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The Structure of Hyperalkaline Aqueous Solutions Containing High Concentrations of Gallium - a Solution X-ray Diffraction and Computational Study

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Highly concentrated alkaline NaOH/Ga(OH)₃ solutions with $1.18 \text{ M} \leq [\text{Ga(III)}]_{\text{T}} \leq 2.32 \text{ M}$ and $2.4 \text{ M} \leq [\text{NaOH}]_{\text{T}} \leq 4.9 \text{ M}$ (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, that 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)₃Ga–O–Ga(OH)₃²⁻ could not unambiguously be shown, however, from the comparison of experimental IR, Raman and ⁷¹Ga NMR spectra with calculated ones, its formation can be safely excluded. Moreover, higher mononuclear stepwise hydroxo complexes, like Ga(OH)₆³⁻, that have been claimed to exist by others in the literature, was 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 computer industry. It is similar to aluminium, but less common and less frequently used. Nevertheless, with the development of 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 beside 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 the typical oxide occurs in 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 Ga³⁺ and 1.18 Å for Al³⁺, while ionic radii are 0.62 Å for Ga³⁺ and 0.54 Å for

Al³⁺. 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 obvious that interatomic potentials have a special role in forming structures. These pieces of information are still not enough to answer the above question.

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 $\text{Ga}(\text{OH})_4^-$, the first possible candidate is the dimeric $(\text{OH})_3\text{Ga}-\text{O}-\text{Ga}(\text{OH})_3^{2-}$; 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 experiments¹⁵ with caustic gallates containing $[\text{NaOH}]_{\text{T}} = 0.4 \text{ M}$ yielded a molecular mass of ~270 for the gallium bearing species, indicating the possible presence of a dimeric gallate complex ($M_{\text{r}} = 257.4$, 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 $\text{Ga}(\text{OH})_6^{3-}$ structural units are known and their structure is well established.^{18–21} It is suggested, that the solution species $\text{Ga}(\text{OH})_6^{3-}$ is formed in strongly alkaline solutions.²² The statement was based on observations from solubility²³ and conductivity¹⁶ measurements.

The Raman and ⁷¹Ga NMR spectra of highly concentrated NaOH/Ga(OH)₃ solutions²⁴ (with $0.23 \text{ M} \leq [\text{Ga}(\text{III})]_{\text{T}} \leq 2.32 \text{ M}$ and $1 \text{ M} \leq [\text{NaOH}]_{\text{T}} \leq 15 \text{ M}$) were found to be consistent with the predominance of the well-known tetrahedral hydroxo complex, $\text{Ga}(\text{OH})_4^-$. The observations suggested, that this is the only spectroscopically significant species present in these NaOH/Ga(OH)₃ solutions, even at the highest $[\text{Ga}(\text{III})]_{\text{T}}$ and $[\text{NaOH}]_{\text{T}}$. The ⁷¹GaNMR chemical shifts observed for these solutions ($225 \pm 2 \text{ ppm}$, relative to $\text{Ga}(\text{H}_2\text{O})_6^{3+}$), which are highly concentrated with respect to gallium, are practically identical to those observed for alkaline (pH = 13) solutions with significantly lower $[\text{Ga}(\text{III})]_{\text{T}}$.² Thus, the chemical shift is consistent with the presence of tetrahedral complex (or complexes). 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 observation, that the area of this peak is linearly proportional to $[\text{Ga}(\text{III})]_{\text{T}}$, indicates 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.*, $\text{Ga}(\text{OH})_6^{3-}$) or the oxo-bridged dimer (*i.e.*, $(\text{OH})_3\text{Ga}-\text{O}-\text{Ga}(\text{OH})_3^{2-}$) 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 diffraction and quantum mechanical calculations. The other is to elucidate if solution species other than the well-established tetrahedral

