Local order in concentrated aqueous solutions of yttrium chloride and bromide

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Abstract. X-ray diffraction patterns of equimolecular concentrated aqueous solutions of yttrium chloride and bromide have been investigated from $s = 0.4$ Å^{-1} up to $s = 15$ Å^{-1}. An assumed coordination of eight water molecules around each yttrium cation, at a distance of 2.36 Å, reproduces the intensity at high s values in agreement with the values obtained by some of the present authors from EXAFS experiments. Narrow interference maxima at $s = (4\pi \sin\theta)/\lambda \simeq 0.9$ Å^{-1} may be interpreted as the existence of a local order of the hydrated yttrium cations surrounded by anions and free water molecules. Structural models with and without close packing of the hydrated cations were built to *simulate* that local order.

1. Introduction

X-ray diffraction methods have produced a great deal of information about the distances between ions and water molecules that are in direct contact in (liquid) aqueous solutions. These results, more or less accurate, have been considered as unequivocally interpreted. The existence of medium-range ion–ion correlations, at distances of the order of 8–10 Å^{-1}, has been discussed by many authors [1–12] (cited by us in previous papers), and has been the subject of some controversy. Prins and Fonteyne [1] observed, at about 1 Å^{-1}, in the x-ray patterns of aqueous solutions of salts of heavy ions an interference maximum at decreasing s values when the concentration of the solute diminishes. These maxima were interpreted as a 'superarrangement' of the heavy ions in the liquid solutions. Later Alves-Marques and others [3, 10–13] demonstrated that similar local correlations between ions may exist even in concentrated aqueous solutions of salts of light ions. A large variety of aqueous solutions of ions where the cation has an electric charge larger, equal or smaller than the charge of the anion was investigated. The suggestion that the condition for existence of a close packing of ions is the different valence of the ions that constitute the solute (the close-packed ions being the ions of higher valence) was proposed in [11]. In this present article our hypothesis is corroborated for equimolecular solutions of yttrium chloride and bromide.

The existence of large hydration shells around the yttrium ions (the ions of higher valence in these solutions), strongly attracted by the anions, suggests the close packing of these large hydrates with the relatively smaller anions and free water molecules being

accommodated in the holes of the close packing. The distances between these close-packed cation hydrates are calculated from a face-centred cubic lattice with similar macroscopic density constituted by the same particles as existing in the solution. As the chloride and bromide ions have approximately the same size when compared with the size of the unit of composition (one hydrated yttrium, three anions and about ten free water molecules) we assume that the structure of both ionic solutions will be alike. The yttrium–yttrium interference maxima at 0.9 $Å^{-1}$ are visible in the patterns of both solutions but less visible with yttrium bromide than with yttrium chloride (figure 1). This phenomenon was already observed by us when we compared x-ray patterns of aluminium chloride and bromide solutions [3], patterns of magnesium chloride and bromide solutions [3] and patterns of solutions of indium nitrate and perchlorate [13]. (The comparison of indium chloride and bromide solutions do not give like results because, in these ionic liquids, anions are included in the first coordination shell of the indium cations [10]). When the electron cloud of the anions is very dense the constructive interferences of the x-rays scattered by the solution are less marked at the $s = (4\pi \sin\theta)/\lambda$ values corresponding to the cation–cation interference. The close-packing structure of yttrium ions does not extend, plausibly, beyond a shell of twelve next neighbours.
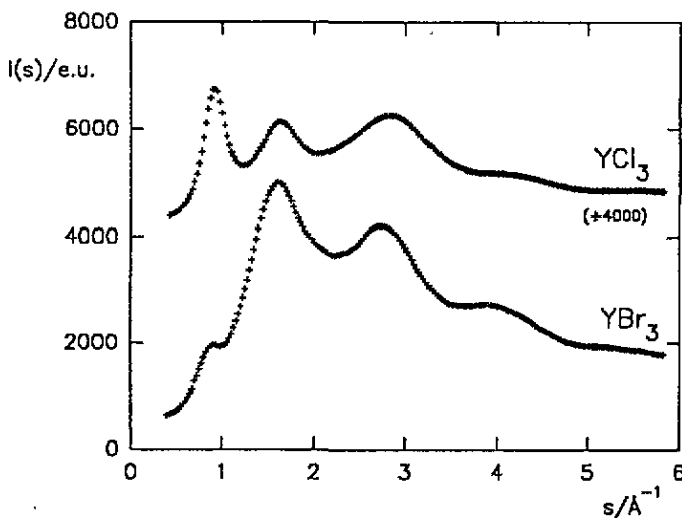

Figure 1. Experimental x-ray intensities for aqueous solutions: 2.73 mol dm^{-3} YCl_3, 2.67 mol dm^{-3} YBr_3.

