with 1.18 M $\leq$ [Ga(III)]$_T$ $\leq$ 2.32 M and 2.4 M $\leq$ [NaOH]$_T$ $\leq$ 4.9 M (where the subscript T denotes total or analytical concentrations) have been prepared and investigated by solution X-ray diffraction and also by *ab initio* quantum chemical calculations. The data obtained are consistent with the presence of only one predominant Ga(III)-bearing species in these solutions, which is the tetrahedral hydroxo complex Ga(OH)$_4{}^-$. This finding is in stark contrast to that found for Al(III)-containing solutions of similar concentrations, in which, besides the monomeric complex, an oxo-bridged dimer was also found to form. From the solution X-ray diffraction measurements, the formation of the dimeric (OH)$_3$Ga–O–Ga(OH)$_3{}^{2-}$ could not unambiguously be shown, however, from the comparison of experimental IR, Raman and ^{71}Ga NMR spectra with calculated ones, its formation can be safely excluded. Moreover, higher mononuclear stepwise hydroxo complexes, like Ga(OH)$_6{}^{3-}$, which have been claimed to exist by others in the literature, were not possible to experimentally detect in these solutions with any of the spectroscopic techniques used.

Introduction

Gallium is a metal of importance especially for the new electronic technologies and the computer industry. It is similar to aluminium, but less common and less frequently used. Nevertheless, with the development of the computer industry its significance is growing. Its appearance in Nature is minute. It can be found together with aluminium, for example in the Bayer liquors, from which alumina is extracted. Here gallium practically is only a trace element besides aluminium. The annual production of gallium is between 260 and 320 tons in 2011 worldwide, while aluminium production was more than 30 Million tons in 2006.

Gallium extraction requires a precision technique but no special treatment is needed. The separation of gallium from aluminium is done by standard methods.[1] Gallium is a typical semiconductor and most of its industrial use is due to that. Since both aluminium and gallium are in the 13th column of the periodic table, the physicochemical characteristics are also very much alike (except that aluminium is not a semiconductor). Both have (positive) trivalent ions as most predominant ones and their typical hydroxide complex occurs in the form of M(OH)$_4{}^-$. It is even more interesting that the atomic sizes and atomic characteristics are also similar: covalent radii are 1.26 Å for Ga^{3+} and 1.18 Å for Al^{3+}, while ionic radii are 0.62 Å for Ga^{3+} and 0.54 Å for Al^{3+}. Based upon this data, the structure of their compounds even in the solution phase should be very much similar or at most minor differences could be expected. Therefore, if any difference can be detected in their structural features, it can be ascribed to the small deviations in dimensions or to the differences in their physicochemical properties.

It is a general question in structural chemistry, what the predominant feature is that determines the structure of a compound: the ionic (atomic) sizes, or the physical or chemical behaviour of the compounds. We have plenty of structural data available, but this question is still open. It seems to be obvious that interatomic potentials have a special role in forming structures. These pieces of information are still not enough to answer the above question.

[a] *Institute of Molecular Pharmacology, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Pusztaszeri út 59-67, H-1025 Budapest, Hungary*

[b] *Department of Inorganic and Analytical Chemistry, University of Szeged, Dóm tér 7, Szeged, H-6720 Hungary. E-mail: sipos@chem.u-szeged.hu; Fax: +36 62 544 340; Tel: +36 62 544 054*

[c] *Materials and Solution Structure Research Group, University of Szeged, Institute of Chemistry, Rerrich Béla tér 1, Szeged, H-6720 Hungary*

[d] *Department of Physical Chemistry and Material Science, University of Szeged, Aradi Vértanúk tere 1, Szeged, H-6720 Hungary*

[e] *Department of Organic Chemistry, University of Szeged, Dóm tér 8, Szeged, H-6720 Hungary*

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Up to pH = 13, the hydrolysis of Ga(III) is well established.[2–5] With increasing pH, Ga(III) undergoes hydrolysis with the progressive formation of stepwise mononuclear hydroxo complexes and a further species related to the tridecamer (Keggin polymer).[3,6–9] Around neutral pH, Ga(OH)$_3$ or GaOOH is precipitated, which readily dissolves in slightly basic solutions, to form Ga(OH)$_4^-$ in the form of tetrahydroxo complexes.

Our knowledge about the structure of Ga(III)-bearing species forming in strongly alkaline (pH > 13) solutions is relatively little. Besides Ga(OH)$_4^-$, the first possible candidate is the dimeric (OH)$_3$Ga–O–Ga(OH)$_3^{2-}$; a solution species analogous to this has been observed in alkaline aluminate solutions.[10] Solid Ga(III)-compounds containing the above dimeric unit have been prepared and their crystal structure is known.[11–13] It is however uncertain if it exists in strongly alkaline solutions. On the IR spectra of NaOH–Ga(OH)$_3$ solutions, at high concentrations, vibration bands appeared at ∼500 and ∼740 cm^{-1}. They were assigned to Ga–O–Ga bonds and polymerised species;[14] this suggests the possible formation of oxo-bridged oligomer(s) in aqueous solution. Dialysis experiments[15] with caustic gallates containing [NaOH]$_T$ = 0.4 M yielded a molecular mass of ∼270 for the gallium bearing species, indicating the possible presence of a dimeric gallate complex (M_r = 257.4, without hydrate water molecules). Conductivity measurements were also explained in terms of the formation of polynuclear aggregates.[16,17]

At very high concentrations of base, the progressive formation of higher stepwise (penta- or hexahydroxo) complexes may become (at least in principle) possible. Solid Ga(III) hydroxo complex salts with Ga(OH)$_6^{3-}$ structural units are known and their structure is well established.[18–21] It is suggested that the solution species Ga(OH)$_6^{3-}$ is formed in strongly alkaline solutions.[22] The statement was based on observations from solubility[23] and conductivity[16] measurements.

