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Colloidal Characteristics of Molybdenum Blue Nanoparticles Dispersion for Catalytic Applications

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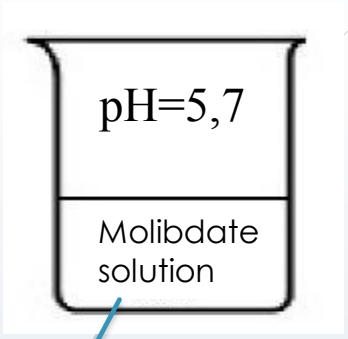
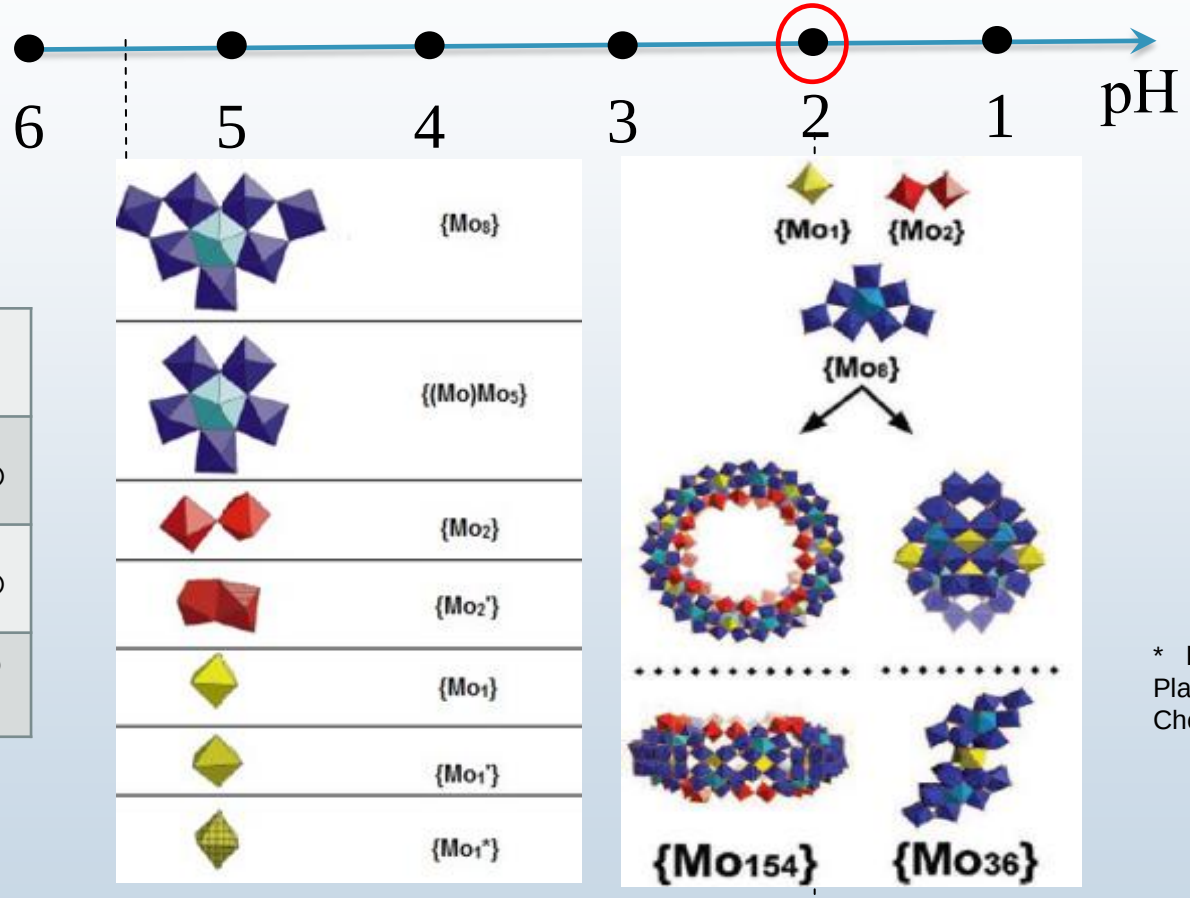
Formation of molybdenum blue particles in molybdate solutions



