The Hydration of Tungstate and Molybdate Ions in Aqueous Solution

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The structure in aqueous solution of the hydrated tungstade and molybdate ions WO_4^{2-} and MoO_4^{2-} has been derived from large angle X-ray scattering measurements using MoO_4^{2-} as an isomorphous substituent for WO_4^{2-}. The W(Mo)–O bond lengths are 1.78_6 Å and do not differ from those found in crystal structures. A fairly well-defined hydration shell of about 12 water molecules surrounds the XO_4^{2-} ions at a W(Mo)–H_2O distance of 4.06 Å.

The determination of the solvation number of ions in solution in often ambiguous, different methods giving different results. Large-angle X-ray scattering (LAXS) measurements offer a possibility of a direct structure determination of the solvated ions, but the information obtained from the scattering data is often obscured by overlapping contributions from other types of interactions. In aqueous solutions, cation-water distances within the hydration spheres are usually in the range between two and three Å, in close proximity of the dominant H_2O–H_2O interactions at about 2.9 Å. For hydration anions the distances are longer and not as well defined.

X-ray scattering data for solutions containing tetrahedral oxoanions (ClO_4^-, SO_4^{2-}, SeO_4^{2-} and PO_4^{3-}) have indicated the presence of hydration shells around these ions [1–4] but difficulties in separating the corresponding contributions to the scattering data can prevent accurate structure determinations [5–6]. The disturbing influence of intermolecular interactions can, at least approximately, be eliminated by utilizing differences between distribution curves for solutions of similar composition. In the case of an isomorphous substitution, when an ion in the solution can be replaced by an ion with a different scattering power without changing the structure, the elimination is complete and the difference curve will contain contributions only from interactions involving the substituted ions.

The method of isomorphic substitution was introduced by Bol et al. [7], and it was also used in neutron scattering experiments by Neilson et al. [8].

In the present work an attempts has been made to get more detailed information on the hydration of tetrahedral oxoanions by comparing scattering curves for tungstate and molybdate solutions of the same composition. The WO_4^{2-} and the MoO_4^{2-} ions both form regular tetrahedra with nearly the same metal oxygen bond length. In the isomorphous crystal structures of $Na_2WO_4 \cdot 2\,H_2O$ [9] and $Na_2MoO_4 \cdot 2\,H_2O$ [10] the average lengths have been reported to be 1.77_8 Å for the W–O bond and 1.773 Å for the Mo–O bond. It seems likely, therefore, that an exchange of MoO_4^{2-} for WO_4^{2-} ions in an aqueous solution would leave its structure and, therefore, its intermolecular interactions unchanged. By taking the difference between the RDFs for the two solutions, these interactions would cancel out and the difference curve would contain contributions involving the W(Mo) atoms only. It would then give an unobscured picture of the surroundings of these atoms.

Experimental

Preparation of solutions

Solutions, which were about 2 M in WO_4^{2-} or MoO_4^{2-}, were prepared by dissolving weighed amounts of $Na_2WO_4 \cdot 2\,H_2O$ or $Na_2MoO_4 \cdot 2\,H_2O$ in distilled water. Densities were determinated with an Anton Paar digital densimeter DMA 35. The composition of the solutions are given in Table 1.

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Table 1. Composition of solutions. Concentrations are given as mol l^{-1} (upper figures) and as the number of atoms in the stoichiometric unit of volume $V/Å^3$ (lower figures).

Solution	Concentrations				Density	V
	Na	WO_4^{2-}	MoO_4^{2-}	H_2O	$g\ cm^{-3}$	A^3
Na_2WO_4	4.04	2.02	–	50.7	1.506	822.0
	2	1	–	25.1		
Na_2MoO_4	4.07	–	2.035	50.8	1.334	816.0
	2	–	1	25.0		

X-ray scattering measurements

The scattering from the molybdate solution was measured with AgKα-radiation ($\lambda = 0.5608$ Å) in a $\theta - \theta$ diffractometer described previously [11]. The scattered radiation was reflected by a focusing single crystal LiF monochromator before reaching the scintillation counter, which was equipped with a pulse height analyzer and a discriminator.

