Colloidal Aspects of the Formation of the Interactions between Humic Substances and Surfactants

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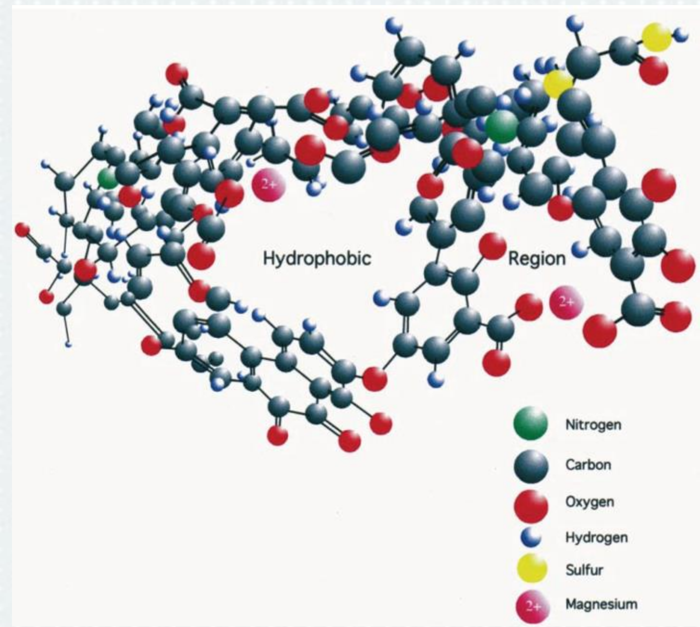
Aims / motivation

- **surfactants are nowadays used everywhere**
- **increased solubility of harmful substances (API, hydrophobic subs., metals)**
- **undesirable foaming of ground and waste waters**

Picture shot from within the lagoons during fall, 2014. Is the greying of this foam evidence of the use of a surfactant to clarify clouded water after dredging?

Aims / motivation

- **potential sorbent => humic substances (or HS rich materials)**
  - **reactive functional groups: –COOH, –Ar–OH, –Al–OH**
  - **hydrogen bonds**
  - **aromatic structures: π–π interactions**
  - **hydrophobic interactions**



- **crucial questions – quantification of binding properties and potential**

  – finding the optimal application form

Research approaches

Conventional approaches:

- batch sorption approaches =>
  affinity + sorption capacity + sorption isotherms

Our innovative approach – combination of:

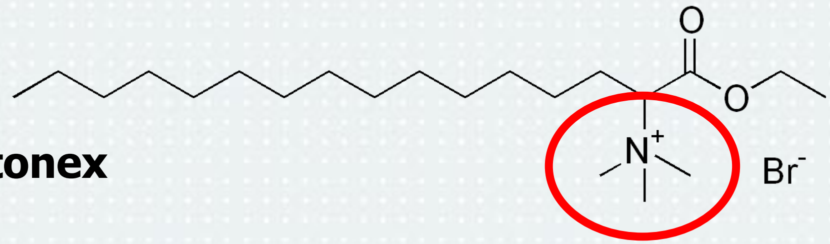
- colloidal chemistry approaches (size, PDI, zeta, Mw)
- thermochemical analysis (ITC, TGA, EA)
- advances spectroscopy (differential UV/VIS, FCS, FTIR)
  (more in presentation of Dr. Smilek)
- combination with sorption experiments