$12MoO_4^{2-} + 21H^+ = H_7Mo_{12}O_{41}^{3-} + 7H_2O$
$24MoO_4^{2-} + 43H^+ = H_7Mo_{24}O_{78}^{5-} + 18H_2O$
$24MoO_4^{2-} + 45H^+ = H_9Mo_{24}O_{78}^{3-} + 18H_2O$
$36MoO_4^{2-} + 64H^+ = \mathbf{Mo_{36}O_{112}^{8-}} + 32H_2O$

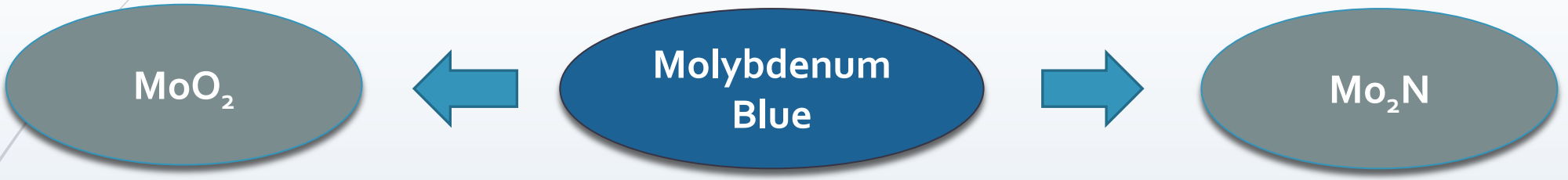
In present of reduction agent



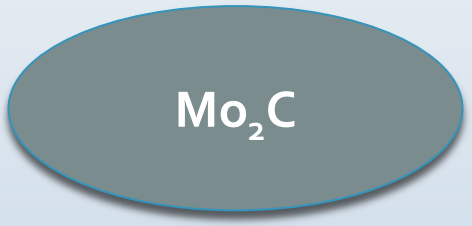
* Müller A., Serain C. Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity // Acc. Chem. Res. 2000. V. 33. P. 2.