The Raman and [71]Ga NMR spectra of highly concentrated NaOH–Ga(OH)$_3$ solutions[24] (with 0.23 M ≤ [Ga(III)]$_T$ ≤ 2.32 M and 1 M ≤ [NaOH]$_T$ ≤ 15 M) were found to be consistent with the predominance of the well-known tetrahedral hydroxo complex, Ga(OH)$_4^-$, which is the only spectroscopically significant species in these solutions, even at the highest [Ga(III)]$_T$ and [NaOH]$_T$. The [71]GaNMR chemical shifts observed for these solutions (225 ± 2 ppm, relative to Ga(H$_2$O)$_6^{3+}$), which are highly concentrated with respect to gallium, are identical to those observed for alkaline (pH = 13) solutions with significantly lower [Ga(III)]$_T$.[2] Thus, the chemical shift is consistent with the presence of tetrahedral complex(es). Raman spectra are also consistent with this statement in terms of the invariance of the centre of the peak of the symmetrical GaO$_4$ stretching (605 cm^{-1}). The area of this peak is linearly proportional to [Ga(III)]$_T$, indicating that either there is only one spectroscopically significant species present or the different species present are not distinguishable by Raman spectroscopy. In summary, species like higher hydroxo complexes (i.e., Ga(OH)$_6^{3-}$) or the oxo-bridged dimer (i.e., (OH)$_3$Ga–O–Ga(OH)$_3^{2-}$) were not *directly* detected by any of these two spectroscopic techniques, however, their presence could not be excluded.

The aim of the current work is threefold. One is to systematically investigate the structure of gallium bearing hydroxo complexes that are formed in strongly alkaline NaOH–Ga(OH)$_3$ solutions† using solution X-ray diffractometry and quantum mechanical calculations. The other is to elucidate if solution species other than the well-established tetrahedral Ga(OH)$_4^-$ might exist and are present in experimentally detectable quantities in such systems. In particular, the detection of the dimeric species, analogous to (OH)$_3$Al–O–Al(OH)$_3^{2-}$, was the central question, as in the concentration range of the current studies, its formation is expected to be favoured. Based on these data, we also aimed at comparing the structure of such alkaline gallate solutions with analogous aluminate containing ones.

Experimental

Solution preparation

Concentrated NaOH stock solutions (*ca.* 20 M) were prepared from Millipore MilliQ water and *a.r.* grade NaOH (Hungaropharma, 99% purity) as described previously.[25] Preparation of the alkaline gallate stock solution was carried out by dissolving a freshly prepared Ga(OH)$_3$ in a known amount of base solution. Details of the preparation have been described elsewhere.[24] Solution series for the X-ray diffraction measurements were prepared by accurate gravimetric dilution of the gallate and sodium hydroxide stock solutions. The concentrations of the Ga(III)-bearing solutions and their acronyms used in the text were as follows: n52: [NaOH]$_T$ = 4.82 M and [Ga(III)]$_T$ = 2.32 M; n51: [NaOH]$_T$ = 4.90 M and [Ga(III)]$_T$ = 1.18 M; n21: [NaOH]$_T$ = 2.40 M and [Ga(III)]$_T$ = 1.18 M. For comparison, two NaOH solutions with no added Ga(III) were also recorded (n5: [NaOH]$_T$ = 4.82 M; n2: [NaOH]$_T$ = 2.40 M). Further details are summarised in Table 1.

X-ray diffraction measurements

X-ray diffraction measurements were performed in a thermostated room at a temperature of 25 °C on a θ–θ type diffractometer, made by Philips, using MoK$_\alpha$ radiation with a wavelength of 0.711 Å. The observed range of scattering angles (2θ) was between *ca.* 1.5° and 110°. The scattered intensity was recorded in 155 data points, equally spaced over the range of scattering angles and each counted over a 6 min sampling period. This gave a total of 40 000 to 240 000 counts per point. The method of measurement and data treatment were as previously reported,[26] including corrections for background, polarization, absorption, multiple scattering, subtraction of the scattering pattern of the empty cell, and conversion of the corrected intensities into absolute units. Since the samples were of high purity and some of them very concentrated, the material of the polymer windows was *ca.* 75 μm thin foils of bi-oriented polypropylene. These appeared fully resistant to the alkaline solutions and produced little background scattering.

The experimental structure function $kH(k)$ is defined as

$$kH(k) = k\left[I_{abs}(k) - \sum_\alpha x_\alpha f_\alpha^2(k) \sum_\alpha x_{\alpha,inc}(k)\right] M(k) \qquad (1)$$

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† In this paper, based on the analogy with aluminates, NaOH–Ga(OH)$_3$ solutions will also be called *gallates* or *sodium gallates*; naturally, they are not to be confused with the conjugated base of the gallic acid, which is also called this way.

