Supplementary Material (ESI) for Chemical Communications

Supplementary Information

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"Phosphoesterase activity of $[Mo_7O_{24}]^{6-}$ cluster: diffusion ordered NMR spectroscopy as a tool for obtaining insights into the reactivity of polyoxometalates"

Luk Van Lokeren, Els Cartuyvels, Gregory Absillis, Rudolph Willem and Tatjana N. Parac-Vogt*[b]

DOSY NMR

Acquisition

All diffusion experiments were performed by pulsed field gradient ^{1}H NMR spectroscopy by means of a BPP-LED pulse sequence,[1] with shaped gradient pulses of amplitude G and duration δ modulated as the G[sin($2\pi/\delta$)] function. All diffusion experiments were carried out at 298K without sample spinning on a Bruker Avance II 500 MHz equipped with a BGU z-gradient unit providing a maximum gradient strength of 51 G/cm. The amplitude of the field gradient was varied from 2 to 95% of its maximum value over 32 increments, while the gradient recovery delay (τ) and the eddy current delay (t_e) were fixed at 0.1 and 5 ms, respectively. The diffusion delay (Δ) was set to 50 ms and the corresponding gradient pulse duration (δ) to 6 ms, in order to achieve an intensity attenuation range of at least 95%. The number of number of scans was set to 8 with a recycling delay of 5 s.

In order to match the kinetic time scale of the concentration variation of the species of interest, with the duration of a diffusion NMR experiment (22 minutes), and also in order to avoid convection artefacts, the DOSY acquisition was perfomed at 298 K, on a sample of reaction mixture that was allowed to evolve with time, likewise at 298 K, which significantly lowered the rate of the overall catalytic process. Thus, over the diffusion NMR measurement time of 22 minutes, the ^{1}H resonance amplitude variation of the species of interest turned out never to exceed 0.5% in the worst case, during the whole reaction period.

Processing

The DOSY NMR data were processed by Inverse Laplace Transform (ILT),[2] using a maximum entropy algorithm, MaxEnt,[3] as implemented in the Gifa Processing package interfaced with TOPSPIN software. The ILT-MaxEnt 2D DOSY spectra obtained display the negative logarithmic scale of the diffusion coefficient on the vertical axis in f1, and the chemical shift (in ppm), for each measurable moiety of the corresponding diffusing species, on the horizontal f2 axis. The resulting 2D spectrum was integrated over a given resonance range along the chemical shift axis, which provides an intensity function depending only on the -logD variable. A sum of Gaussian functions was fitted to these data. The peak maxima thus obtained were used as the representative diffusion coefficients. The accuracy of the diffusion coefficients is about 1%, as usually for monogaussian decays.[4]

Calculation and Estimation of Diffusion Coefficients

In solution, the Debye-Einstein equation allows to determine the diffusion coefficients only *based* on translational motions:

$D = k_B T/f_T$

where k_B is the Boltzmann constant, T the temperature in Kelvin and f_T the friction factor. Assuming spheroid particles, the equation can be rewritten as the well-known Stokes-Einstein equation:[5]

$D = k_B T f_S / c\pi\eta b$

where η is the viscosity of the solvent, b is the minor semi-axis of the structural unit, c is a parameter tending asymptotically to 6 as the particle size increases, holding in general for structures with 1 nm diameter or more and f_S is a shape factor accounting for the shape of the structural unit. The shape factors corresponding to spherical, prolate and oblate ellipsoids can be expressed as follows: [6]

$f_S = 1$ for spherical particles

$$f_S = \frac{\ln\left(\rho + \sqrt{\rho^2 - 1}\right)}{\sqrt{\rho^2 - 1}}$$ for prolate particles

$$f_S = \frac{\arctan\sqrt{\rho^2 - 1}}{\sqrt{\rho^2 - 1}}$$ for oblate particles

where ρ is the axial ratio a/b, i.e. the ratio of the major semi-axis a to the minor semi-axis b. The Stokes-Einstein equation allows an accurate calculation of the diffusion coefficient from the dimensions of a particle as determined from X-ray diffraction structural data.[7] (Table 1)

Table 1: Comparison of experimental and calculated diffusion coefficients for species with assumed shape and estimated semi-axis (from X-ray diffraction data[7]). The estimated maximum error on the diffusion coefficient is 0.1 × 10^{-10} m^2/s