Solutions — **Sols** — Precipitates

Catalytic Application of Molybdenum Blue



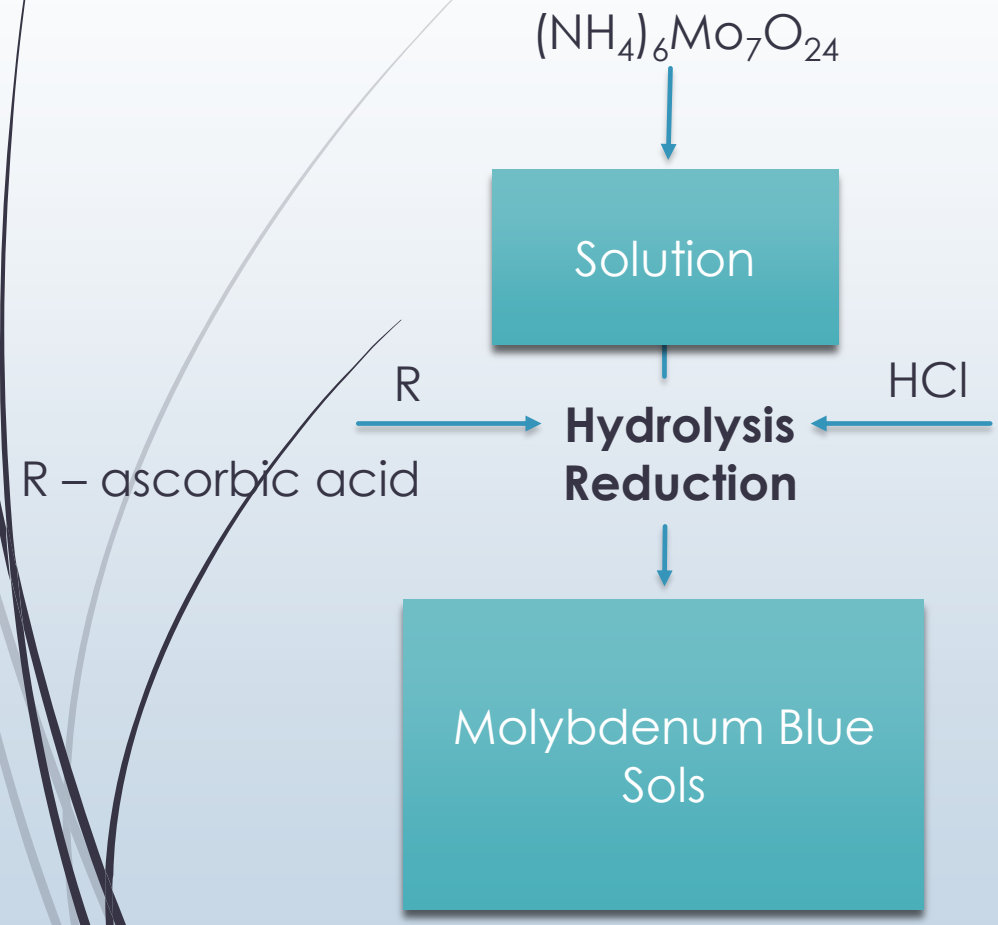
- Reforming of hydrocarbons
- Partial oxidation of hydrocarbon
- Photocatalysis
- electrochemical-catalyst

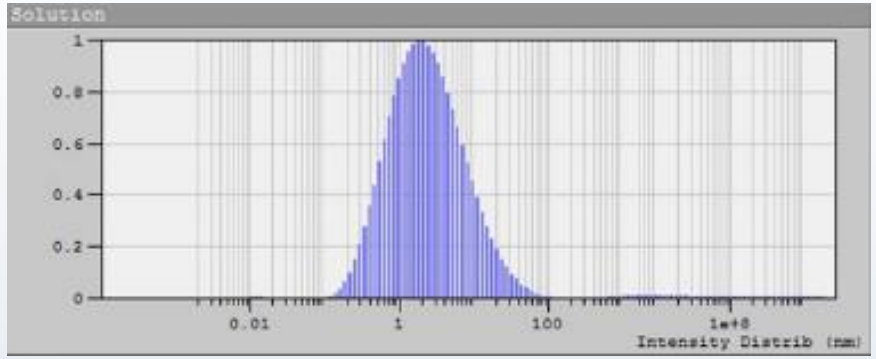


- Photo- and electrochemical-catalyst
- Hydrodenitrogenation
- CO hydrogenation
- NH_3 synthesis
- Hydrogenation
- Hydrogenolysis
- Isomerization

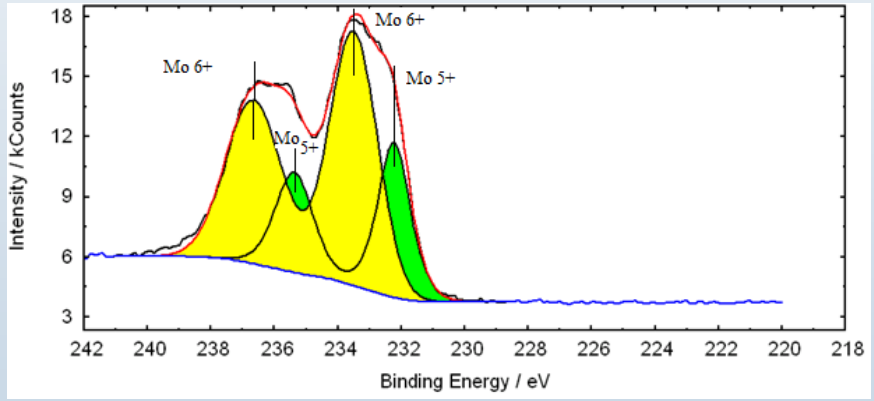
- Desulfurization
- Hydrogenation
- Isomerization
- Dry reforming of Methane
- Steam reforming of methanol
- Water gas shift reaction
- Electro-catalyst for hydrogen evolution reaction