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Table 1 The codes, compositions and various parameters of the solutions studied by solution XRD: total concentrations in M; densities (ρ); linear absorption coefficients (μ); average number densities (ρ_0) and molar ratios among the various components

Solution	[NaOH]$_T$ (M)	[Ga(OH)$_3$]$_T$ (M)	ρ (g cm^{-3})	μ (cm^{-1})	ρ_0 (10^{-24} cm^3)	Ga(OH)$_3$: NaOH : H$_2$O
$n2$	2.4327	0	1.0886	1.2703	0.1044	0 : 1 : 22.64
$n5$	4.7353	0	1.1728	1.4513	0.1072	0 : 1 : 11.54
$n21$	2.4806	1.1846	1.1984	5.993	0.0406	1 : 2.09 : 44.84
$n51$	4.9464	1.1885	1.2685	6.1919	0.0426	1 : 4.16 : 43.34
$n52$	4.8601	2.321	1.3481	10.683	0.0462	1 : 2.09 : 20.91

where k is the scattering variable, $k = 4\pi/\lambda \times \sin(\theta)$, λ the wavelength of incident radiation, $I_{abs}(k)$ the corrected intensity converted to absolute units, x_α the mole fraction, $f_\alpha(k)$ the coherent scattering factor, and $I_{\alpha,inc}(k)$ the incoherent scattering of an α type scattering unit. $M(k)$ is the modification function

$$M(k) = \exp(-bk^2)\left[\sum_\alpha x_\alpha f_\alpha(k)\right]^2 \qquad (2)$$

where the sum is extended over each type of X-ray scattering unit in the sample solution. The value of b is arbitrary, selected as $b = 0.003$. Four types of scattering units were considered as being present in the solutions: Na$^+$ and OH$^-$ ions, H$_2$O molecules and Ga^{3+} ions. The arbitrary use of a composite "group" scattering unit, representing both OH$^-$ and H$_2$O instead of individual O and H atoms, is proved to be useful for the description of the X-ray scattering of many H-containing molecules and ions. This is necessary because of the low sensitivity of X-rays in the detection of separate H atoms. Accordingly, throughout this paper, whenever a scattering unit is denoted by O, it refers to the composite scattering of both OH$^-$ and H$_2$O. All necessary scattering factors and incoherent intensity contributions were computed as analytical expressions. The parameters required to compute the scattering factors were taken from the literature.[27,28] The incoherent intensities were calculated according to Pálinkás and Radnai[29] for O, H, Na, and Ga and according to Hajdu for H$_2$O.[30]

The experimental pair distribution functions $g(r)$ were computed from the structure functions according to

$$g(r) = 1 + \frac{1}{2\pi^2 r \rho_0}\int_{k_{min}}^{k_{max}} kH(k)M(k)j_0(kr)\,dk \qquad (3)$$

where r is the interatomic distance, k_{min} and k_{max} are the lower and upper limits of the range of experimental data, ρ_0 is the bulk number density of the X-ray scattering units, and j_0 is the 0th order spherical Bessel function.

Computational methods

The complexes studied by computational methods included Ga(H$_2$O)$_6^{3+}$, Ga(OH)$_4$(H$_2$O)$_2^-$ and (OH)$_3$Ga–O–Ga(OH)$_3^{2-}$. Optimizations and frequency analyses were performed using the GAUSSIAN 09 program with density functional theory (DFT) at the M052x/6-311++G** computational level. We systematically modeled solvent effects by representing H$_2$O as a polarizable continuum, according to the method implemented in the PCM-SCRF (self-consistent reaction field) procedure in the Gaussian program.

We take into account some cases explicitly the hydration shell of these complexes, but the calculated properties do not change significantly compared to the PCM method, so we do not discuss those results. Chemical shifts are properties that depend on the interaction of static magnetic fields (the strong external field and the small internal fields of the nuclei) with the magnetic field created by the electron's movement inside a molecule. In this paper we applied the GIAO (gauge invariant atomic orbitals) method which uses basis functions that have explicit field dependence NMR shielding tensors at DFT levels of theory on optimized structure of complexes.[31] Raman and ^{71}Ga NMR spectroscopic measurements were performed using solutions with concentrations similar to those used for the X-ray diffractometric measurements. The results of these measurements were described in a previous publication[24] and are used here for comparison with the theoretical results. Also for comparative purposes, IR data were taken from the literature.[14]

Results and discussion

Experimental structure functions

The experimental structure functions are shown in Fig. 1. One feature clearly visible is the complete change of the shape of the double peak in the region of 2.0–3.5 Å^{-1} with changing chemical composition of the solutions. This double peak in the structure function of water at around 2.5 Å^{-1} is
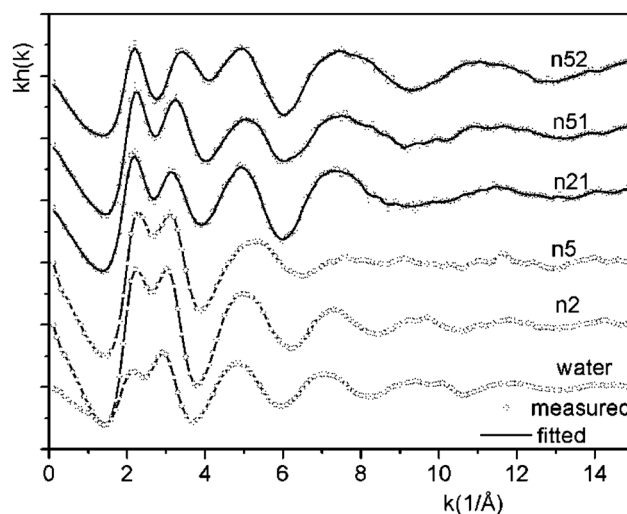

Fig. 1 Experimental (circles) and fitted (solid lines) solution X-ray structure functions for sodium hydroxide and sodium gallate solutions. For definition of acronyms used for the various solutions, see Table 1.

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characteristic of the three dimensional tetrahedral hydrogen bonded network.

By contrast, when the samples water and $n2$ and $n5$ are compared, it can be seen that changes in sodium hydroxide concentration do not affect seriously the double peak, rather, cancel out the waves at $k > 6$ Å^{-1}. This can be due either to interference or to a structural effect. However, in the case of gallate solutions, the disruption of long-range hydrogen bonded structures can be seen.