The scattering from the tungstate solution was measured in a Rigaku Theta-Theta Wide Angle Goniometer CN2182D5 using MoKα-radiation ($\lambda =$ 0.7101 Å) and a focusing graphite monochromator. In order to use it for solution scattering measurements a special liquid sample holder was constructed which could be inserted into the solid sample holder of the instrument. The solution was transferred into the container of the sample holder by means of a burette. The height of the solutions surface was adjusted to the correct value, as determined from scattering measurements, by adding or withdrawing solution with the burette, which was permanently connected by a teflon tube to the container.

Intensities were measured for $1.5° < \theta < 70°$, where 2θ is the scattering angle. The whole angular range was covered using four slit widths (1/6°, 1/2°, 1° and 2°). The interval in θ was 0.1° up to $\theta = 10°$ and 0.25° for $\theta > 20°$. About 10^5 counts were collected for each point, and each angular region was scanned twice. The intensity measurements were done automatically with an ABC800 computer connected to the microprocessor of the diffractometer. Angles and intensities were stored and later processed (background corrections, averaging, normalization to common slit width) in the computer. Specially written programs in Basic for collection of data (SOLXRAY) and for the processing of data (SCALE) were used.

Data Treatment

The intensity data were handled by means of the KURVLR program as described in previous papers [12], [13]. Corrections were made for polarization in the sample and in the monochromator and for incoherent radiation slipping through the monochromator. Normalization to a stoichiometric unit of volume containing one W(Mo) atom was done by comparing observed and calculated intensities in the high-angle region of an intensity curve. Radial distribution functions, $D(r)$, were calculated from the reduced intensity values, $i(s) = I_{\text{obs}}(s) - \sum n_i f_i^2$, with $s = 4\pi(\sin\theta)/\lambda$, according to the expression

$$D(r) = 4\pi r^2 \varrho_0 + 2r\pi^{-1} \int_0^{s_{\max}} s \cdot i(s) \sin(rs) \cdot M(s)\, \mathrm{d}s .$$

Here $\varrho_0 = \left(\sum_i n_i f_i(0)\right)^2 V^{-1}$, V = the stoichiometric unit of volume chosen, n_i = the number of atoms "i" per unit volume, and f_i = the scattering factor of atom "i" corrected for anomalous dispersion. The sharpening factor

$$M(s) = f_{\text{Mo}}^2(0)/f_{\text{Mo}}^2(s) \cdot \exp(-0.010\, s^2).$$

For the upper integration limit, $s_{\max}$, the same value, 15.5 $Å^{-1}$ was used for both the AgKα and MoKα radiation. Theoretical peaks were calculated by a corresponding Fourier transformation of the theoretical intensities for the pair interactions,

$$i_{pq}(s) = \sum f_p f_q \sin(r_{pq} s)\,(r_{pq} s)^{-1} \cdot \exp(-\tfrac{1}{2}\sigma_{pq}^2 s^2),$$

using the same sharpening function and the same $s_{\max}$ value as for the experimental data and assuming the rms variation in the distance to be σ_{pq}.

Intensity contributions from an assumed even electron distribution surrounding a complex outside a sphere of radius R were calculated from the expression

$$i(s) = n_j \frac{4\pi R^3}{V} \cdot \frac{\sin Rs - Rs\cos Rs}{(Rs)^3} \cdot \sum_p f_p \frac{\sin s r_p}{s r_p} \sum_i n_i f_i \exp(-Bs^2).$$

Here n_j is the number of molecules in the stoichiometric unit volume, V, and r_p is the distance of an atom from the center of the molecule. The first summation is taken over all atoms in the molecule and the second summation over all atoms in V. The exponential factor $\exp(-B s^2)$ is included to allow for the non-sharpness of the emergence of the continuum [12].

Analysis of the data

Observed intensity values, $s\,i(s)$, for the sodium molybdate and sodium tungstate solutions are shown in Figure 1.