Synthesis of Molybdenum Blue Sols



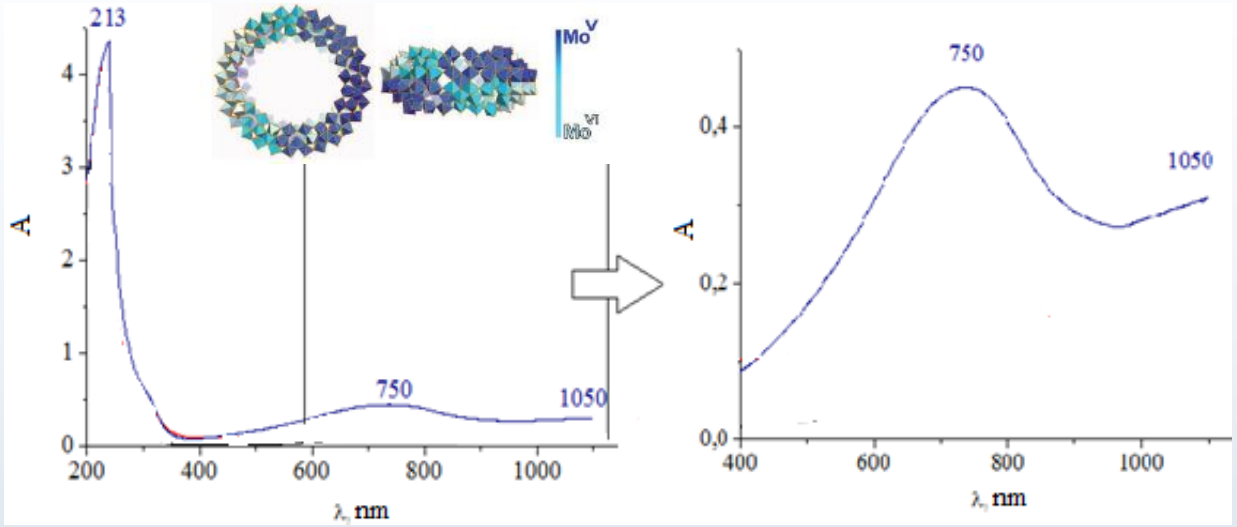


DLS particle size distribution of molybdenum oxide clusters

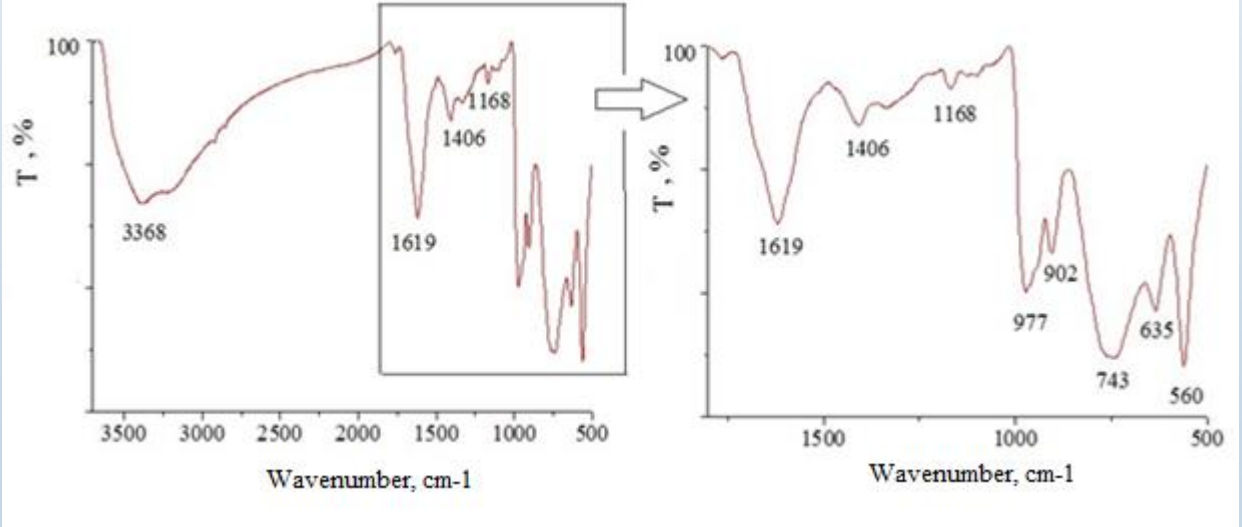


XPS spectrum of Mo (a) of molybdenum oxide clusters

Molybdenum Blue Particles Characterizations

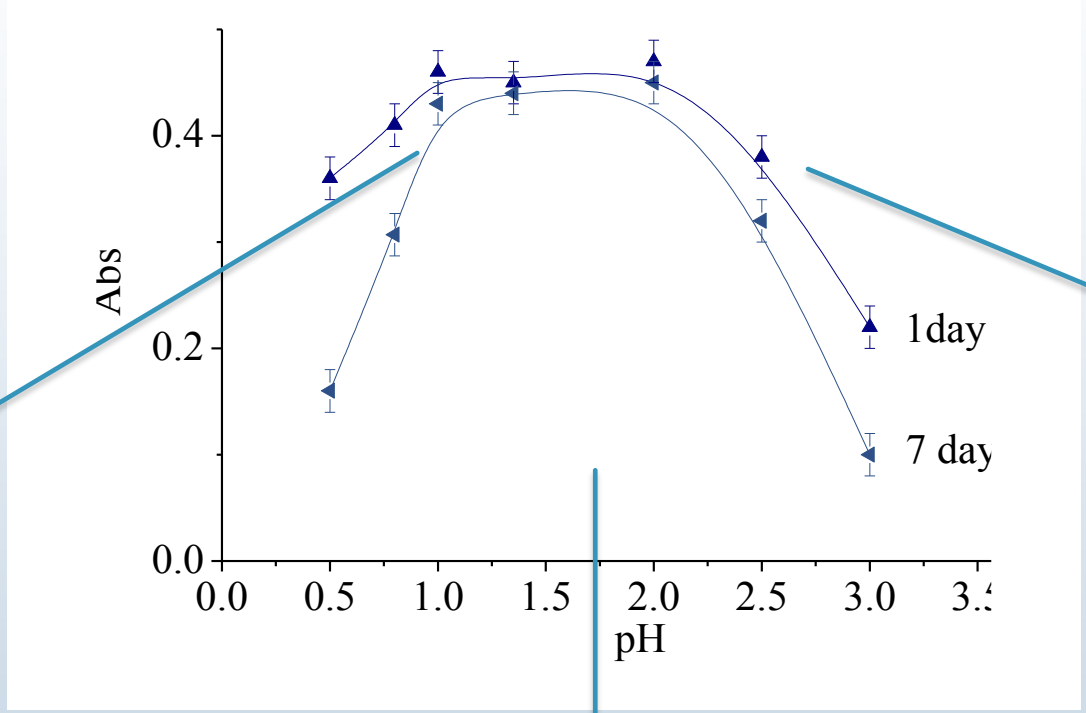