Experimental pair distribution functions

The structural features (bonding and non-bonding distances and coordination numbers) of the solutions can be seen directly from the pair distribution functions. The experimental pair distribution functions, $g(r)$, were computed from the structure functions according to eqn (3), using the valuable experimental data up to $k_{max} = 16$ Å^{-1}. The non-physical ripples present in the $g(r)$ at mainly small r values were removed or reduced using the generally accepted Fourier-filtering data treatment procedure, and the structure function was corrected for residual systematic errors. The $g(r)$ pair distribution functions are shown in Fig. 2. It is evident that some of the spurious ripples remain, but the experimental results are not seriously affected.

Water

The pair distribution function of water is already well known from the literature. The shape of the present curve is in excellent agreement with published functions.[32] The main peak, at 2.84 Å, corresponds to hydrogen-bonded first neighbor distances, with
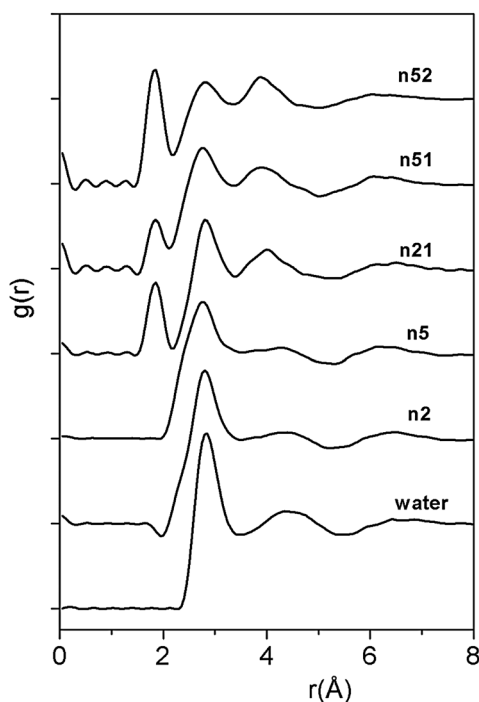

Fig. 2 Experimental X-ray pair distribution functions for sodium hydroxide solutions, and sodium gallate solutions. The solutions are as defined in Table 1.

an average coordination number of about 3.5 to 4.5 molecules. The second broad peak at around 4.5 Å can be interpreted as a distorted tetrahedral structure within a 3-dimensional hydrogen-bonded network.

NaOH solutions

Compared to that of pure water, the pair distribution functions of the $n5$ (~ 5 M NaOH) and $n2$ (~ 2 M NaOH) solutions show a broadening of the first peak, with a substantial decrease in height and a significant shift of the peak positions down to 2.7 Å. This feature can be easily explained by taking into account the Na$^+$–O first neighbour distance which is around 2.4 Å[32] (O stands for oxygen from water and also from OH$^-$ ions, as under these conditions, the formation of the contact ion pair NaOH^0 is significant, see ref. 33 and the references cited therein; this notation will be used in the rest of the article when all type of oxygens are mentioned). Another significant change can be observed on the $g(r)$ where the minimum after the first peak is filled that can be explained by the presence of hyper-coordinated hydroxide ions as it has been reported in our earlier work.[34]

Gallate solutions

The sharp peak at 1.85 Å is a well defined peak in each gallate solution. The gradual emergence of a shoulder on the left-hand side of the main peak in gallate solutions (Fig. 2) can also be ascribed to this Na$^+$–O contribution. It is interesting to note that while the concentration of sodium is the same in all solutions except $n21$, the shoulder is more pronounced the higher the gallate concentration is. An explanation of this is that a decreasing contribution from the hydrogen bonded H$_2$O–H$_2$O distances is observed instead of an increase in the Na$^+$–O contribution, leading to a greater distinction of the two.

A structural rearrangement can also be observed in the range of longer distances, from 3.5 to about 6 Å including a peak at ~ 4 Å. It is not possible to assign these changes to one or two pair contributions only. In this range the disruption of characteristic water structure occurs and the formation of another type of structural entity accounted for the gallate solutions appears. This is obviously due to a structural rearrangement, readily explained by the breaking of the longer-range structure of bulk water and the development of a more compact, shorter range local order in the more concentrated electrolyte solutions.

The following structural features are observed:

(a) The Ga–O distance was found to be 1.85 Å in all of the gallate solutions studied.

(b) The coordination number of the nearest O units around each gallium is 4, within the limit of the experimental errors.

(c) The position of the Na–O shoulder is unchanged (relative to the Ga(III)-free solutions), within the precision of the measurements.

(d) The O–O peak position decreases with the addition of NaOH to water (from 2.85 to 2.65 Å), but this trend is reversed by increasing the concentration of Ga(III) (up to 2.85 Å in the $n52$ solution).

(e) The sodium ions are coordinated by about 6 O-containing units (referencing to our notation, so the O comes from either OH$^-$ or H$_2$O) over the series of gallate solutions.

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(f) If the integrated area corresponding to the Na–O contribution is subtracted from the composite second peak, the remaining coordination number has an uninterpretable meaning if we assumed that only O–O scattering contributes to this peak. The coordination numbers thus obtained show a clear tendency to increase with increasing gallate concentration. Therefore, this part of the radial distribution function cannot be clearly interpreted based only on O–O contribution, but a more complex structural arrangement should be assumed.