Except for more pronouned peaks for the tungstate solution the intensity curves are closely similar. In the low-angle region, however, the tungstate curve shows the presence of a peak at about $s = 0.8$ Å^{-1}, which does not occur for the molybdate solution. The corresponding θ angle is $\approx 2.4°$ for the tungstate $\approx 1.9°$ for the molybdate solution. Although these values are close to the lower limit for the observable intensity region the data seem to indicate that the difference is real. This does not, however, imply any structural difference between the solutions, as will be shown in the following discussion.

The radial distribution functions, $D(r) - 4\pi r^2 \varrho_0$, are given in Figure 2. The first peak in the RDF occurs at 1.8 Å and corresponds to the W(Mo)−O distances in the tetrahedral WO_4^{2-}(MoO_4^{2-}) ions. More diffuse peaks at ≈ 3 Å can be ascribed to H_2O(O)−H_2O(O) and Na^+-H_2O interactions. The major part of the pronounced peak at ≈ 4.1 Å is supposed to be due to the hydration layer around the anions: In these solutions no polynuclear complexes are expected to be present, [15−18], [20], which is in agreement with the observed $D(r)$ functions [19].

In the difference between the two $D(r)$ functions (Fig. 3), which should contain only interactions involving the W(Mo) atoms, only two peaks are present in the region up to about 4.5 Å. The first peak is closely reproduced by a theoretical peak calculated for four W(Mo)−O interactions at a distance of 1.786 Å, which is in agreement with the structures for the WO_4^{2-}(MoO_4^{2-}) ions found in crystals [9], [10], [14], [21]. The much larger peak at 4.1 Å is not well resolved from longer distances, but shows a well-defined shape towards low r values. A theoreti-

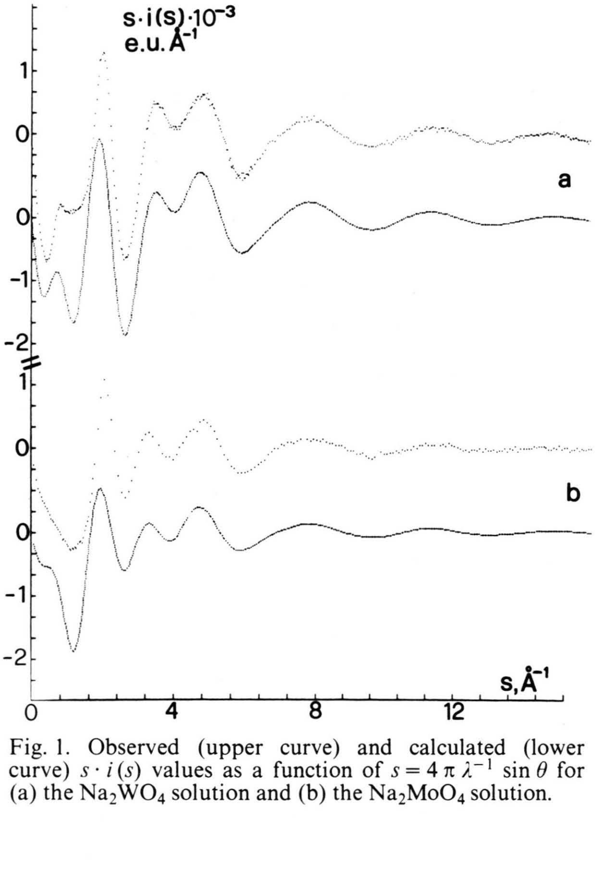

Fig. 1. Observed (upper curve) and calculated (lower curve) $s \cdot i(s)$ values as a function of $s = 4\pi\lambda^{-1}\sin\theta$ for (a) the Na_2WO_4 solution and (b) the Na_2MoO_4 solution.