Electronic absorption spectra of of molybdenum clusters



FTIR spectra of of molybdenum clusters

pH range of Aggregative Stability of Molybdenum Blue Sols

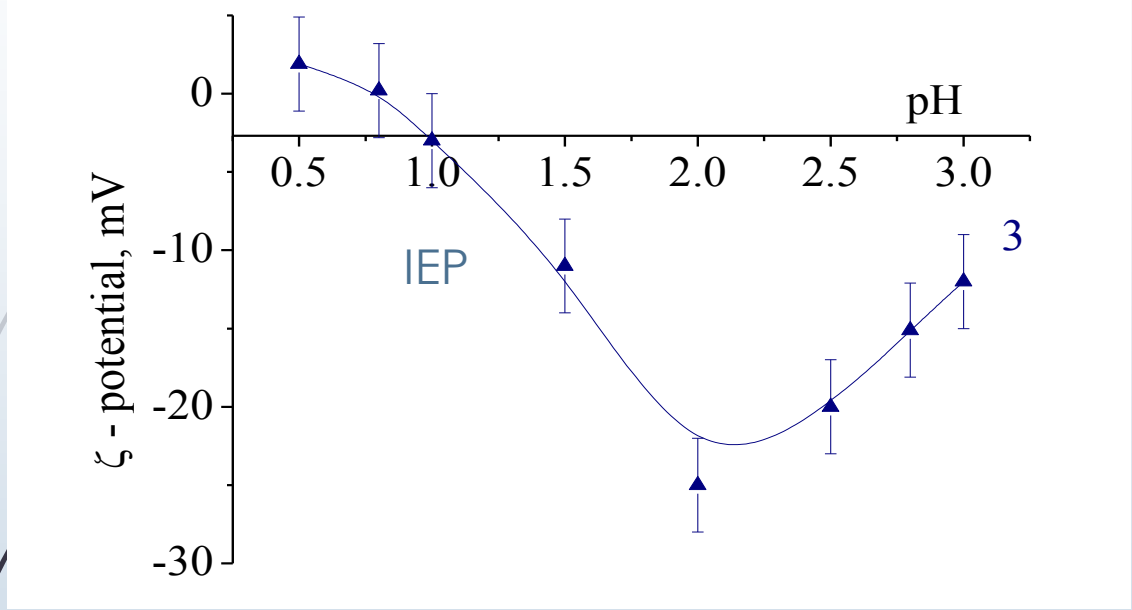


Coagulation

Clusters decomposition

Aggregative Stable Sols

Electrokinetic potential of Molybdenum Blue Particles



$$\zeta = \frac{3\eta U_{эф}}{2\varepsilon\varepsilon_0} \cdot \frac{1}{f_1(\kappa r)},$$

U_{ef} is electrophoretic mobility, ε is the dielectric constant of the medium, ε_0 is the electric constant, η is the sol viscosity, r is the particle radius, and κ is the reciprocal of the Debye length.

the function $f_1(\kappa r)$:

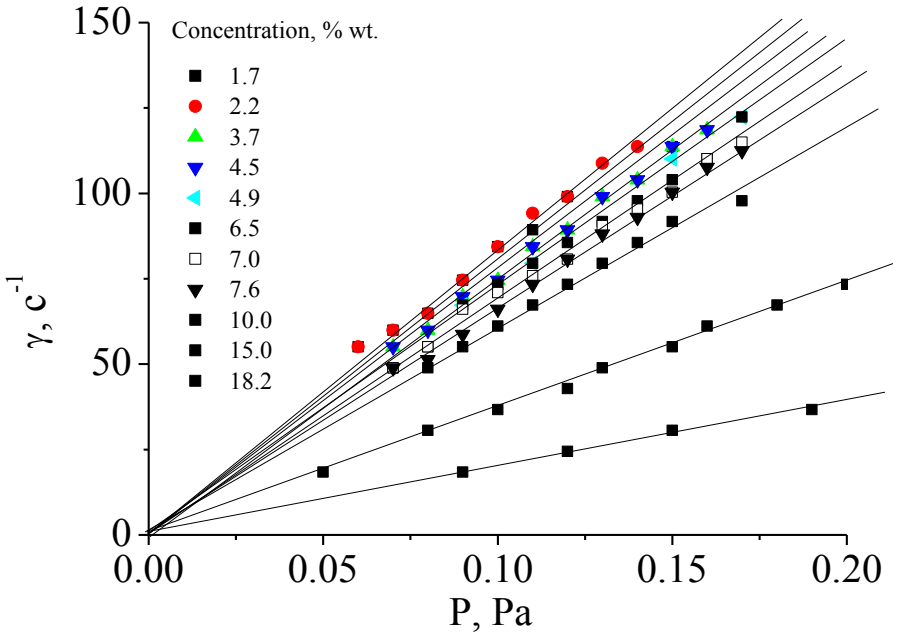
$$f_1(\kappa r) = 1 + \frac{1}{2}\left[1 + \left(\frac{2{,}5}{\kappa r[1+2\exp(-\kappa r)]}\right)\right]^{-3}$$

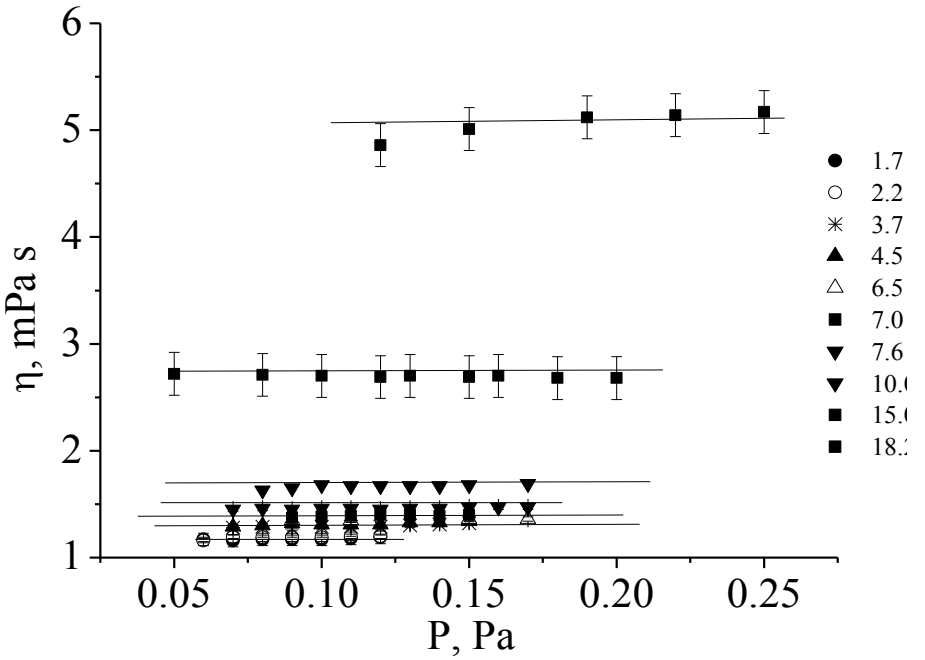
pH		Cluster structure
3,0 – 4,5	Mo_{138}	$[Mo_{138}O_{410}(OH)_{20}(OH_2)_{46}]^{40-}$
3,3-2,5	Mo_{142}	$[Mo_{142}O_{400}(OH)_{52}(OH_2)_{38}]^{28-}$
1,7	Mo_{148}	$[Mo_{142}O_{436}(OH)_{15}(OH_2)_{56}]^{27-}$
1,4	Mo_{150}	$[Mo_{150}O_{442,5}(OH)_{11,5}(OH_2)_{64}]^{24,5-}$
1,5-2,0	Mo_{154}	$[Mo_{154}O_{462}(OH)_{14}(OH_2)70]^{14-}$

* Botar B., Ellern A., Kogerler P. Mapping the formation areas of giant molybdenum blue clusters: a spectroscopy study // Dalton Transactoions. 2012. V. 41. P. 8951 – 8959.