Geometric models of structure

To refine further the structural features listed above average geometrical models were constructed and tested against the experimental data. The usual procedure is to apply a nonlinear least-squares method (LSQ) in which the theoretical structure functions are calculated with adjustable structural parameters and geometrical rules arising from the models used to compute the nonadjustable parameters. The theoretical structure functions are then compared with the corresponding experimental ones to achieve the best fit according to

$$R = \frac{\sum\limits_{k=k_{\min}}^{k_{\max}} \left[kH_{\text{theor}}(k) - kH_{\text{exp}}(k) \right]^2}{\sum\limits_{k=k_{\min}}^{k_{\max}} k^2 H_{\text{exp}}(k)^2} = \text{minimum} \qquad (4)$$

The theoretical structure function has its usual form where the summation spans over each pair of α, β type contributions, $r_{\alpha\beta}$ is the distance, $l_{\alpha\beta}$ is its root-mean-square deviation (rmsd) value related to the temperature factor, and $c_{\alpha\beta}$ is the frequency factor (coordination number) of the α, β type contribution. $kH_{\text{cont}}(k)$ denotes the term for those contributions in which the distances are supposed to be randomly distributed, and $\delta_{\alpha\beta}$ is the Kronecker delta. The following strategy for the refinement of the structure was adopted. First, a univariate fit was carried out to determine the average distance values for Ga–O pair distributions. The same procedure was applied to obtain the corresponding $l_{\alpha\beta}$ and $c_{\alpha\beta}$ values. Once these parameters were determined and the existence of four coordinate Ga atoms consequently established, the contributions of OH–OH pairs within the Ga(OH)$_4^-$ tetrahedra were determined from geometrical constraints. Next, the contributions of the monomer structural units were subtracted from the experimental $kH(k)$ and the Na–O parameters determined approximately. Finally, an attempt was made to determine the parameters of the bulk water in the system. Once a rough estimate for each main parameter had been obtained, a systematic refinement was performed by testing the following species in the model:

(1) Monomeric gallate ions, corresponding to the formula Ga(OH)$_4^-$. A regular tetrahedral shape due to the strong interaction between gallium and hydroxide ions was assumed and the OH–OH distances and coordination numbers were computed accordingly.

(2) Gallate ions in dimeric form, corresponding to the formula Ga$_2$O(OH)$_6^{2-}$, as two tetrahedral blocks are connected

via an O-bridge. All distances and coordination numbers were computed from the geometrical constraints.

(3) Hydrated sodium ions were characterized by structural parameters of Na–O contributions. No regular geometry was assumed. Contact ion pairs between sodium and hydroxide, NaOH^0, were considered in these fitting parameters. Distances and rmsd values of the Na–OH pairs were set equal to those of Na–H$_2$O, thus handling them equivalently.

(4) NaGa(OH)$_4^0$ complex ions were assumed to have a sodium ion in touch with more than one OH group, *e.g.*, on the face of the gallate tetrahedron.

(5) The first neighbour distance and the coordination number around the O atoms were adjusted during the fitting procedure.

(6) Rmsd values were adjusted to take account of the Ga–OH contributions and for all others with relatively high average weights. In all other cases rmsd values were fixed, and set equal to an approximate value chosen from the literature.[32]

(7) The "continuous" part of the structure function was omitted from the structural analysis, as it is irrelevant to the local order of current interest.

During the analysis, the model comprised an appropriate mixture of the above elements. Initially, an assumption of fully hydrated ion pairs merged in the "remaining water structure" was adopted, without accounting for any ion pair formation.

This model was then developed by dropping the assumption of complete hydration to consider the system with ion pairs. Finally, a compact structure in which all the gallate ions were regarded as forming contact ion pairs with sodium and these "compact" structural units were hydrated by the remaining water molecules. In the last case, no separate hydrated ions were supposed in the solution. The structural parameters obtained from models are shown for solution *n*21, as example, in Table 2.

The fitted various contributions to the total radial distribution function for solution *n*52 is shown in Fig. 3. It is important to note that among the model assumptions, (4) and (7) have the smallest significance and could be even neglected without important change in the goodness of fit.

Local structure around gallium

As far as tetrahedrally coordinated gallium is concerned, no previous measurements to clarify its local structure appear to have been made in highly concentrated alkaline solutions. The coordination number of the O-containing scattering units around the Ga atoms in all of the present gallate solutions is four, within the limit of experimental error. It should be noted here that the results of the LSQ fit agree reasonably well with those obtained from the direct reading of the pair distribution functions (Table 3). The accurate values of distances, together with the coordination number values and the literature information establish that the basic structural geometry of the gallate ions in all of our solutions is tetrahedral. Based on literature data, the primary Ga–O distance in purely O-coordinated Ga(III) compounds depends on the coordination number of the metal ion. In octahedral complexes, it was found to be $r_{\text{Ga–O}} = 1.95 \pm 0.03$ Å

Table 2 Structural parameters obtained from least-squares fitting of the experimental data by theoretical structure functions, using average geometrical models, for solution n21

Ga(OH)$_4^-$ (monomeric gallate)

$r_{Ga–OH}$	$l_{Ga–OH}$	$c_{Ga–OH}$	$r_{OH–OH}$	$l_{OH–OH}$	$c_{OH–OH}$
1.80	0.095	4.1	2.93	0.16	6.0*

NaGa(OH)$_4^0$ (contact ion-pair)

$r_{Na–O}$	$l_{Na–O}$	$c_{Na–O}$	$r_{Ga–Na}$	$l_{Ga–Na}$	$c_{Ga–Na}$
2.41	0.138	1.2	3.85	0.19	1.1

Na$^+$–O (with all oxygens)

$r_{Na–H_2O}$	$l_{Na–H_2O}$	$c_{Na–H_2O}$
2.47	0.14	4.9

O–O (all oxygens)

$r_{OH–H_2O}$	$l_{OH–H_2O}$	$c_{OH–H_2O}$
2.81	0.16	3.8

The distances, ($r_{\alpha\beta}$), the rmsd deviations ($l_{\alpha\beta}$) in Å, and the coordination numbers ($c_{\alpha\beta}$) are given. Asterisk indicates that the parameter was fixed during the fitting procedure or calculated from geometrical constraints.