2. Experimental details

The Warren–Mavel technique [14] was used to obtain the diffraction patterns of YCl_3 and YBr_3 equimolecular aqueous solutions. YCl_3 was obtained from Alfa-Ventron (99.9%), YBr_3 from Johnson Matthey–Alfa (99.99%). Aqueous solutions were prepared from their hydrated salts and the composition was determined by chemical analysis (2.73 mol dm^{-3} for YCl_3, 2.67 mol dm^{-3} for YBr_3).

The experiments were carried out on station 9.1 at Daresbury Laboratory [15–17]. The Warren–Mavel technique was chosen in order to obtain scattered intensities nearly free from Compton scattered intensities as well as from fluorescence radiation emitted by the Y

Table 1. CP and WCP molecular models for 2.73 mol dm^{-3} YCl$_3$ aqueous solution. Radial distances r between the different pairs of particles, r.m.s. fluctuations Δr, number of particles w concerned in each kind of correlation. The distribution of distances is assumed to be trapezoidal [3], r_{th} is the value of the threshold of the continuous (uniform) distribution of random distances and Δr_{th} the corresponding r.m.s. fluctuation. Distances are in Å. The volume of the structural unit containing one cation hydrate is 608 Å^3.

Correlations	r	Δr	CP molecular model			WCP molecular model		
			w	r_{th}	Δr_{th}	w	r_{th}	Δr_{th}
cation–cation	9.5	1.2	12	12	1.2	0	5.3	0.6
cation–water(h)	2.36	0.09	16	12	1.4	16	5.3	0.6
	7.7	0.8	48					
	9.8	1.3	96					
	11	1.3	48					
water(h)–water(h)	2.72	0.10	24	12	1.6	24	5.3	0.6
	3.85	0.16	24			24		
	4.72	0.26	8			8		
	5.7	0.8	24					
	6.3	0.8	24					
	7.8	1.0	96					
	8.3	1.2	96					
	9.5	1.4	96					
	10	1.4	144					
	11	1.4	48					
	12	1.4	192					
	13	1.4	48					
cation–anion	4.76	0.29	12	9.6	1.3	12	6.6	0.8
	8.2	1.2	24					
water(h)–anion	3.17	0.13	24	9.6	1.3	24	6.6	1.0
	5.3	0.6	48			48		
	6.8	0.9	24			24		
	6.1	0.9	24					
	7.4	1.0	48					
	8.6	1.0	48					
	9.6	1.2	48					
	11	1.3	24					
anion–anion	4.76	0.39	12	9.2	1.3	12	6.2	0.9
	6.7	0.9	9					
	8.2	1.2	24					

element that is present in the samples.

The incident radiation, monochromatized by a Si(111) channel-cut crystal had a wavelength about 40 eV above the K absorption edge of Ag (25.520 keV). Data were collected using the fluorescence detection technique of Warren–Mavel with a 30 μm thick Ag foil placed in the scattered beam path. The detector was a Harshaw NaI(Tl) scintillation counter. The solutions were contained in a plate cell between two nitrocellulose windows 30 μm thick held 0.4 mm apart. Transmission geometry was used and symmetric θ–2θ scans were made in 0.2° steps from $s = 0.4$ Å^{-1} up to $s = 20$ Å^{-1}. At each data point constant counts were accumulated in the detector (instead of counting for a fixed time interval) in order to ensure constant counting statistics throughout. Diffraction patterns of the empty cell, in the same conditions of the filled one, were also obtained in order to correct the experimental results. Transmission measurements of the incident beam intensity

Table 2. Structural data of the identical correlations in CP and WCP molecular models for 2.73 mol dm^{-3} YCl$_3$ aqueous solution.