** Shishido S., Ozeki T. The pH dependent nuclearity variation of [Mo_{154-x}] type polyoxomolybdates and tecktonic effect on their aggregations // J. Amer. Ceram .Soc. 2008. V. 130. P. 10588-10595.

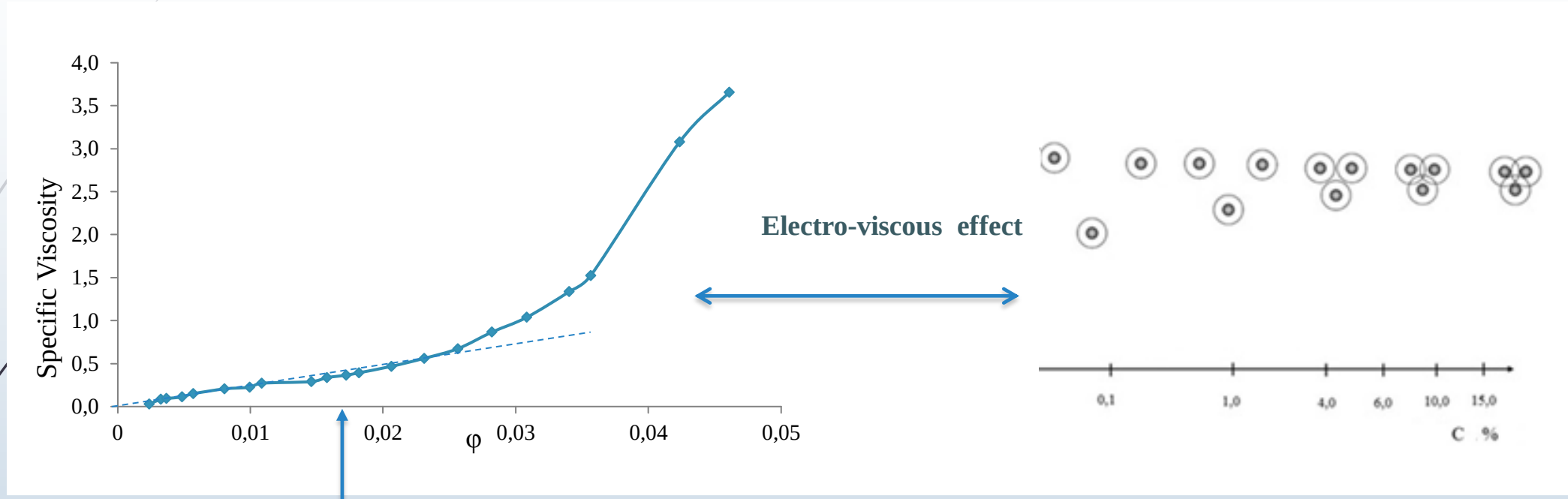
Rheology properties of Molybdenum Blue Sols





* T = 20°C
Brookfield LV-DV-II Pro with ULA adapter

Rheology properties of Molybdenum Blue Sols



Conclusions

- Molybdenum blues synthesized using ascorbic acid are sols containing Mo_{154-x} nanoparticles
- Molybdenum blues are aggregative stable in the pH range from 0.8 to 2.0.
- In the pH range from 0.8 to 2.0, molybdenum blue particles have a negative charge, the maximum value of the electrokinetic potential does not exceed 30 mV.
- Molybdenum blues are Newtonian liquids, the viscosity of which is mainly determined by the concentration of the dispersed phase. Electro-viscous is observed at a concentration of more than 10% wt. due to the presence of DEL on the surface of particles.

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Thank you
for your attention!