- <u>application form of HA based sorbents</u>

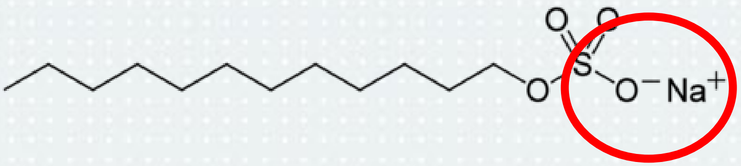
Materials / methods

1. Materials

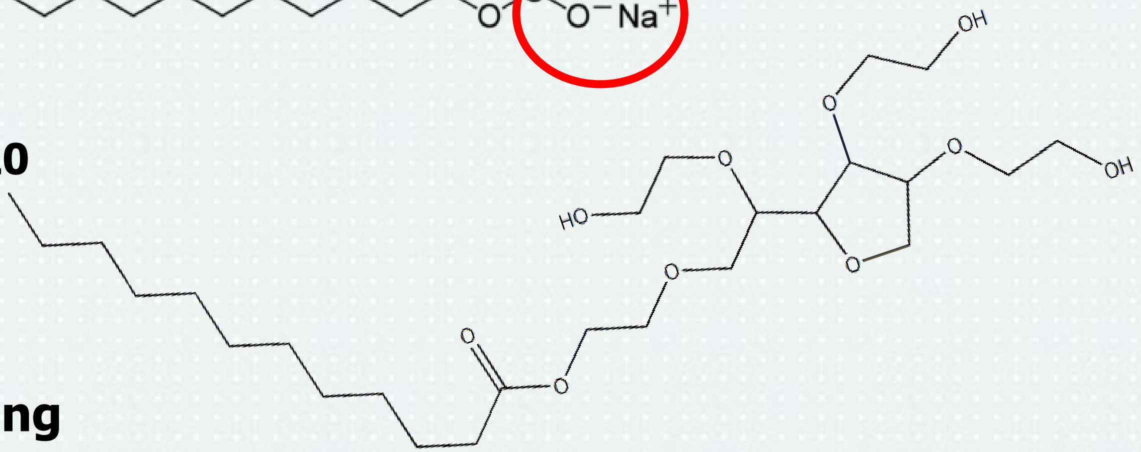
- ➢ **Sorbent => humic substances from lignite – South Moravia, Czech Republic**
- ➢ **Surfactants**
  - ✓ **cationic – CTAB, TTAB, Septonex**



  - ✓ **anionic – SDS**



  - ✓ **non-ionic – tween 20**



2. Methodology

- ➢ **dynamic light scattering**
- ➢ **thermochemical analysis of formed complexes (TGA, EA)**
- ➢ **structural analysis of formed complexes (FTIR)**

Colloidal aspects of interaction

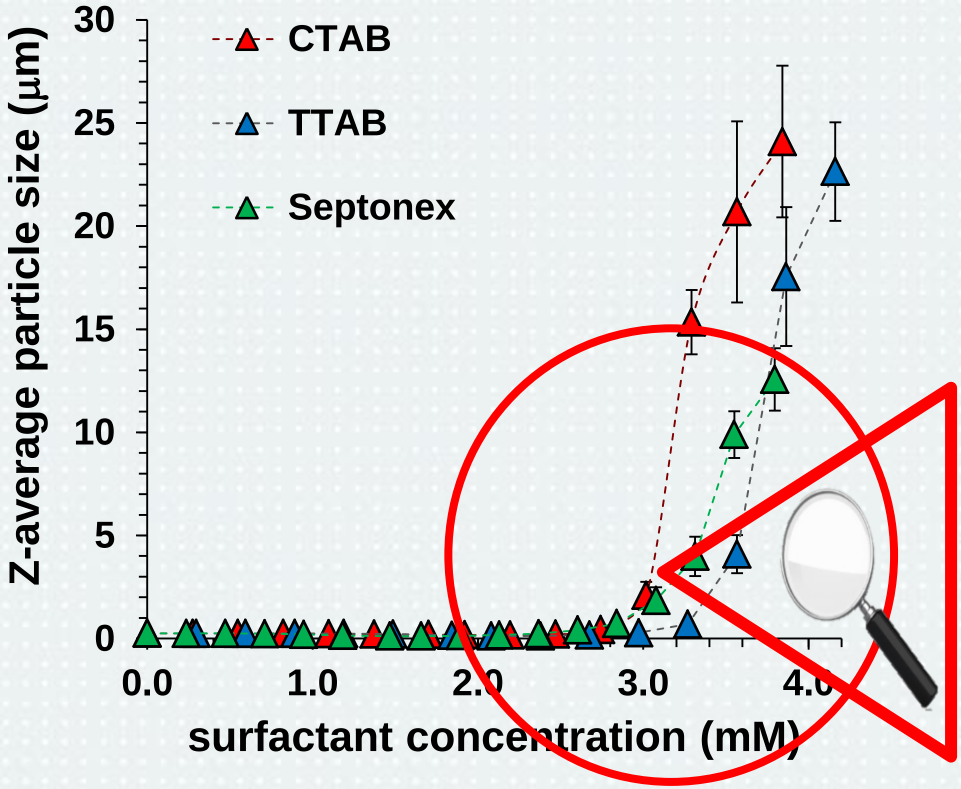
- dynamic light scattering (DLS) – extremely sensitive for presence of bigger particles or aggregates
- MPT-2 titration unit => titration mode