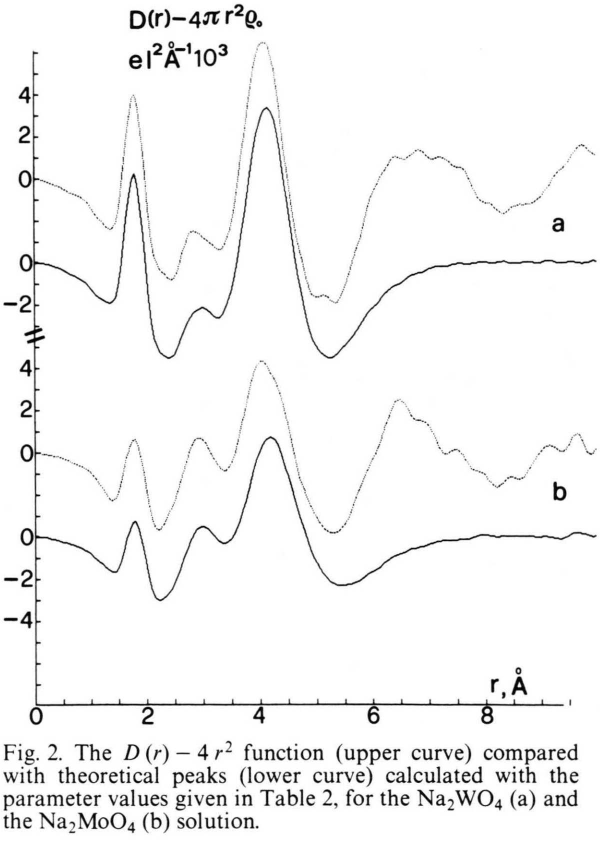

Fig. 2. The $D(r) - 4r^2$ function (upper curve) compared with theoretical peaks (lower curve) calculated with the parameter values given in Table 2, for the Na_2WO_4 (a) and the Na_2MoO_4 (b) solution.

cal peak calculated for 12 (W$-$Mo)$-H_2O$ interactions is in agreement with the short distance part of the observed peak (Figure 3).

If the derived interactions are subtracted from the difference curve the remaining part shows no significant structural features, but has a shape expected for a continuous electron distribution surrounding the complexes at a distance of about 5 Å (Table 2). The assumption of an "isomorphous" substitution is thus confirmed.

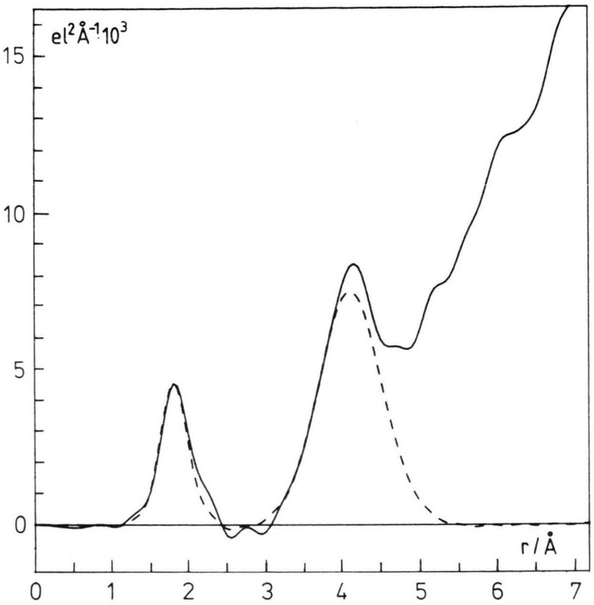

Fig. 3. The difference (solid line) between the $D(r)$ functions for the Na_2WO_4 and the Na_2MoO_4 solutions, compared with the theoretical peaks for the (W$-$Mo)$\ldots$O interactions at 1.786 Å and the (W$-$Mo)$\ldots H_2O$ interactions at 4.06 Å (dashed line) calculated with the parameter values given in Table 2.

Table 2. Parameter values used for the calculation of theoretical curves. Distances, r (Å), rms variations, σ (Å) and frequences factors, N, are given. Estimated standard deviations for some of the values are given within brachets.

		r	σ	N
Intramolecular interactions:				
WO_4^{2-}	W(Mo)$-$O	1.786(8)	0.08(1)	4
MoO_4^{2-}	W(Mo)$-H_2O$	4.06(2)	0.34(3)	12(1)
H_2O(Na)	H_2O-H_2O	2.90	0.4	2.8
	H_2O-H_2O	4.3	0.6	6.8
Intermolecular interactions:				
WO_4^{2-}(MoO_4^{2-})	$R = 5.0$ Å		$B = 0.2$ Å^2	
H_2O(Na)	$R = 4.9$ Å		$B = 0.2$ Å^2	

