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Molecular Weights of Cyclic and Hollow Clusters Measured by DOSY NMR Spectroscopy

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Abstract: The Stokes−Einstein expression of the diffusion coefficient as a function of the hydrodynamic radius of the diffusing object does not explicitly carry the mass dependency of the object. It is possible to correlate the translational self-diffusion coefficients D with the molecular weight M for an ensemble of cyclic or hollow clusters ranging from about 200 to 30 000 $g \cdot mol^{-1}$. From this correlation, the mass of a cluster can be deduced from its diffusion coefficient. Consistency of diffusion as a power law of mass and Stokes−Einstein formulation is completely fulfilled with the selected compounds of this contribution.

Introduction

Einstein, in his series of papers on the study of the Brownian motion, proposed to use the diffusion coefficient as a way to access the size of molecules.[1] Translational self-diffusion can currently be measured by Diffusion Ordered Spectroscopy (DOSY).[2] Obtained through pulse field gradient (PFG) NMR experiments, such diffusion coefficients are measured with high accuracy. In recent years, measurements of diffusion based on NMR, because they split the chemical shift dimension and the diffusion dimension, provided a large range of applications for mixture analysis,[3−5] polymer analysis,[6,7] ion pairing,[8,9] or supramolecular chemistry.[10−12]

In this study, Poly-Oxo-Metalates (POMs) clusters have been considered as potential candidates to evaluate the diffusion to mass relation. For a long time, POMs were strictly inorganic objects. Presently, many organic−inorganic units appear in polyanions chemistry or building blocks of Metal Organic Frameworks (MOFs). In particular, the Versailles POMs group has produced a large variety of host−guest cyclic Oxo-Thio-Molybdenum compounds including organic ligands that are amenable to ^{1}H DOSY.[13−20] In order to investigate the nature of the relation between D and M with well-defined objects, we have first considered a series of oxothiomolybdenum rings self-assembled around polycarboxylate ligands ranging from Mo_{10}

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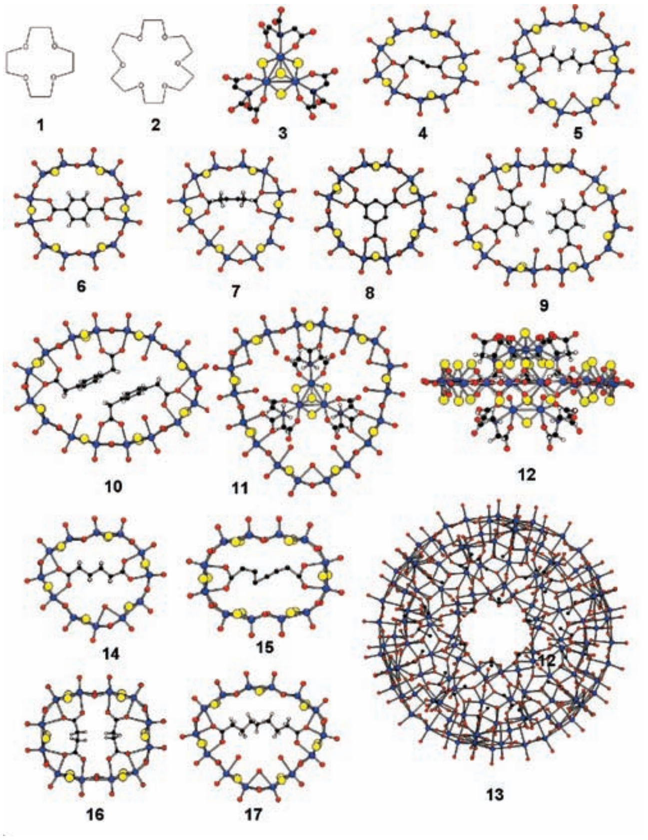

Figure 1. Structural representations of compounds used in the present study.

to Mo_{23} nuclearities.[13−20] In addition to this series of compounds, we selected two crown-ethers for their low molecular weights, i.e., 12-Crown-4 and 18-Crown-6, a complex built around the incomplete cubane core, Mo_3S_4[21,22] chosen to give an intermediate value between crown ethers and Mo-rings and one of Müller's "giant" compounds, namely $(NH_4)_{42}[Mo_{72}Mo_{60}O_{372}(H_2O)_{72}(CH_3COO)_{30}]$,300•$H_2O$,10•$CH_3COONH_4$, $[Mo_{132}]$,[23] a hollow icosahedral polyanion, with acetate ligands inside the cavity, for extending the upper limit of molecular weights.