Correlations	r	Δr	w	r_{th}	Δr_{th}
				CP and WCP molecular models	
cation–water(f)	3.00	0.10	3	4.47	0.6
	3.72	0.19	3		
	5.8	0.6	8		
water(h)–water(f)	2.60	0.06	12	3.55	0.6
	3.04	0.19	12		
	3.49	0.26	8		
	4.74	0.5	12		
	5.4	0.8	12		
anion–water(f)	3.36	0.26	12	3.37	0.6
	3.38	0.26	6		
water(f)–water(f)	4.24	0.5	3	3.47	0.6
	4.76	0.5	12		
	4.78	0.5	8		
	5.3	0.8	3		

after crossing the liquid sample were recorded during the exposure to control the thickness of the sample.

The measured intensities were corrected for background, polarization and absorption. The corrected intensities were converted to a scale of electron units using the Krogh-Moe method [18].

The pair correlaton function $g(r)$ was calculated from experimental data by the method of Finbak adopted by Warren [19]:

$$g(r) = 1 + \left(2\pi^2 r \rho_e \sum_{uc} Zj\right)^{-1} \int_0^{s_{max}} s i'(s) e^{-bs^2} \sin(rs) \, ds \qquad (1)$$

where ρ_e is the average scattering density of the sample in electrons Å^{-3}, Zj the atomic numbers and $i'(s)$ the reduced intensity:

$$i'(s) = \left(I_{eu}(s) - \sum_{uc} f_j^2\right)/F^2(s) = i(s)/F^2(s). \qquad (2)$$

$F(s) = \sum_{uc} f_j / \sum_{uc} Zj$ was used as a sharpening factor and in the modification function e^{-bs^2} b was equal to 0.008 Å^2. Different values of s_{max} were tried for the Krogh–Moe method and Fourier inversion. For the data analysis we used s values up to 15 Å^{-1}. This cut-off produces spurious peaks and decreases the spatial resolution, but it is not relevant for distances greater than 2Å.

The structural units, i.e. the units of composition, uc, are always referred to one cation: for the YCl$_3$ solution one Y^{3+}, three Cl$^-$ and 19.4 H$_2$O molecules; for the YBr$_3$ solution, one Y^{3+}, three Br$^-$ and 18.3 H$_2$O molecules. No smoothing of the data was performed.

The coherent scattering factors f_j corrected for anomalous dispersion were obtained from Cromer and Mann [20] for Cl$^-$ and Br$^-$ and from Cromer and Waber [21] for Y^{3+}. For H$_2$O we used those from Hajdu [22]. Incoherent scattered x-ray intensities corrected for the Breit–Dirac recoil factor were calculated from Pálinkás and Radnai [23] for Cl$^-$, and from Hajdu [24] by interpolation for Br$^-$. For Y^{3+} an extrapolation was done from the Y atom of Pálinkás [25] based on Freeman and Watson [26].
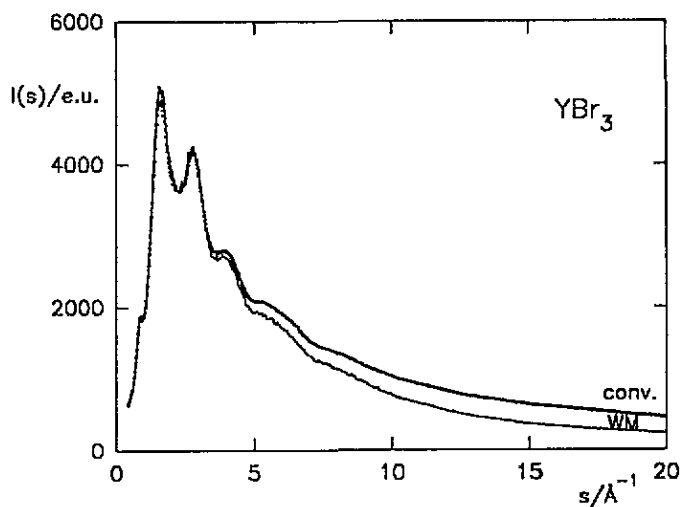
Table 3. CP and WCP molecular models for 2.67 mol dm^{-3} YBr$_3$ aqueous solution. Radial distances r between the different pair of particles, r.m.s. fluctuations Δr, number of particles w concerned in each kind of correlation. The distribution of distances is assumed to be trapezoidal [3], r_{th} is the value of the threshold of the continuous (uniform) distribution of random distances and Δr_{th} the corresponding r.m.s. fluctuation. Distances are in Å. The volume of the structural unit containing one cation hydrate is 622 Å^3.