Table 3 Approximate values of the structural parameters from a direct reading of the pair distribution functions (peak maxima r_1, r_2, r_3, and minima, r_{min}, in Å), and coordination numbers (c_i) calculated from the integration to the peak maxima ($i < 4$) and to the first minimum on the $g(r)$ function (i). O refers to either OH$^-$ or H$_2$O units

	r_1 Ga–O	r_2 Na–O	r_3 O–O	r_{min}	c_1 Ga–O	c_2 Na–O	c_3 O–O
n21	1.80	2.45	2.85	3.10	4.0	6.1	3.8

solutions,[2,37] $r_{Ga–O}$ was found to be 1.80–1.83 Å. In crystalline solid Ga(III) compounds, for the tetrahedrally O-coordinated Ga(III),[38–41] $r_{Ga–O} = 1.82 \pm 0.04$ Å (e.g., in alkali-gallosilicates 1.83 Å, in Ga-bearing zeolites 1.78–1.85 Å and in β-Ga$_2$O$_3$, 1.83–1.86 Å). From our own measurements, from the primary $r_{Ga–O} = 1.83 \pm 0.03$ Å and also from the 4.0 ± 0.1 coordination number, the geometry of the Ga(III) in our systems is tetrahedral. This finding is in accordance with the previous Raman and ^{71}Ga NMR results.[24] From this, it also follows that higher complexes (e.g., Ga(OH)$_6^{3-}$) do not form even at the highest concentration of base. If such a complex is present at all, its concentration is below the detection limit of the experimental technique used.

An attempt was also made to describe the structure of the (more concentrated) solutions by including a dimeric species (HO)$_3$Ga–O–Ga(OH)$_3^{2-}$ which has two tetrahedrally coordinated gallium atoms with an O atom shared at a common vertex (listed as model 2 in the previous section). In this model structure the Ga···Ga distance is estimated to be around 3.1 Å. From Fig. 3 it can be seen that based on the X-ray diffraction measurement one can conclude that no significant amount of dimeric species exists in the solution, even in the case of the highest concentration of gallium studied here.
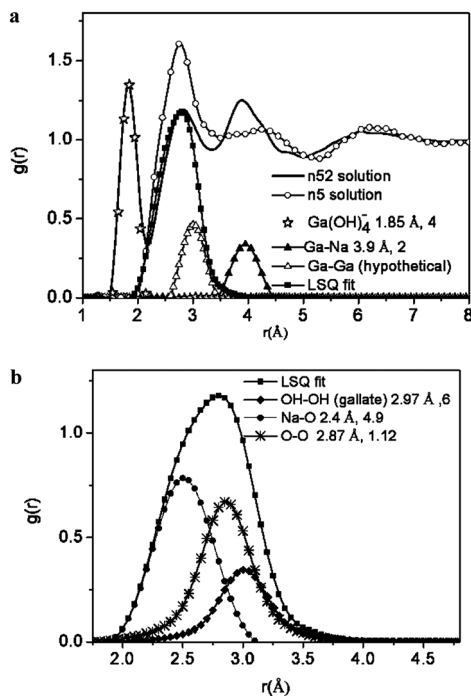

Fig. 3 (a) Results of the LSQ fitting procedure for the n52 sodium gallate solution at the structure function level, showing the experimental X-ray structure function (solid line), and the individual pair interactions used for fitting as well as hypothetical contribution of gallate dimer as direct evidence, and that the dimer structure does not play important role. For comparison, the structure function obtained for the solution n5 (line with open circles) is also shown (b). Deconvoluted peak of the LSQ fit at around 2.86 Å. The individual pair interactions used for fitting, the type of atoms, distances and coordination numbers are also shown.

(e.g., in aqueous solutions for Ga(H$_2$O)$_6^{3+}$, $r_{Ga–O} = 1.95$–1.96 Å, in the solid α-GaO(OH) 1.98 Å, in the solid complex salt Na$_{10}$[Ga(OH)$_6$]$_2$(OH)$_4$ 1.95 Å).[2,35,36] In alkaline Ga(III)-bearing

Comparison of the observed and calculated ^{71}Ga-NMR, IR and Raman spectra

The structures, for which ab initio calculations were performed are shown in Fig. 4. The primary Ga–O bond lengths were found to be 1.85 Å for the monomeric and 1.81 Å for the dimeric gallate species, respectively. A similar shortening in the Al–O bond length, which was experimentally observed for alkaline aluminate solutions upon increasing the concentration of Al(III), was explained in terms of transformation of the monomer into the dimer.[42] The ^{71}Ga NMR chemical shifts of Ga(OH)$_4^-$ and (HO)$_3$Ga–O–Ga(OH)$_3^{2-}$ have been calculated, and (relative to that of Ga(H$_2$O)$_6^{3+}$) have been found to be 301 and 304 ppm, respectively. Although these are significantly different from those experimentally observed for strongly alkaline gallate solutions (~225 ± 3 ppm), the data indicate that the chemical shielding of the nucleus in the Ga-atom is very similar in the monomeric and in the (hypothetical) dimeric gallate complex. Therefore, ^{71}Ga NMR is likely to be unable to distinguish between these two species. Note that similar results were obtained, when the ^{27}Al NMR spectra of the aluminate-monomer and that of the dimer were compared, the experimental spectra of strongly alkaline aluminate solutions, which