Considering these compounds depicted in Figure 1, which possess comparable shapes, a wide range of molecular weights from about 200 to 30 000 $g \cdot mol^{-1}$ can be covered, spanning a little more than 2 orders of magnitude.

Besides, all these objects share to some approximation the same feature, they do not differ too much in density and interactions with the solvent and they do not seem to exhibit a microscopic constant density along a radius from center to the object border (Figure 1). Moreover, to a first approximation, for cyclic as well as hollow quasi-spherical objects, all of them are under fast rotational tumbling, and may therefore be considered as dynamical hollow spheres. It would be of interest to know if the family of compounds selected on a similar geometrical basis would share the same behavior toward their diffusion to mass relation, governed by a common power law.

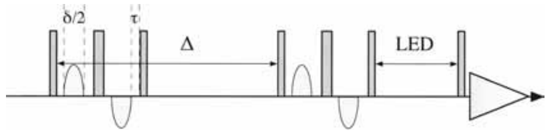

Figure 2. Pulse sequence BiPolar—Pulse Field Gradient—STimulated Echo—Longitudinal Eddy current Delay.

Experimental Section

Chemicals. Crown ethers 12-crown-4 and 18-crown-6 and ligands nitrilotriacetate (abbreviated nta^{3-}), glutarate (glu^{2-}), trans,trans-muconate ($Muco^{2-}$), terephtalate ($TerP^{2-}$), tetramethylterephtalate (TMT^{2-}), trimesate ($Trim^{3-}$), isophtalate ($IsoP^{2-}$), phenylenediacetate (PDA^{2-}), adipate ($Adip^{2-}$), suberate (Sub^{2-}), and succinate ($Succ^{2-}$) in acidic forms were purchased from Acros or Aldrich chemicals and used without further purification.

Syntheses. Compounds $Na_2[Mo_3S_4(Hnta)_3].5H_2O$ (**3**), $Cs_2[Mo_{10}O_{10}S_{10}(OH)_{10}(glu)].11H_2O$ (**4**), $Rb_2[Mo_{12}O_{12}S_{12}(OH)_{12}(H_2O)(Muco)].21H_2O$ (**5**), $Cs_2[Mo_{12}O_{12}S_{12}(OH)_{12}(TerP)].12DMF\ 0.2H_2O$ (**6**), $(NMe_4)_2[Mo_{12}O_{12}S_{12}(OH)_{12}(H_2O)_3(TMT)].17H_2O$ (**7**), $K_3[Mo_{12}O_{12}S_{12}(OH)_{12}\ (Trim)].22H_2O$ (**8**), $Rb_4[Mo_{16}O_{16}S_{16}(OH)_{16}(H_2O)_2(IsoP)_2].28H_2O$ (**9**), $Li_4[Mo_{16}O_{16}S_{16}\ (OH)_{16}(H_2O)_4(PDA)_2].20H_2O$ (**10**), $Cs_5[Mo_{18}O_{18}S_{18}(OH)_{18}(H_2O)_9(Mo_3S_4(nta)_3)].36H_2O$ (**11**), $K_9[Mo_{18}O_{18}S_{18}(OH)_{18}(H_2O)_9(Mo_3S_4(nta)_3)][Mo_2O_2S_2(nta)_2].36H_2O$ (**12**), $(NH_4)_{42}[Mo_{132}O_{372}(H_2O)_{72}(CH_3COO)_{30}]$,$300H_2O$,$10CH_3COONH_4$, (**13**), $Rb_2[Mo_{12}O_{12}S_{12}(OH)_{12}(H_2O)\ (Adip)].11H_2O$ (**14**), $K_2[Mo_{12}O_{12}S_{12}(OH)_{12}(Sub)].28H_2O$ (**15**), $Rb_3(NMe_4)[Mo_{12}O_{12}S_{12}(OH)_{12}(H_2O)_2(Succ)_2].11H_2O$ (**16**), and $(NMe_4)_2[Mo_{14}O_{14}S_{14}(OH)_{14}(H_2O)_3(Azel)].29H_2O$ (**17**) used in the present study were prepared as described in the literature[13,15−20] and checked by routine methods (FT-IR, EDX, TGA, NMR).