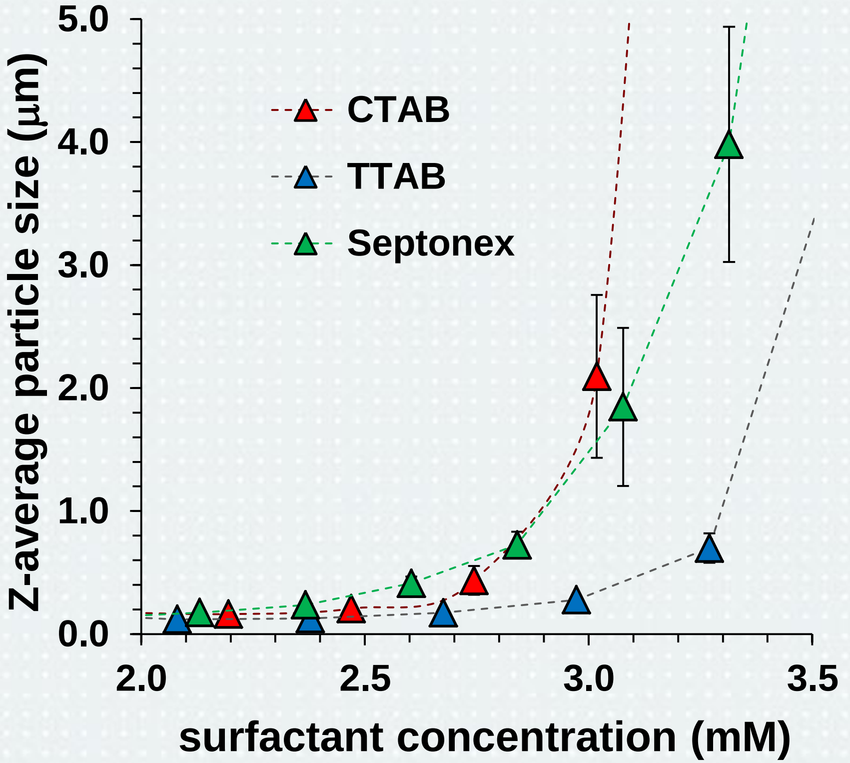
- initial stages of aggregation of HA + surfactant
- additionally
  - zeta potential – measure of system stability and changes in charge
  - intensity of scattered light => formation of bigger particles
  - controlled pH and conductivity

Colloidal aspects of interaction II

1. cationic surfactants

- oppositely charged => positive interaction
- 10 g/l of lignite humic acids + surfactants