$\text{Ga}(\text{OH})_4^-$ might exist and are present in experimentally detectable quantities in such systems. In particular, the detection of the dimeric species, analogous to the $(\text{OH})_3\text{Al}-\text{O}-\text{Al}(\text{OH})_3^{2-}$ was the central question, as at 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 (Hungrapharma, 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*: $[\text{NaOH}]_{\text{T}} = 4.82 \text{ M}$ and $[\text{Ga}(\text{III})]_{\text{T}} = 2.32 \text{ M}$; *n51*: $[\text{NaOH}]_{\text{T}} = 4.90 \text{ M}$ and $[\text{Ga}(\text{III})]_{\text{T}} = 1.18 \text{ M}$; *n21*: $[\text{NaOH}]_{\text{T}} = 2.40 \text{ M}$ and $[\text{Ga}(\text{III})]_{\text{T}} = 1.18 \text{ M}$. For comparison, two NaOH solutions with no added Ga(III) were also recorded (*n5*: $[\text{NaOH}]_{\text{T}} = 4.82 \text{ M}$; *n2*: $[\text{NaOH}]_{\text{T}} = 2.40 \text{ M}$). Further details are summarised in Table 1.

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	$[\text{NaOH}]_{\text{T}}$ (M)	$[\text{Ga}(\text{OH})_3]_{\text{T}}$ (M)	ρ (g cm ⁻³)	μ (cm ⁻¹)	ρ_0 (10 ⁻²⁴ cm ³)	Ga(OH) ₃ :NaOH:H ₂ O
<i>n2</i>	2.4327	0	1.0886	1.2703	0.1044	0 : 1 : 22.64
<i>n5</i>	4.7353	0	1.1728	1.4513	0.1072	0 : 1 : 11.54
<i>n21</i>	2.4806	1.1846	1.1984	5.993	0.0406	1 : 2.09 : 44.84
<i>n51</i>	4.9464	1.1885	1.2685	6.1919	0.0426	1 : 4.16 : 43.34
<i>n52</i>	4.8601	2.321	1.3481	10.683	0.0462	1 : 2.09 : 20.91

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 α 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, 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

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

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

$$M(k) = \exp(-bk^2) [\sum_{\alpha} x_{\alpha} f_{\alpha}(k)]^2 \quad (2)$$

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_2O molecules and Ga^{3+} ions. The arbitrary use of a composite “group” scattering unit, representing both OH^- and H_2O instead of individual O and H atoms, 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_2O . 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 Radnai²⁹ for O, H, Na, and Ga and according to Hajdu for H_2O .³⁰ The experimental pair distribution functions $g(r)$ were computed from the structure functions according to

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

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 $\text{Ga}(\text{H}_2\text{O})_6^{3+}$, $\text{Ga}(\text{OH})_4(\text{H}_2\text{O})_2^-$ and $(\text{OH})_3\text{Ga}-\text{O}-\text{Ga}(\text{OH})_3^{2-}$. 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_2O 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 function that have an explicit field dependence NMR shielding tensors at DFT levels of theory on optimized structure of complexes.³¹ Raman and ⁷¹Ga 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 publication²⁴ 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 \AA^{-1} with changing chemical composition of the solutions. This double peak in the structure function of water around 2.5 \AA^{-1} is characteristic to 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 $k > 6 \text{\AA}^{-1}$. 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.

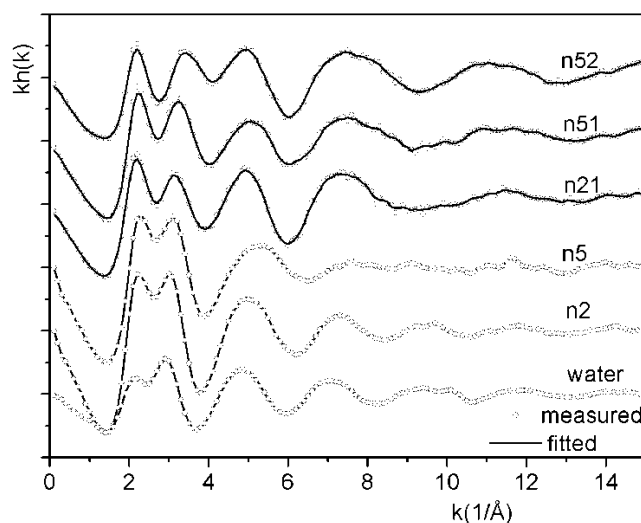


Fig. 1 Experimental (circles) and fitted (solid lines) solution X-ray structure functions for sodium hydroxide and sodium gallate solutions. For definition of acronyms used for the various solutions, see Table 1.