DOSY NMR Experiments. The spectra were recorded on a Bruker avance 400 MHz using a BBI Bruker 5 mm gradient probe, which allows to use field gradients up to about 60 $G \cdot cm^{-1}$. The temperature was regulated at 298 K, and the NMR tube was not spun. The diffusion NMR experiments were performed with a pulsed-gradient stimulated echo (LED-PFGSTE) sequence, using bipolar gradient.[24] DOSY spectra were generated by using the program GIFA software,[25] the DOSY Module of NMRNotebook from NMRTEC,[26] using inverse Laplace Transform[27] driven by maximum entropy, to build the diffusion dimension.

The samples were prepared by dissolving the solid samples to deuterated water with an average concentration of about 5×10^{-3} molar. DOSY experiments have been carried out in water (D_2O) at 298 K and the diffusion coefficients have been measured on protons of the organic moieties for each of these compounds. The pulse sequence used for the present study is presented in Figure 2.

Sequence delays were $\Delta = 200$ ms (diffusion delay), $\tau = 1.2$ ms (after gradient recovery delay), and Te = 3 ms (LED recovery delay). For each data set, 2048 complex points were collected for each 35 experiments in which the gradient strength was exponentially incremented from 1 to 47.5 Gcm^{-1}. The gradient duration $\delta/2$ was adjusted to observe a near complete signal loss at 47.5 Gcm^{-1}. Typically, the $\delta/2$ delay was chosen in the 0.7−1.5 ms range. A 1 s recycle delay was used between scans for all data shown. The number of scan was adapted to the sample, but never less than eight scans. The total experiment time, including a 4 min temperature equilibration step, ranged from 15 min to several hours

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Table 1. Mass and Diffusion Coefficient of All the Compounds of This Study in D_2O[a]

compounds[b]	ref	MM_{anion}[c] (g/mol)	D ($\mu m^2.s^{-1}$) in D_2O	V_{uc}[d] (A^3)	Z[d]	V_{uc}/Z (A^3)[f]	M_{uc}/Z (g/mol)	V anion (A^3)	R_{Sphere}[f] (nm)	R_H[f] (nm)[f]
12-crown-4, **1**	36	176.2	782	223.33	2	111.67	176.2	151.12	0.39	0.32
18-crown-6, **2**	37	264.3	623	979.82	2	489.91	264.3	226.67	0.45	0.40
$[Mo_3S_4(Hnta)_3]^{2-}$, **3**	22,23	983.5	389	2112.50	2	1056.25	1258.7	842.54	0.69	0.63
$[Mo_{10}Glu]^{2-}$, **4**	13	1740.2	395	5512.60	4	1378.15	2204.2	1 492.45	0.84	0.62
$[Mo_{12}Muco]^{2-}$, **5**	18	2090.3	342	3584.90	2	1792.45	2639.0	1 792.71	0.89	0.72
$[Mo_{12}TerP]^{2-}$, **6**	17	2096.3	358	2865.10	1	2865.10	3275.2	1 813.29	0.89	0.69
$[Mo_{12}TMT]^{2-}$, **7**	18	2188.4	335	4253.00	2	2126.50	2642.5	1 876.84	0.91	0.74
$[Mo_{12}Trim]^{3-}$, **8**	20	2139.3	315	6645.00	2	3322.50	3310.9	1 834.73	0.90	0.78
$[Mo_{16}(IsoP)_2]^{4-}$, **9**	17	2940.5	295	3112.20	1	3112.20	3696.4	2 521.87	1.00	0.84
$[Mo_{16}(PDA)_2]^{4-}$, **10**	17	3032.6	279	5881.40	2	2940.70	4104.6	2 600.86	1.01	0.88
$[Mo_{18}(Mo_3S_4(nta)_3)]^{5-}$, **11**[d]	19	4040.8	259							0.95
$\{[Mo_{18}(Mo_3S_4(nta)_3)][Mo_2O_2S_2(nta)_2]\}^{9-}$, **12**	19	4836.0	240	9665.80	2	4832.90	5705.4	4 035.16	1.17	1.03
$[Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-}$, **13**	23	21684.4	144	97 702.10	4	24425.53	28618.0	18 597.26	1.71	1.71
$[Mo_{12}Adip]^{2-}$, **14**[e]	16	2094.3	454	8471.50	4	2117.88	2765.0	1 796.14		
$[Mo_{12}Sub]^{2-}$, **15**[e]	16	2104.3	530	3924.80	2	1962.40	2606.3	1 804.72		
$[Mo_{12}(Succ)_2]^{4-}$, **16**[e]	15	2164.3	547	4401.40	2	2200.70	2693.0	1 918.01		
$[Mo_{14}Azel]^{2-}$, **17**[e]	16	2494.5	457	10719.80	4	2679.95	3022.5	2 138.94		