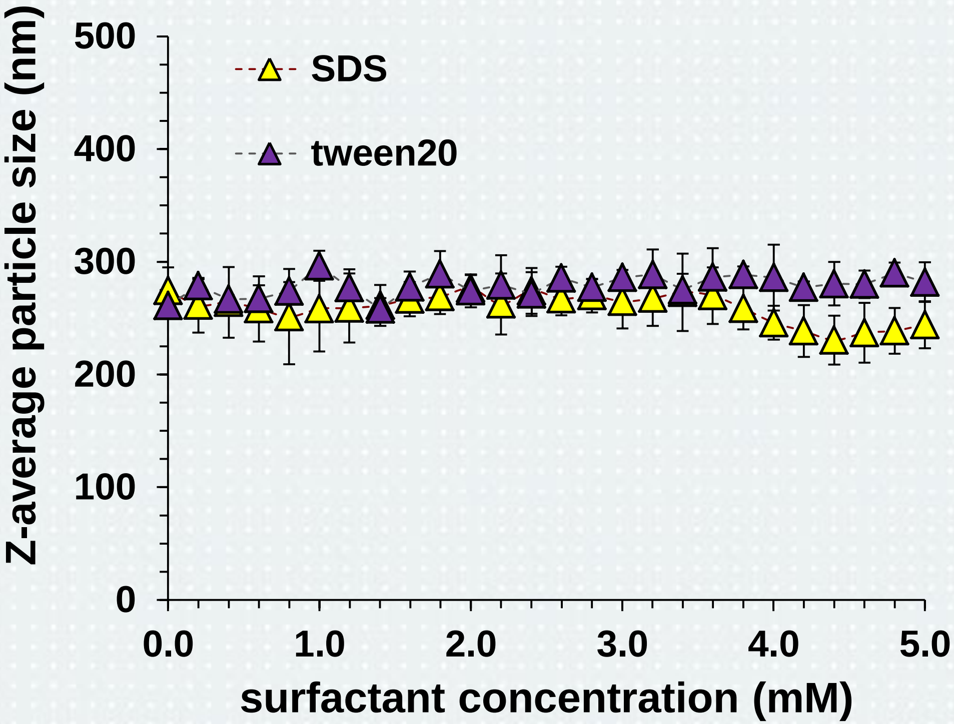
Colloidal aspects of interaction III

2. anionic and non-ionic surfactants

- **same or no charge => no electrostatic interaction**
- **10 g/l of lignite HA + surfactants**

- **negligible effect on observed average particle size of HA**

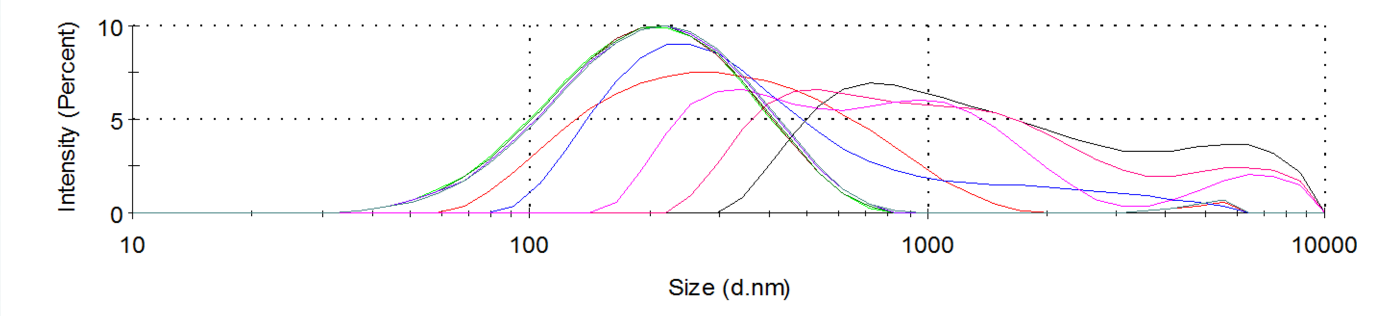
- **interaction resulting in phase separation of HA and SDS (anionic) or tween 20 (non-ionic)**