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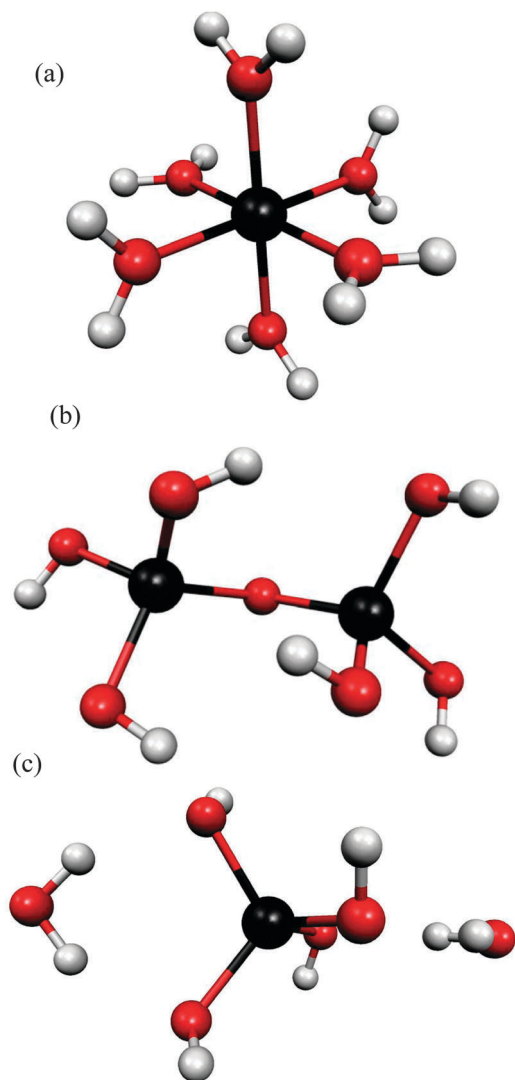
Fig. 4 Ball and stick models of Ga(III)-ion containing structures: (a) octahedrally coordinated $Ga(H_2O)_6^{3+}$ ions, (b) the dimeric species, $(HO)_3Ga-O-Ga(OH)_3^{2-}$ and (c) the monomeric $Ga(OH)_4^-$ with two hydrating H_2O molecules.

Fig. 5 Calculated IR (up) and Raman spectra (down) of the species shown in Fig. 4, (a) octahedrally coordinated $Ga(H_2O)_6^{3+}$ ions, (b) the dimeric species, $(HO)_3Ga-O-Ga(OH)_3^{2-}$ and (c) the monomeric $Ga(OH)_4^-$ with two hydrating H_2O molecules.

were either rich or poor in the dimeric aluminate species, were practically identical.[43]

Calculated IR and Raman spectra of the three gallate structures are shown in Fig. 5. On the experimentally observed IR spectra, absorption bands were seen at ~ 740 and ~ 500 cm^{-1} in strongly alkaline gallate solutions.[14] Calculated absorption bands (in this spectral region) were found at 739 and 482 cm^{-1} for the monomeric and at 840 and 768 cm^{-1} for the dimeric species, respectively (Fig. 5a). On the experimentally found Raman spectra of analogous solutions,[24] only one band at 605 cm^{-1} was observed. Calculations resulted in a strong Raman band at 600 cm^{-1} for the monomeric and at 552 cm^{-1} (with a shoulder at 592 cm^{-1}) for the dimeric species, respectively (Fig. 5b). Both sets of data strongly indicate that the calculated spectral parameters are consistent with the presence of the monomeric gallate species and with the absence of the dimeric
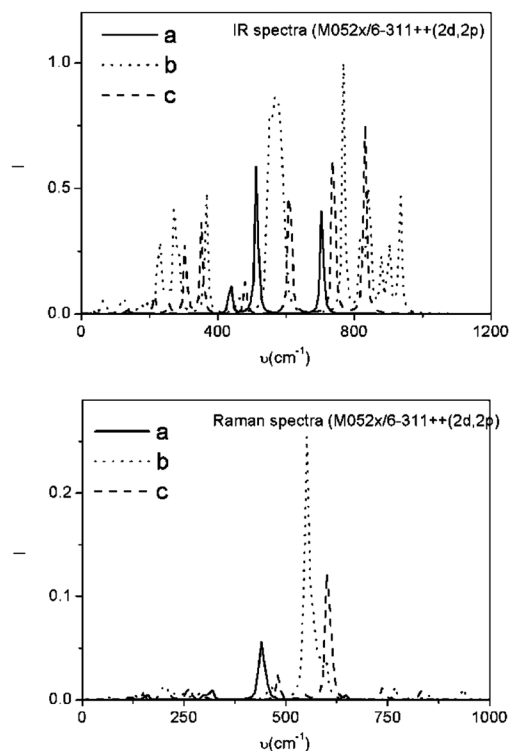
one in these strongly alkaline gallate solutions. This is a striking difference between the strongly alkaline gallate and aluminate solutions. In aluminates with similar concentrations, the dimeric species $(OH)_3Al-O-Al(OH)_3^{2-}$ is present in significant and experimentally detectable concentrations.[42–44]

For analogous Ga-containing solutions, the experimental observations and the findings from quantum chemical calculations are consistent with the absence of the dimeric gallate species, $(OH)_3Ga-O-Ga(OH)_3^{2-}$. This finding is particularly surprising, as solid crystalline compounds with this dimeric unit as the building block have been possible to be prepared from concentrated $NaOH-Ga(OH)_3$ solutions.[11,13,43,44]

Hydration structure of the gallate ion and the first-neighbour oxygen–oxygen distances

Adding the approximate effective radii of Ga, OH, and H_2O results a Ga–OH$_2$ distance of between 4.0 and 4.4 Å for hydrated gallate species. The distance depends slightly on the location and orientation of the hydrating water molecule. For trivalent, hydrated Ga^{3+} ions, a strong tendency to form a stable and highly symmetrical second hydration layer with hydrogen bonds significantly shorter than those present in pure water has been observed. This was explained in terms of the strong coulombic field of Ga^{3+}, which strongly polarizes its first neighbour molecules. In contrast, as the $Ga(OH)_4^-$ is both an anion and much larger, it seems likely to have only a very loosely bound hydration shell like perchlorate, sulphate

or iodide. This fact and the complexity of the entire structure in the range up to the expected Ga–OH$_2$ distance have made the determination of the gallate hydration parameters quite uncertain.