[a] The ligands abbreviations used for naming the compounds are as follows: nitrilotriacetate (nta^{3-}), glutarate (glu^{2-}), muconate ($Muco^{2-}$), terephtalate ($TerP^{2-}$), tetramethylterephtalate (TMT^{2-}), trimesate ($Trim^{3-}$), isophtalate ($IsoP^{2-}$), phenylenediacetate (PDA^{2-}), adipate ($Adip^{2-}$), suberate (Sub^{2-}), succinate ($Succ^{2-}$), and azelaate ($Azel^{2-}$). [b] The complete formulas of these salts are given in the Experimental Section. [c] Molecular masses of anions correspond to the exact formula of the unsolvated compounds obtained in the solid state by X-ray-diffraction studies. [d] Compound **11** had not its structure determined explaining the lack of crystalline parameters. [e] Compounds **14**−**17** exhibit a chemical exchange of organic species between solution and cluster no size or hydrodynamic radius can be extracted. [f] UC stands for Unit Cell and R_H for hydrodynamic radius.

per sample. For each data set, the spectral axis was processed with sine-bell, and Fourier transform was applied in order to obtain 1024 real points. A spline baseline correction was finally applied. The columns (axis of varying gradient) of this data set were then processed for inverse Laplace transform using the Inverse Laplace technique[27] using the Gifa software.[25] The DOSY reconstruction was realized with 512 points in the diffusion dimension and 2000 MaxEnt iterations.

Results

Table 1 contains the data concerning their crystallographic state before being dissolved and their diffusion coefficient measured in water. As expected, from compound **1** to complex **13**, the self-diffusion coefficient decreases while the molecular weight increases. From the values of Table 1, we can analyze the data (Figure 3) with the function given by eq 4. It exhibits a power law having a d_F value of 3.00 ± 0.02. A usual representation is to plot the variation of $\log D$ versus $\log M$, both entities being experimental measurements, without any model. As shown in the inset of the Figure 3, the relation of $\log D$ vs $\log M$ is linear over 2.1 decades with a slope of −0.338, i.e., a d_F value of 2.96, very close but not identical to the direct fit with eq 4.

Interestingly, for the compounds **14**−**17** (not shown in Figure 3) the values of D appear significantly higher than those of the other compounds of similar molecular weight. In previous works,[15,16] we have evidenced that for these four complexes, a partial decoordination of the encapsulated ligand followed by an exchange process between coordinated and uncoordinated ligands. Therefore, an average D value between free and encapsulated ligand is obtained for these compounds. When meeting such an experimental limitation, one must exclude such POMs with exchanging organic species from the set of selected objects used for assessing a general behavior between diffusion and mass. They obviously can be characterized at a further stage of refinement, for studying interactions between molecules and solvent.

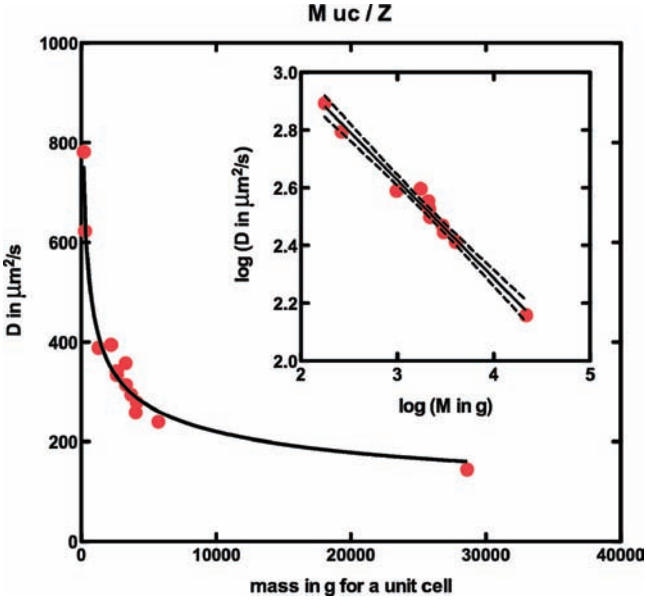

Figure 3. Correlation between diffusion and mass of clusters. Red dots represent ring or hollow polyanions without exchange (**1** to **13**). Inset: representation of the power law between diffusion and mass of the clusters, with 95% interval plot as dotted lines.

