SAXS Investigations of Very Large Polyoxomolybdate Clusters in Solution

A. Knöchel[1], A. Müller[2], P. K. Pranzas[1, 3], C. Serain[2], R. Willumeit[3] and R. Gehrke[4]

[1]Institut für Anorg. und Angew. Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg
[2]Institut für Anorg. Chemie, Universität Bielefeld, Postfach 100 153, D-33501 Bielefeld
[3]GKSS Forschungszentrum, Max-Planck-Straße, D-21502 Geesthacht
[4]HASYLAB, Notkestraße 85, D-22603 Hamburg

Polyoxometalates (POM) build very large clusters with desirable or predictable properties relevant for materials science. In 1995 a "big wheel" shaped POM with a diameter of approx. 3,4 nm and more than 700 atoms - for a long time the largest inorganic compound that was characterized with single-crystal X-ray structure analysis - was published [1]. POM assemblies, in which the large rings show chain-like arrangements, have also been synthesized [2, 3]. The structures of the above mentioned compounds were solved by X-ray crystallographic analysis, whereas their behaviour in solution is unknown. In order to understand the aggregation processes small-angle X-ray scattering (SAXS) experiments were performed at the SAXS instrument POLYP at beamline A2 of HASYLAB. Freshly prepared and 36 hours aged solutions of the POM $Na_{15}[Mo_{144}O_{409}(OH)_{28}(H_2O)_{56}]$ x ca. 250 H_2O (1) with concentrations of 5 g/L in methanol and water were measured in vacuum-tight measuring cells with Kapton windows and a sample thickness of 1 mm. Distances between the sample and the one-dimensional position-sensitive detector of 0.49 and 1.91 m were chosen. The used measuring times were about 20 minutes.

From the resulting scattering curves radii of gyration R_g were calculated. For the freshly prepared methanolic POM (1) solution a R_g value of 1.726 ± 0.0028 nm was calculated and for the corresponding POM solution in water a R_g value of 1.729 ± 0.0061 nm. For the 36 hours aged POM solution in methanol a radius of gyration of 7.54 ± 0.026 nm was obtained. These values indicate that the sizes of the POM clusters are identical in methanol and water and that an aging process with the formation of larger structures takes place in the solution. Model calculations showed that there is only a slight deviation in the shape of the POM clusters from that of a sphere. With the help of *Gnom* [4], an indirect transform program for small-angle scattering data processing, distance distributions were calculated from the scattering curves. In both solvents, H_2O and methanol, an equal size distribution was obtained, which is shown in figure 1 for the methanolic solution.

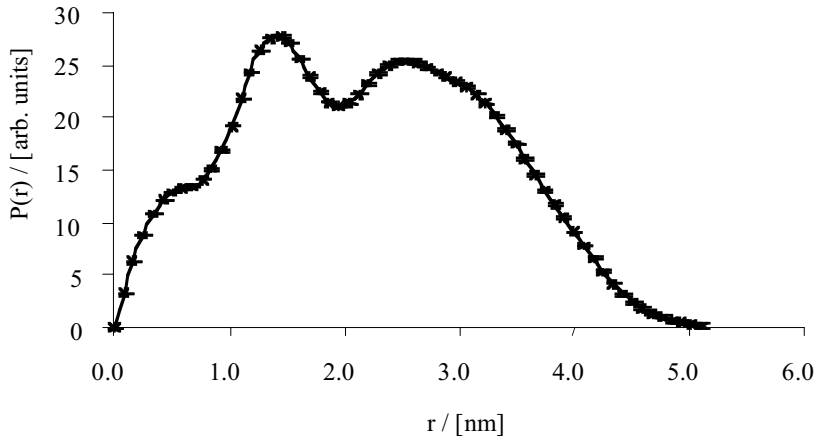

Figure 1: Distance distribution P(r) of the "big wheel" polyoxometalate (1) in methanol (C = 5 g/L), calculated from a SAXS scattering curve. The relative frequency P(r) is plotted versus distance r in nm between scattering centers.

The maximum diameter of the scattering particles D_{max} is 5.1 nm, at 1.4 und 2.6 nm two maxima are visible. The structural interpretation of this distribution is very complex, because the relative frequency P(r) is depending on the particle geometry as well as on the distribution of the inhomogenities inside the particles. First model calculations using the model of two hollow cylinders with various arrangements to each other indicate that this distance distribution can be interpreted as a chain of circular POM clusters. This result indicates that the "big wheel" basic structure, which was found by crystallographic investigations, also exists in solution. The distance distribution of the same solution as shown in figure 1 - just 36 hours later - is shown in figure 2.

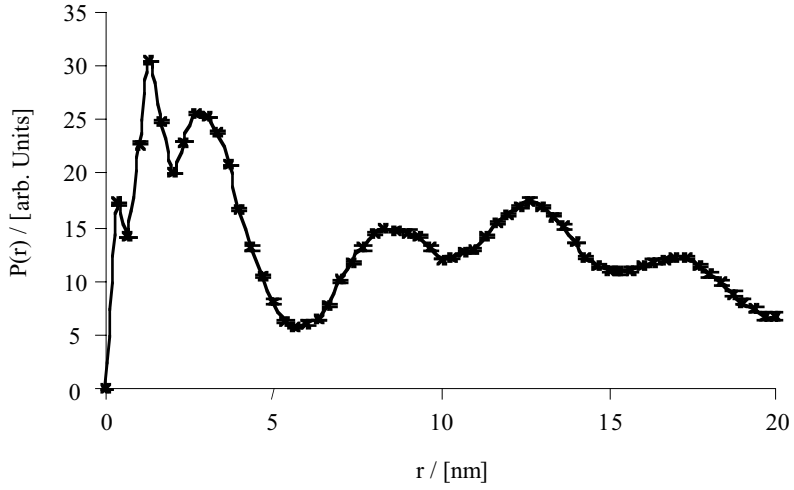

Figure 2: Distance distribution P(r) of the same POM solution in methanol as shown in figure 1, 36 hours after preparation. The relative frequency P(r) is plotted versus distance r in nm between scattering centers.

In this distribution the "big wheel" structure again is visible, but also structures with sizes larger than 20 nm. To obtain information about bigger particles measurements with distances between sample and detector larger than 1.91 m are necessary. This indicates that big agglomerates are formed in the POM solution over a period of a few hours.

Information about the structure of POM clusters and about the process of aggregation is essential for synthesizing even larger structures and to develop new compounds with special attributes. Small-angle X-ray scattering (SAXS) proved to be a suitable analytical method for such investigations, as it allows measurements directly in solution.

References

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