Correlations	r	Δr	CP molecular model			WCP molecular model		
			w	r_{th}	Δr_{th}	w	r_{th}	Δr_{th}
cation–cation	9.6	1.2	12	12	1.4	0	5.3	0.6
cation–water(h)	2.36	0.08	16	12	1.4	16	5.3	0.6
	7.8	0.8	48					
	10	1.3	96					
	12	1.3	48					
water(h)–water(h)	2.72	0.16	24	12	1.6	24	5.3	0.6
	3.85	0.16	24			24		
	4.72	0.26	8			8		
	5.7	0.8	24					
	6.3	0.8	24					
	7.9	1.0	96					
	8.4	1.2	96					
	9.6	1.4	96					
	10	1.4	144					
	11	1.4	48					
	12	1.4	192					
	14	1.4	48					
cation–anion	4.79	0.32	8	9.6	1.3	8	6.7	0.8
	5.0	0.32	4			4		
	8.3	1.16	24					
water(h)–anion	3.17	0.13	16	9.6	1.3	16	6.7	1.0
	3.48	0.13	8			8		
	5.0	0.39	8			8		
	5.3	0.6	32			32		
	6.0	0.8	8			8		
	6.9	0.9	16			16		
	7.0	0.9	8			8		
	6.1	0.9	24					
	7.5	1.0	48					
	8.6	1.0	48					
	9.6	1.2	48					
	11	1.3	24					
anion–anion	4.26	0.32	2	9.2	1.3	2	5.8	0.8
	4.74	0.45	0.5			0.5		
	4.79	0.45	4			4		
	5.6	0.6	2			2		
	6.8	0.9	9					
	8.3	1.2	24					

For the 2.67 mol dm^{-3} YBr$_3$ aqueous solution some data were collected using the usual detection system with the same incident wavelength as in the fluorescence detection technique. Figure 2 shows plots of the intensities $I_{eu}(s)$ for the data collected with the fluorescence detection, 'Warren–Mavel' (WM) technique, and the usual 'conventional' (conv.) intensities, scaled to match each other in the low-s range values.

Table 4. Structural data of the identical correlations in CP and WCP molecular models for 2.67 mol dm^{-3} YBr$_3$ aqueous solution.

| Correlations | r | Δr | CP and WCP molecular models | | |
			w	r_{th}	Δr_{th}
cation–water(f)	3.39	0.16	2	4.16	0.6
	3.45	0.16	4		
	7.6	1.0	4		
water(h)–water(f)	2.80	0.19	8	3.51	0.6
	2.84	0.19	16		
	5.1	0.6	8		
	5.2	0.6	16		
anion–water(f)	2.60	0.10	1	3.51	0.6
	3.39	0.16	10		
	4.51	0.39	1		
	4.73	0.45	4		
	5.9	0.8	2		
water(f)–water(f)	4.75	0.45	4	3.49	0.6
	4.79	0.45	1		
	4.84	0.45	4		
	6.8	1.0	11		

Figure 2. X-ray diffraction intensities for 2.67 mol dm^{-3} YBr$_3$ aqueous solution: ——, fluorescence detection method, 'Warren–Mavel' (WM); ······, conventional detection method (conv.).

3. Results and interpretation

Previous experimental Raman results [27] permit us to assume identical yttrium hydrate structures in both solutions. In both molecular models used to interpret the data for the YCl$_3$ and YBr$_3$ the value of 2.36 ± 0.02 Å for the Y–OH$_2$ distance in hydrates with eight water molecules fits very well with our experimental $g(r)$ functions (figure 3). This value (obtained from our present data) is slightly greater than 2.33 Å (or 2.34 Å) previously