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 eq 3, using the valuable experimental data up to $k_{max} = 16 \text{ \AA}^{-1}$. 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 spurious ripples remain, but the experimental results are not seriously affected.

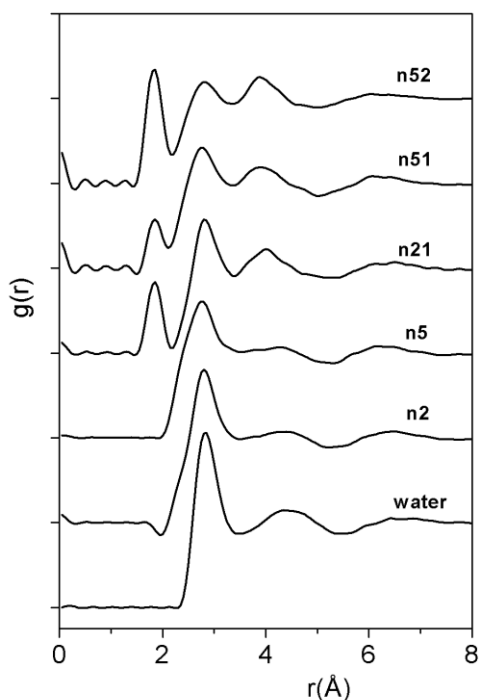


Fig. 2 Experimental X-ray pair distribution functions for sodium hydroxide solutions, and sodium gallate solutions. The solutions are as defined in Table 1.

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.^{32,33} The main peak, at 2.84 Å, corresponds to hydrogen-bonded first neighbor distances, with an average coordination number of about 3.5 to 4.5 molecules. The second broad peak 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 $\text{Na}^+\text{-O}$ (either oxygen of water or hydroxide; this notation will be used in the rest of the article when all type of oxygens are mentioned) first neighbour distance, which is around 2.4 Å.³³ Another significant change can be observed on the $g(r)$ where the minimum after the first peak is filled in 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 $\text{Na}^+\text{-O}$ 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 $\text{H}_2\text{O-H}_2\text{O}$ distances is observed instead of an increase in the $\text{Na}^+\text{-O}$ 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 structural entities 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:

- The Ga-O distance was found to be 1.85 Å in all of the gallate solutions studied.
- The coordination number of the nearest O units around each gallium is 4, within the limit of the experimental errors.
- The position of the Na-O shoulder is unchanged (relative to the Ga(III)-free solutions), within the precision of the measurements.
- 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).
- The sodium ions are coordinated by about 6 O-containing units (referencing to our notation, so the O comes from either OH^- or H_2O) over the series of gallate solutions.
- 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 shows a clear tendency to increase with increasing gallate concentration. Therefore, this part of the radial distribution function can not 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

$$R = \frac{\sum_{k=k_{\min}}^{k_{\max}} [kH_{\text{theor}}(k) - kH_{\text{exp}}(k)]^2}{\sum_{k=k_{\min}}^{k_{\max}} k^2 H_{\text{exp}}(k)^2} = \text{minimum} \quad (4)$$

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 $\text{Ga}(\text{OH})_4^-$ 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 for 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 $\text{Ga}(\text{OH})_4^-$. 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 $\text{Ga}_2\text{O}(\text{OH})_6^{2-}$, 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 for Na– H_2O , thus handling them equivalently.

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

(5) The first neighbour distance and 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.³³

(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.