Coordination structure of the sodium ion: hydration and contact ion pair formation

The hydration structure of sodium ions in solution has been intensively investigated by direct structural methods,[32,45] but with a surprisingly scattered range of results. The hydration numbers that have been reported usually vary between 4 and 6[32] and to have been found to strongly correlate with the Na–O bond distance.[45] Computer simulation studies have explained these variations by invoking the existence of relatively weak forces between sodium and water, which result in a loss of regular symmetry in the first hydration shell. The present results regarding the coordination structure of the sodium ions in solution conform with the observations. The Na–O distances are in good agreement with that obtained in our previous studies on highly concentrated sodium hydroxide solutions (2.45 Å).[34] The average coordination number of Na$^+$ in the most highly concentrated NaOH solution ($n1$) is 5.4. This represents a significantly lower degree of symmetry than would be the case in a truly octahedral structure. The coordination state of the sodium ion in the sodium gallate solutions is more complicated. In the most dilute solution ($n21$) the coordination number of sodium is close to 4.9, and for the most concentrated solution it is 3.9.

It has to be noted here that the coordination numbers in the first coordination shell of sodium ions contain information on the amount of formed GaO$_x$–Na ion pairs. It can be concluded that in the most dilute case the coordination number is 1 and it increases to 2 in the case of most concentrated solution of gallium. The average total coordination number of sodium (GaO$_x$–Na together with Na–O) is almost not affected by gallium concentration.

Structural changes in bulk water

An assumption usually made in the structural analysis of dilute solutions is that water which is not directly coordinated to a solute species may be treated as bulk water and the experimental structure function of pure water can be simply subtracted from that of the solution. In these cases, a weighting factor is calculated from the stoichiometric ratio of water. This approximation is, however, not valid with the present solutions except, perhaps, $n21$. This makes any attempt to characterize quantitatively the structure of the bulk or, more precisely, of the remaining water, rather difficult. The only reliable statement that can be made is that the original structure of the water is largely disrupted.

Comparison with aluminate structures

A complete series of sodium aluminate solutions has been measured several years ago and the structure of aluminate solutions was analyzed in detail.[42–44] The analysis has been performed along a similar way to the gallate solutions, mostly because we wanted to study the eventual similarities or find the differences between the two systems. The main results of the aluminate structural analysis are:

(i) The monomeric aluminate form with tetrahedral structure is confirmed.[8]

(ii) Beyond that, a more extended structure with two tetrahedra (that is: dimeric aluminate species) is possible, both from experimental[8,42–46] and from computational[47] means further structural units are also possible, even if they were not fully confirmed. Moreover, spectroscopic and other studies reported the extended network of numerous structural forms in aluminate solutions, however, they are scarcely confirmed.

(iii) Some other features of aluminate structures are also signalled, and even nowadays they are still a question of doubt. The most important feature of aluminate structures is that a variety of structural forms is mentioned, which can be a result of the uncertainty in the method itself or, in the various forms present in the structure.

As far as gallate structure is concerned, the situation seems to be simpler. As the present work witnesses, there is much less doubt in describing the predominating structural forms in gallate solutions, see, *e.g.*, the predominant structural form of aluminate structures is the monomeric one, and any other complex structural units could be excluded. As far as ion pair formation is concerned, it is also negligible in gallates (O-bridged Ga species in solution), while these are very probable in aluminates. Since the atomic/ionic sizes are very similar, these differences in features can be ascribed to the different chemistry and physics of gallates and aluminates. It seems to be validated that gallates are more compact structures than aluminates are.

Summary and conclusions

As a result of the progressive fitting procedure described above, the best fitted model for the most dilute $n21$ solution includes only Ga(OH)$_4{}^-$ monomers, hydrated sodium ions, and bulk water. The hydration structure of the gallate ion could not be adequately described due to the low weight of Ga–OH$_2$ pair contributions. For the same reason and because of the difficulty in distinguishing between OH$^-$ and H$_2$O, the hydration structure of the OH$^-$ ions could also not be determined. Direct evidence was found for the formation of a sodium gallate contact ion pair, at the same time we concluded that the total hydration number of sodium hardly changes as the Ga(III) concentration increases.

At the other extreme, in the most concentrated $n52$ solution, there is hardly enough water to completely hydrate any of the ions in solution. The existence of contact ion pairs is thus ensured by simple stoichiometric and packing constraints.

In summary, the speciation in highly concentrated alkaline solutions is dominated by a gallate ion that is four coordinate and has tetrahedral symmetry. Significant concentrations of species with higher (octahedral) or lower degrees of symmetry (*e.g.*, GaO$_2{}^-$ units) as well as the dimeric gallate species,

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$(OH)_3Ga–O–Ga(OH)_3{}^{2-}$, can be excluded. At very high concentrations, however, all ions tend to be involved in contact ion pairs sharing the available water and/or hydroxide species.

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