Compound	Shape	Semi-axis (Å)	D_{exp} (10^{-10} m^2/s)	D_{calc} (10^{-10} m^2/s)
PhP	spherical	3.17	6.4	6.6
$[(PhP)_2Mo_5O_{21}]^{4-}$ (92%)	prolate	3.30 / 8.44	4.2	4.3
PhPMo7 (8%)	spherical	4.80		4.4
NPP	spherical	3.64	5.5	5.8
NPP2Mo5	prolate	3.30 / 10.34		3.9
NPPMo6	oblate	3.43 / 4.71		4.9
NPPMo7	spherical	5.31		3.9
Dimer	oblate	6.03 / 7.60		3.0
Complex **A**			4.1	3.9
Complex **B**			2.8	3.0
NP	spherical	3.50	5.7	6.0

Reaction: Figure

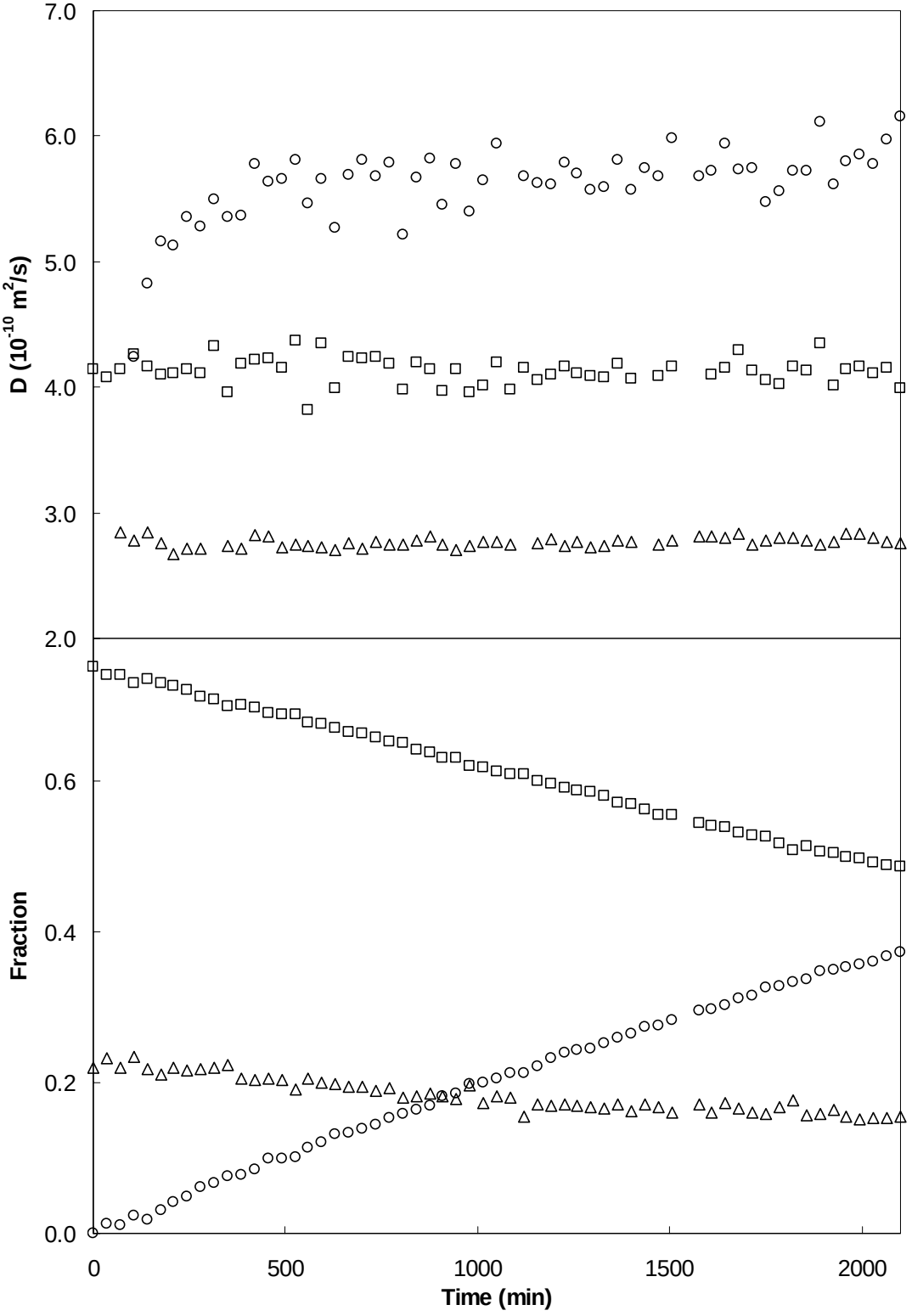

Figure 1: Evolution of the fraction and the diffusion coefficient of complex A (□), complex B (△) and NP (○) upon reaction of NPP with molybdate (concentration, ratio, pH + temperature). Upper panel: time dependence of the diffusion coefficient. Lower panel: time dependence of the species molar fraction.

References for supporting information

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