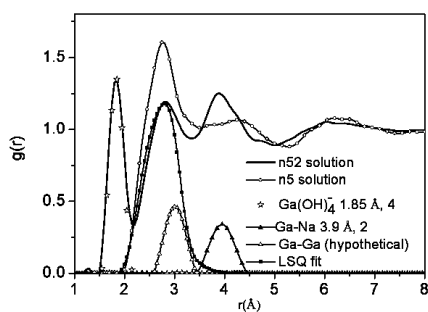
During the analysis, the model comprised an appropriate mixture of the above elements. Initially, an assumption of fully hydrated ion pairs merged in the “remaining water structure” was adopted, without accounting for any ion pair formation.

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 and/or form contact ion pairs with hydroxide ions was assumed. In the last case, no separate hydrated ions were supposed in the solution. The structural parameters obtained from models giving the best fit to the experimental data are shown for solution *n21*, as example, in Table 2.

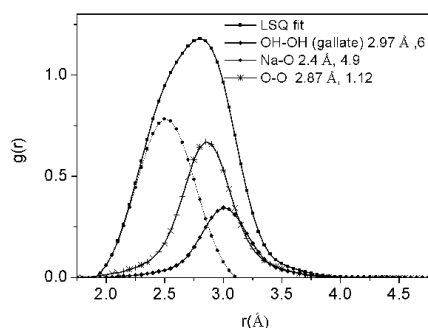
Table 2. Structural parameters obtained from least-squares fitting of the experimental data by theoretical structure functions, using average geometrical models, for solution *n21*.

Ga(OH) ₄ [−] (monomeric gallate)					
<i>r</i> _{Ga-OH}	<i>l</i> _{Ga-OH}	<i>c</i> _{Ga-OH}	<i>r</i> _{OH-OH}	<i>l</i> _{OH-OH}	<i>c</i> _{OH-OH}
1.80	0.095	4.1	2.93	0.16	6.0*
NaGa(OH) ₄ ⁰ (contact ion-pair)					
<i>r</i> _{Na-O}	<i>l</i> _{Na-O}	<i>c</i> _{Na-O}	<i>r</i> _{Ga-Na}	<i>l</i> _{Ga-Na}	<i>c</i> _{Ga-Na}
2.41	0.138	1.2	3.85	0.19	1.1
Na ⁺ -O (with all oxygens)					
<i>r</i> _{Na-H₂O}	<i>l</i> _{Na-H₂O}	<i>c</i> _{Na-H₂O}			
2.47	0.14	4.9			
O-O (all oxygens)					
<i>r</i> _{OH-H₂O}	<i>l</i> _{OH-H₂O}	<i>c</i> _{OH-H₂O}			
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 indicate that the parameter was fixed during the fitting procedure or calculated from geometrical constraints.



3a



3b

Fig. 3a. Result 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 a direct evidence, 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; **3b.** Deconvoluted peak of LSQ fit around 2.86 Å. The individual pair interactions used for fitting, the type of atoms, distances and coordination numbers are also shown.

The fitted various contributions to the total radial distribution function for solution *n52* 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 LSQ fit agrees 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 $r_{\text{Ga-O}} = 1.95 \pm 0.03 \text{ \AA}$ (e.g., in aqueous solutions for $\text{Ga}(\text{H}_2\text{O})_6^{3+}$ $r_{\text{Ga-O}} = 1.95\text{--}1.96 \text{ \AA}$, in the solid $\alpha\text{-GaO}(\text{OH})$ 1.98 \AA , in the solid complex salt $\text{Na}_{10}[\text{Ga}(\text{OH})_6]_2(\text{OH})_4$ 1.95 \AA).^{2,35,36} In alkaline Ga(III)-bearing solutions,^{2,37} $r_{\text{Ga-O}}$ was found to be $1.80\text{--}1.83 \text{ \AA}$. In crystalline solid Ga(III) compounds, for the tetrahedrally O-coordinated Ga(III),³⁸⁻⁴¹ $r_{\text{Ga-O}} = 1.82 \pm 0.04 \text{ \AA}$ (e.g., in alkali-gallosilicates 1.83 \AA , in Ga-bearing zeolites $1.78\text{--}1.85 \text{ \AA}$ and in $\beta\text{-Ga}_2\text{O}_3$, $1.83\text{--}1.86 \text{ \AA}$). From our own measurements, from the primary $r_{\text{Ga-O}} = 1.83 \pm 0.03 \text{ \AA}$ 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 ⁷¹Ga NMR results.²⁴ From this, it also follows, that higher complexes (e.g., $\text{Ga}(\text{OH})_6^{3-}$) do not form even at the highest concentration of base. If such complex is present at all, its concentration is below the detection limit of the experimental technique used.