Another noticeable observation is the diffusion of $[Mo_{132}]$. A discussion arose for this compound about its possible instability in solution by an ultracentrifugation study.[28] No such evidence occurs during the DOSY experiment. No degradation of the compound is observed. A unique diffusion coefficient is measured for the $[Mo_{132}]$ cluster compared to what is claimed from ultracentrifugation, probably due to the difference in concentration range, and or to the fact that the ultracentrifugation methods may exhibit a concentration gradient while DOSY works under equilibrium conditions. The DOSY experiments were run at much higher concentration than that of the ultracentrifugation measurements. One additional interesting case is compound **12**. The latter is constituted from three

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molybdenum components: an Mo_{18} ring self-assembled around the complex $[Mo_3S_4(nta)_3]^{5-}$ (**3**) to give the compound **11**, which interacts through H-bonds with an additional $[Mo_2O_2S_2(nta)_2]^{4-}$ complex in the solid state leading to **12**.[19] Surprisingly, this supramolecular assembly is maintained in solution since all the three components are traveling together and lead to a unique diffusion coefficient. The shape of the undissociated clusters aggregate is probably coarsely spherical, and do correlate as the others clusters.

Discussion

The Einstein relation of diffusion is given by eq 1,

$$D = \frac{kT}{\gamma} \tag{1}$$

with γ being the drag factor. For a sphere of diameter R_H, γ is equal to $6\pi\eta R_H$. The Stokes–Einstein relation describes the diffusion coefficient as follows:

$$D = \frac{kT}{6\pi\eta R_H} \tag{2}$$

where k is the Boltzmann constant, T the temperature, η the solvent viscosity, and R_H the hydrodynamic radius. It is important to recall that this relation was established[1] by assuming that a spherical particle of colloidal dimension, much larger than the solvent dimension, moves in a fluid continuum. It is therefore more convenient in such conditions to measure or estimate the size of the spherical particles rather than their mass. This equation defines the hydrodynamic radius R_H of the diffusing particles. The hydrodynamic radius R_H is therefore the radius of an equivalent sphere that would diffuse with the same diffusion coefficient under the same conditions as the diffusing particle. It is not an intrinsic characteristic of each molecule. When considering molecular objects, there is no general relationship between the actual size, and the hydrodynamic radius, unless the shapes of the molecules considered are of the same type. For a spherical particle, the hydrodynamic radius R_H may be calculated by using eq 3, where M is the molecular weight, ρ the density of the species, and N_A is Avogadro's number, with the hydrodynamic radius being the geometrical radius of the sphere.

$$R_H = \sqrt[3]{\frac{3M}{4\pi\rho N_A}} \tag{3}$$

However, departures exist between the spherical approximation of a molecule and the actual shape of the objects. Modifications of the Stokes–Einstein formula intend to take into account the size and the shape of the molecule, or in the case of polymers their dimensionality.[7,10] Among the main issues to elucidate in this domain, the relation between the diffusion and the molecular mass has been recently reinvestigated.[7] The relation between D and M for molecules belonging to a same class of objects, i.e., with an approximate constancy in density, about the same shape provides a relation[7] (4) for that given class of molecules:

$$M \approx (C_r/D_r)^{d_F} \tag{4}$$

with d_F being the fractal dimension of the molecular objects. The case of linear polymers was expected to deviate definitely from a spherical approximation, but even small organic molecules do so, as demonstrated in the work of Crutchfield et al.[29] Diffusion follows the same trend for small molecules than for polymers, a relation between diffusion and mass, having a fractal dimension d_F of 1.8. The dimension d_F was found[7] to range from 2.56 to 1.41 for the molecular objects previously studied, but the study did not contain any objects of spheroidal shape, except maybe the globular protein, for which a d_F of 2.56 is found. When one tries to take into account the departure from sphericity with a shape factor that corrects the Stokes–Einstein relation, this additional shape factor cannot take into account the effect of the dimensionality d_F of the objects as a power law.[30] Such correction factors, as they do not change the exponent of the power law of the diffusion relation to mass, will lead to errors in comparing the hydrodynamical radii of arbitrarily shaped objects. Finally, the anisotropy of the objects diffusing leads to the anisotropy of the interactions between solute and solvent. It is the reason why the diffusion to viscosity dependency becomes a power law in case of a spherical solute and an anisotropic solvent.[31]