The parameter values derived from the difference curve can be used for a further analysis of the individual intensity curves. The structural features that remain after subtraction of the derived intra and intermolecular interactions do not differ significantly between the two solutions. In the RDFs they consist of two peaks, one at 2.9 Å and one at 4.3 Å, which correspond approximately to expected H_2O(Na)$-H_2O$ distances in the solutions and which can be well reproduced by two corresponding theoretical peaks (Table 2 and Figure 2).

Theoretical $s \cdot i(s)$ values, calculated with the parameter values derived in this way (Table 2), are compared in Fig. 1 with observed values. The agreement is satisfactory even in the low-angle region. It is interesting to note that, although identical parameter values have been used for the molybdate and tungstate solutions, the low-angle peak at $s \approx 0.8$ Å appears in the theoretical curve for the tungstate solution but not for the molybdate solution, in agreement with the experimental values. This shows that the presence of the low-angle peak in only one of the solutions does not imply a structural difference between them. It results from the different electron densities of MoO_4^{2-} and WO_4^{2-} and their interactions, in this particular case, with long-distance water interactions. The result is of some interest in view of previous discussion of the so called pre-peaks and supports the view that intensity contributions in the low-angle part are much too complex to be ascribed only to one type of interaction. It also indicates that a simple concentration dependence of the peak position is probably fortuitous [22], [23].

Even in the very simplified model used here for the intermolecular interactions the number of parameters is too large to be uniquely determined by the shape of the observed intensity curves in the low-angle region. It seems hardly possible, therefore, to derive a unique model for the intermolecular interaction only on the basis of an analysis of this part of the intensity curves.

Discussion of the results

The tetrahedral structure of the WO_4^{2-} and MoO_4^{2-} ions in solution has been deduced from spectroscopic evidence [20], [24]. The scattering data confirm that the tungstate and the molybdate ions retains their tetrahedral structure in solution with the same bond length as found in crystals. The Mo–O distances in $Na_2MoO_4 \cdot 2\,H_2O$ are 1.752–1.788 Å (av. 1.773 Å) and the W–O distances in $Na_2WO_4 \cdot 2\,H_2O$ are 1.77–1.78 Å (av. 1.77_8 Å); they do not differ significantly from the value of 1.78_6 Å found here in solution. The tetrahedral structure in solution is further confirmed by the close agreement with a theoretical peak calculated for four nearest oxygen neighbors around each metal ion (Figs. 2–3).

A distorted octahedral coordination around W(Mo) is usually found in crystals obtained from acidified tungstate or molybdate solutions but the present results give no indication of any tendency towards a similar coordination in solution.

The presence of a hydration shell around the tetrahedral WO_4^{2-}(MoO_4^{2-}) ions is unambiguously proved by the scattering data (Figure 3). This hydration shell is well defined towards the tetrahedral ion but is rather diffuse towards longer distances. A theoretical peak, calculated for 12 water molecules in the hydration shell at an average distance of 4.06 Å and a rms variation of 0.34 Å, reproduces closely the observed peak (Fig. 3). It seems, therefore, that each oxygen in the XO_4^{2-} group is in contact with, and probably hydrogen bonded to, about three water molecules. In the crystal structures of $Na_2XO_4 \cdot 2\,H_2O$ [9], [10] a similar coordination shell containing sodium ions, water molecules and oxygen atoms, can be distinguished at distances ranging from 3.6 to 4.2 Å. The number of atoms in this shell is 18 and is thus larger than that found in solution. The average X–H_2O distance in the crystals is 3.83 Å, which is shorter than 4.06 Å found in solution. The bond valence analysis of Brown [25]–[27] predicts weak hydrogen bonding for oxoanions in solution. The hydrogen bond lengths, O(XO_4)–O(H_2O), in the crystals are 2.77–2.83 Å. Assuming the same hydrogen bond length in solution the corresponding X–O–H_2O angle can be calculated to be 123 °.

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