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 H₂O 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
<i>n21</i>	1.80	2.45	2.85	3.10	4.0	6.1	3.8

An attempt was also made to describe the structure of the (more concentrated) solutions by including a dimeric species $(\text{HO})_3\text{GaO}(\text{Ga}(\text{OH})_3)^{2-}$ 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 estimated to be around 3.1 \AA . From Fig. 3 it can be seen that based on the X-ray diffraction measurement one can conclude that there are no significant amount of dimeric species exists in the solution, even in the case of the highest concentration of gallium studied here.

Comparison of the observed and calculated ⁷¹Ga-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 \AA for the monomeric and 1.81 \AA 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 to the dimer.⁴² The ⁷¹Ga NMR chemical shifts of $\text{Ga}(\text{OH})_4^-$ and $(\text{HO})_3\text{Ga-O-Ga}(\text{OH})_3^{2-}$ has been calculated, and (relative to that of $\text{Ga}(\text{H}_2\text{O})_6^{3+}$) have been found to be 301 and 304 ppm, respectively. Although these are significantly different from those experimentally observed for strongly alkaline gallate solutions ($\sim 225 \pm 3 \text{ ppm}$), 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 result was 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 were either rich or poor in the dimeric aluminate species, were practically identical.⁴³

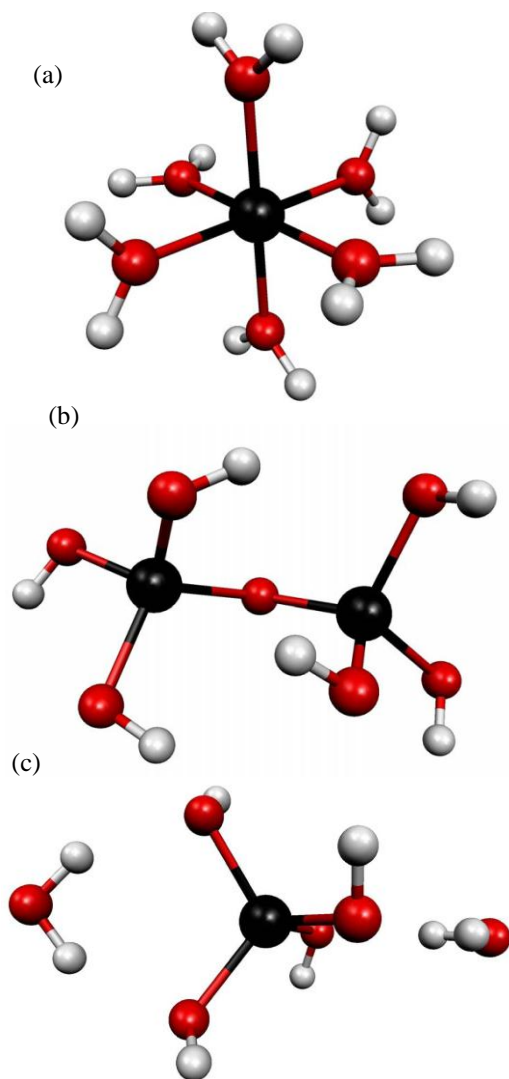


Fig. 4 Ball and stick models for Ga(III)-ion containing structures: a) octahedrally coordinated $\text{Ga}(\text{H}_2\text{O})_6^{3+}$ ion, b) the dimeric species, $(\text{HO})_3\text{GaOGa}(\text{OH})_3^{2-}$ and c) the monomeric $\text{Ga}(\text{OH})_4^-$ with two hydrating H_2O molecules.