As the masses of the clusters correlate with the diffusion coefficient, we may now try to evaluate their sizes. By correlating the unit cell volume to its mass for all of the compounds selected, a linear correlation is found with a common average density of 1.17 ± 0.01, with a correlation factor of 0.998. It is therefore possible to estimate the volume of the clusters diffusing as follows

$$V_{cluster} = V_{au}\frac{M_{cluster}}{M_{au}} \tag{5}$$

where V_{au} and M_{au} are the volume and the mass of the asymmetric unit. As the relation between mass and volume for these clusters is linear, the power law exponent of 3 between the diffusion coefficient and mass will apply to volumes as well. Now the volume estimated by eq 5 can be analyzed as an equivalent sphere of radius R_{Sphere} defined by the following

$$R_{Sphere} = \sqrt[3]{\frac{3V_{cluster}}{4\pi}} \tag{6}$$

$$R_{Sphere} = \sqrt[3]{\frac{3M_{au}}{4\rho f_{cluster}\pi N_A}} \tag{7}$$

where $f_{cluster}$ is the mass fraction of the cluster in the asymmetric unit. As the mass fraction of the cluster to the mass of the asymmetric unit, is linear with a slope of 0.758 ± 0.009 with a correlation factor of 0.999, for the selected family of compounds, a knowledge of the unit cell volume of the crystal and of the number of formula unit in the unit cell is enough to determine the radius of the equivalent sphere of the cluster. The mass that is not in the cluster contains cations and crystallization water. As this mass fraction seems not to vary much with the nature of the counter cations, one may infer that the density of the cation-water counteranion ensemble does not change much in the crystals.

Until now, only the Einstein relation (eq 1), without any assumption on the sphericity of the clusters has been made, and it is the diffusion to the mass as a power law that has been

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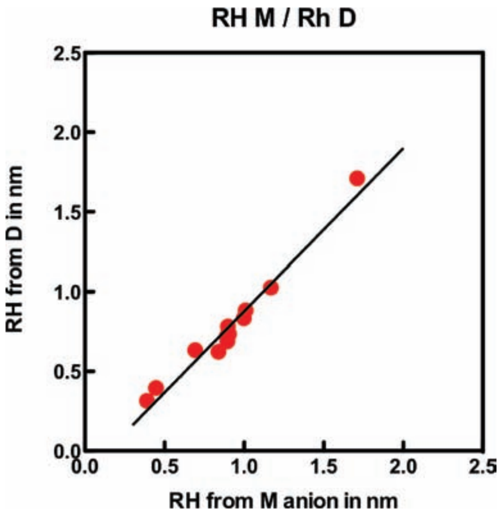

Figure 4. Correlation between the estimated radii of clusters from their crystallographic description (see text) and the diffusion deduced radii of clusters with the hydrodynamic diameter from the Power law and Stokes−Einstein relation. The slope is 1.021 ± 0.062 with a correlation coefficient of 0.965.

used. However, if we want to further re-evaluate the spherical approximation of the Stokes−Einstein hydrodynamic radius for diffusion, in the case of this selection, we need to correlate the estimated R_{Sphere} to R_{H}. Among all of the clusters, [Mo_{132}] species is the one leading to very good agreement between the estimated R_{Sphere}, 1.71 nm, and a radius equal to the geometrical atom-to-atom of 1.45 nm augmented by one water molecule diameter of 0.28 nm, i.e., 1.73 nm. [Mo_{132}] is also the compound closest to a spherical shape. It can therefore be used as a reference for the estimated size. Using the value of 1.71 nm for [Mo_{132}] size leads to size determination for all other clusters using the diffusion coefficients. The relation between the radius from diffusivity and the radius estimated from masses leads to a linear correlation (Figure 4) of slope 1.02 with a correlation factor of 0.965. The quality of the correlation between estimated sizes by diffusion and by volume, indicates that the average density of the clusters is equal to the density of the crystal. The fact that hollow clusters are considered does not impact either the dimensionality of 3 for the power law of diffusion with mass, or their approximation as homogeneous spheres of average density. The latter observation most probably means that the inner volume of the supposedly hollow objects is not empty but filled with the organic linkers and by the solvent.