obtained by EXAFS [27], but this difference is typical of the discrepancies obtained from using EXAFS and x-ray diffraction in liquids. By anomalous x-ray scattering Matsubara and coworkers [28] obtained for YCl_3 solutions results that approach the results given in [27].
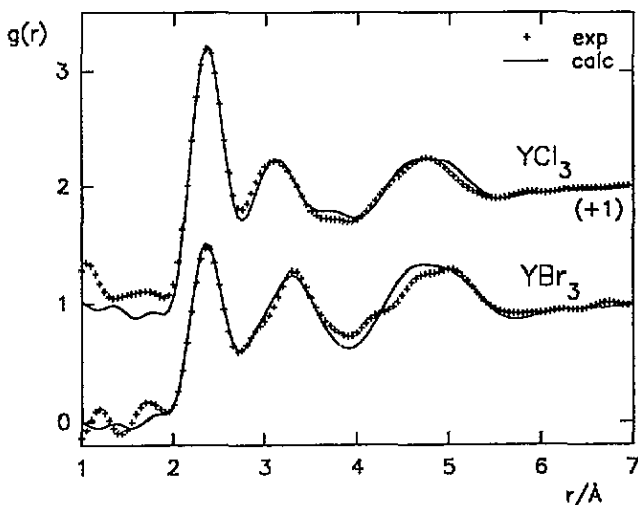

Figure 3. Experimental (+++) and calculated (——) pair correlation function $g(r)$ for 2.73 mol dm^{-3} YCl$_3$ and 2.67 mol dm^{-3} YBr$_3$ aqueous solutions.
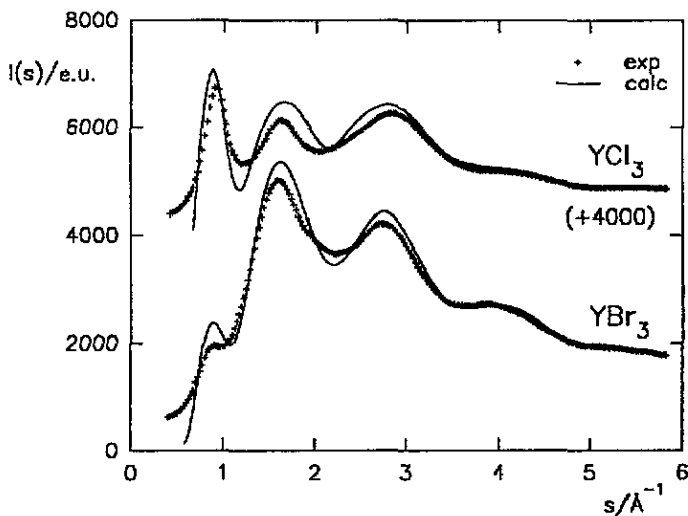

Figure 4. Experimental (+++) and calculated (——) intensity $I_{eu}(s)$ for 2.73 mol dm^{-3} YCl$_3$ and 2.67 mol dm^{-3} YBr$_3$ aqueous solutions.

In order to interpret the narrow interference maxima at $s = 0.9$ Å^{-1} (figure 1) we assume the existence of positional correlations between close-packed hydrated cations with some fluctuations around the characteristic face-centred lattice distance between nearest neighbours. In this molecular model, with 'close packing' (CP) only 12 neighbours are considered to be at that distance from the central yttrium, the others being random uniformly

distributed [3, 10–13, 29]. Without considering any definite hydration of the anions they are approximately located at the midpoints of the cation–cation distances. The free water molecules, about 11, are presumed to be randomly distributed over the vacant sites.

Another molecular model was built assuming only short-range positional correlations between the pairs of ions and molecules, without 'close packing' (WCP) (see tables 1–4).

An appropriate mean of these two models for each yttrium solution has been made (75% CP, 25% WCP for the YCl₃ solution and 50% CP, 50% WCP for the YBr₃ solution). The profiles of the calculated diffracted intensities are compared with the experimental ones (figure 4). Changing contributions up to ±10% of those values does not modify significantly the obtained agreement. A similar comparison has been made using the structure function $si(s)$ (figure 5). Some differences between calculated and experimental values are apparent, but the relative intensities of the main peaks and their positions are well reproduced.
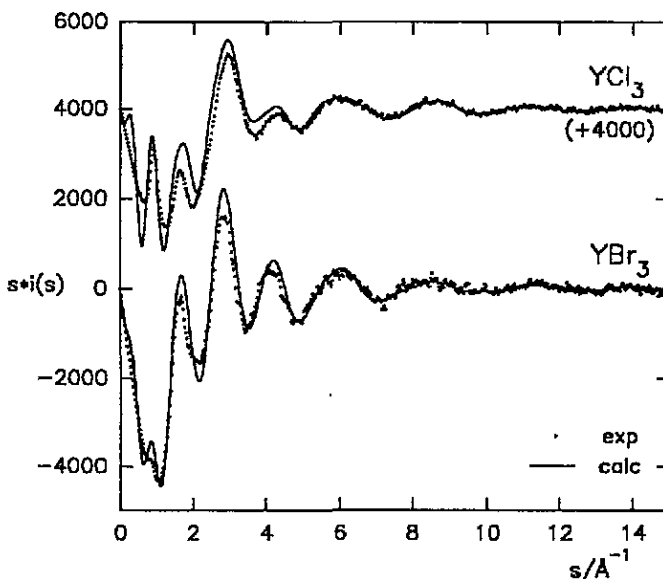