Calculated IR and Raman spectra for the three gallate structures are shown in Fig. 5. On the experimentally observed IR spectra, absorption bands were seen at ~ 740 and $\sim 500\text{ cm}^{-1}$ 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 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 $(\text{OH})_3\text{Al-O-Al}(\text{OH})_3^{2-}$ 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, $(\text{OH})_3\text{Ga-O-Ga}(\text{OH})_3^{2-}$. 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 $\text{NaOH}/\text{Ga}(\text{OH})_3$ solutions.^{11,13,43,44}

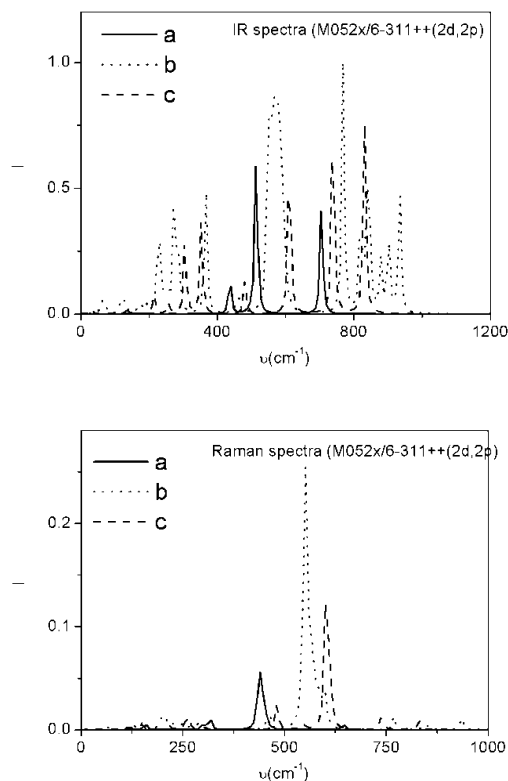


Fig. 5 Calculated IR (up) and Raman spectra (down) of the species shown in Fig. 4, a) octahedrally coordinated $\text{Ga}(\text{H}_2\text{O})_6^{3+}$ ion, b) the dimeric species, $(\text{HO})_3\text{GaOGa}(\text{OH})_3^{2-}$ and c) the monomeric $\text{Ga}(\text{OH})_4^-$ with two hydrating H_2O molecules.

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 \AA 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 $\text{Ga}(\text{OH})_4^-$ 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 $\text{Ga}-\text{OH}_2$ 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,³³ but with a surprisingly scattered range of results. The hydration numbers that have been reported usually vary between 4 and 6, with $\text{Na}-\text{O}$ distances between 2.4 and 2.5 Å. 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 $\text{Na}-\text{O}$ 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 ion contains information on the amount of formed $\text{GaO}_x\text{-Na}$ 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 ($\text{GaO}_x\text{-Na}$ together with $\text{Na}-\text{O}$) 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 tetrahedron (that is: dimeric aluminate species) is possible, both from experimental^{8,42-45} and from computational⁴⁶ 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 in 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 $\text{Ga}(\text{OH})_4^-$ 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 $\text{Ga}-\text{OH}_2$ pair contributions. For the same reason and because of the difficulty in distinguishing between OH^- and H_2O , the hydration structure of the OH^- ions could also not be determined. Direct evidence was found for the formation of sodium gallate contact ion pair formation, 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, $(\text{OH})_3\text{Ga}-\text{O}-\text{Ga}(\text{OH})_3^{2-}$, 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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Notes and references

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† In this paper, based on the analogy with aluminates, $\text{NaOH}/\text{Ga}(\text{OH})_3$ 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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