Through this correlation, a method emerges to estimate the equivalent geometrical sphere from the DOSY results, using [Mo_{132}] as a reference. The parameters necessary to consider that a cluster belongs to the category selected here are to have about the same density as the other clusters and to postulate little variation of the cluster mass fraction relative to the asymmetric unit mass.

[Mo_{132}] acts therefore as a good size reference for DOSY. Actually, it has a quite large mass, and lighter molecules would be accurately determined from [Mo_{132}], as well as massive biological objects. If one wishes to establish a general scale for sizes of spherical objects, as [Mo_{132}] is an icosahedral object, it is almost a spherical object. Almost all of the cyclic POM fall on the correlation, indicating that they are quite well approximated by spheres.

A second interesting consequence of this reinvestigation is that, due to linearity between the volume fraction of the clusters with the volume of the unit cell, the correlation between the asymmetric unit volume and diffusion allows estimation from a solution measurement, the volume of the crystallographic formula unit. With the volume of the unit cell determined by X-ray Diffraction on a polycrystalline powder, one may estimate from the DOSY experiment, *Z*, the number of formula units per unit cell.

In summary, POM clusters are good reference samples for a calibration of the DOSY experiment diffusion coefficient as a function of the mass of the objects. The Stokes−Einstein relation between the diffusion coefficient and the hydrodynamic radius was established for spherical particles of colloidal dimension. The relation obtained in this study is fully consistent for the molecular objects measured with this relation, as they can be approximated as spheres, allowing therefore extension of this relation toward rings or hollow spheres of molecular size using, however, a proper size reference, [Mo_{132}]. Though this conclusion may seem obvious to many, because it corresponds to the usual approximation made when using Stokes−Einstein relation, it has been previously clearly demonstrated that the relation between diffusion and mass follows a power law with fractal exponents for objects that depart from a sphere. For cyclic or hollow objects, having a spheroidal shape, the power exponent for such a family of objects has a value of 3.0, a classical three-dimensional object description, and the hollow character of these clusters does not affect their size estimation.

The two approaches incarnated into the Stokes−Einstein relation and a diffusion coefficient being a power law of the mass of the diffusing objects as described in eq 4 are two different descriptions of diffusing objects. The theoretical background taking into account a convergence of the two descriptions has already been described by the Green−Kubo and Einstein−Helfand relations and comprehensively reviewed by Viscardy and Gaspard.[32−35] However, for objects fulfilling closely enough the condition of sphericity for the shape of the objects and isotropicity for the solvent, both descriptions converge to the Einsteinian formulation of 1905. The diffusion as a power law of mass indicates a deeper aspect of diffusion. Diffusion is intrinsically an interaction process between a solute and a solvent. The dimensionality related to the exponent reflects the geometry of the interactions between solute and solvent and not only the geometry of the solute. When taking into account this aspect, one can select objects and solvents that can lead to a fully isotropic interaction, therefore a power of 3 can be obtained, leading to an identical expression of Stokes−Einstein relation. But in contrast to many assumed cases, the purely molecular "isotropic" cases are rare, not the rule. The selection of clusters in this study therefore constitutes a good set of reference clusters to validate the convergence between diffusion with dimensionality of solute/solvent interaction and the Stokes−Einstein assumption of isotropicity. No such series of molecular clusters has yet properly fulfilled such conditions so closely.[36,37]

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Another point is that if exchange takes place in some host−guest systems, like compound **14-17**, then there is also modulation of *D*, and departure from the proper correlation. A third point is that even in the absence of a crystallographic structure determination, the mass of a cyclic or hollow POM can be estimated by its diffusion in D_2O, a very efficient way to simplify the assignment of POMs in solution.

Conclusions

One can reliably access the mass of an object in water for quasi-spherical objects in an isotropic solvent from the diffusion coefficient, and with proper referencing care, its size. Taking into account the large range of cyclic inorganic clusters of the literature or the giant Mo clusters of Müller's type, we are sure that a direct application of DOSY method can constitute a very efficient and powerful tool for the characterization of these systems in solution, allowing the determination of their molecular weights with a good accuracy. This method appears particularly interesting for assignments of NMR spectrum of POMs mixtures. Moreover, it represents a good complement or alternative to ultracentrifugation studies of such clusters.

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