Figure 5. Experimental (· · · · · ·) and calculated (——) structure function $si(s)$ for 2.73 mol dm⁻³ YCl₃ and 2.67 mol dm⁻³ YBr₃ aqueous solutions.

The pair correlation function $g(r)$ obtained by Fourier inversion of the calculated intensities for both yttrium solutions fits very well in the short range of r values and nicely up to 7 Å (figure 3).

Both molecular models (CP and WCP) are able to describe the diffraction patterns for s greater than about 1 Å⁻¹, as well as the $g(r)$ functions up to 7 Å, but our hypothesis of a 'local' close packing of ions of greater valence (the hydrated yttrium cations in this case) seems necessary to describe the narrow interference maxima observed at 0.9 Å⁻¹ (figure 6).

The existence of these tentative models for the investigated liquids does not mean that the arrangements of the water molecules and ions are exactly the proposed ones but gives a degree of plausibility to our hypothesis of a 'liquid-type close-packing' of the ions of higher valence, the yttrium ions, in these ionic solutions.

Tables 1–4 give the value of the mutual distance of the paired particles, the root mean square of each distance, the weight of the correlation, the value of the threshold of the corresponding continuous (uniform) distribution of random distances of each type of correlation and the fluctuations assumed for these distances. In these molecular models
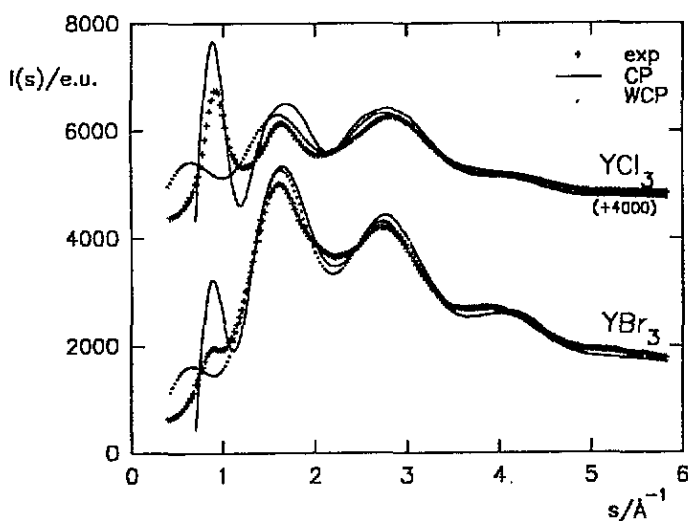
Figure 6. Calculated intensities using a molecular model with local close packing CP (——) and without close packing WCP (······) compared with experimental ones (+++) for 2.73 mol dm^{-3} YCl$_3$ and 2.67 mol dm^{-3} YBr$_3$ aqueous solutions.

the intensities calculated from uniform distributions do not contribute significantly to the narrow maxima at $s \simeq 0.9$ Å^{-1}.

4. Conclusion

The observation of (relatively) narrow maxima of x-ray interferences in the diffraction patterns of concentrated aqueous solutions of yttrium chloride and bromide for 0.7 Å$^{-1} <$ $s < 2.5$ Å^{-1} is well interpreted by local molecular models built up from a 'quasi-close packing' of hydrated yttrium ions. These experiments corroborate, once more, that a (statistical) order extending up to ~ 10 Å around the ions of higher electric charge is plausible in concentrated aqueous solutions of salts constituted by ions of different valence.

Acknowledgments

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