Colloidal aspects of interaction III

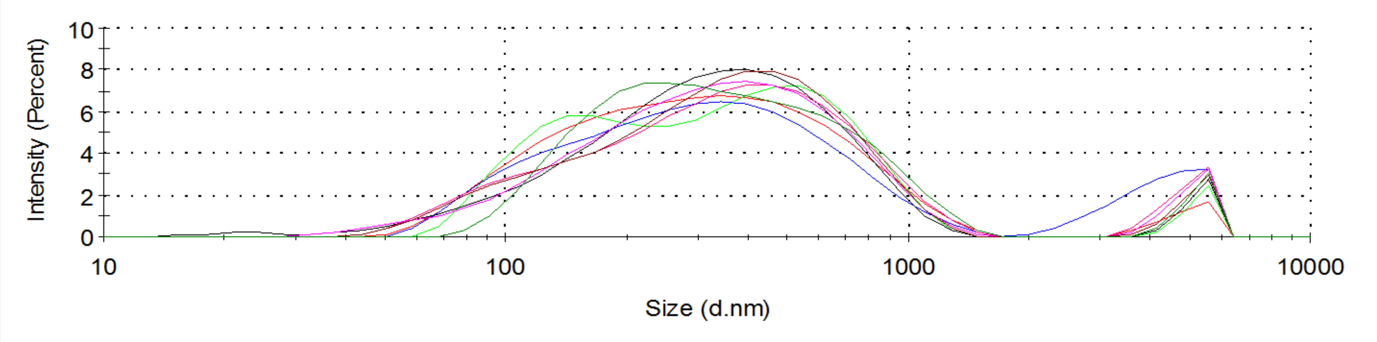
Comparison of size distribution changes

- **cationic surfactant – here data for titration with CTAB**



– shift in particle size distribution towards bigger particles

- **anionic of non-ionic – here data for titration with tween 20**



– almost no shift in particle size distribution to bigger particles

Aggregation concentration

- **DLS titration => aggregation concentration of HA+surfactants**

acidity (mmol/g)		
COOH	**fenolic**	**total**
2.92 ± 0.09	2.21 ± 0.10	5.14 ± 0.34

- **HA acidity (total and COOH)**
  - **direct + indirect => total acidity**
  - **carboxylic (calcium acetate method)**

sample name	CAC (mM)	n_{surf}/n_{TOTAL}	n_{surf}/n_{COOH}
HA + CTAB	2.980±0.012	0.216±0.018	0.380±0.022
HA + TTAB	3.203±0.023	0.223±0.019	0.404±0.024
HA + septonex	2.743±0.050	0.218±0.019	0.383±0.023

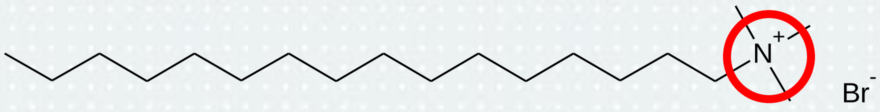
Elemental and thermal analysis

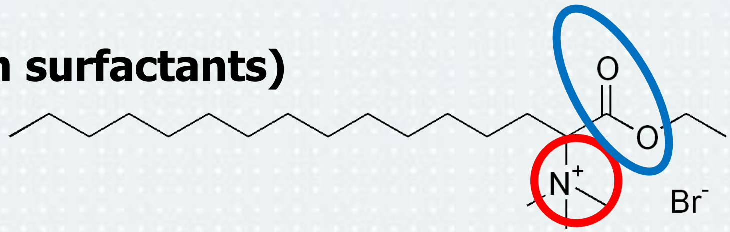
EA on complexes formed after phase separation of HA

- **precipitates only with cationic surfactants**
- **formed precipitates dialyzed and freeze-dried => same content of ash**

Sample name	Elemental composition (At. %)				Elemental atomic ratios (–)			Ash	Humidity
	C	H	O	N	H/C	O/C	N/C	(wt. %)	(wt. %)
HAs	41.95	38.52	18.48	0.78	0.918	0.441	0.019	1.83	6.35
HA–CTAB	33.14	60.73	4.49	1.64	1.832	0.136	0.049	0.96	6.11
HA–TTAB	32.46	61.53	4.50	1.51	1.895	0.139	0.046	0.93	6.11
HA–Septonex	34.28	58.49	5.56	1.67	1.706	0.162	0.049	1.08	5.35

- **increased content of N (introduced from surfactants)**

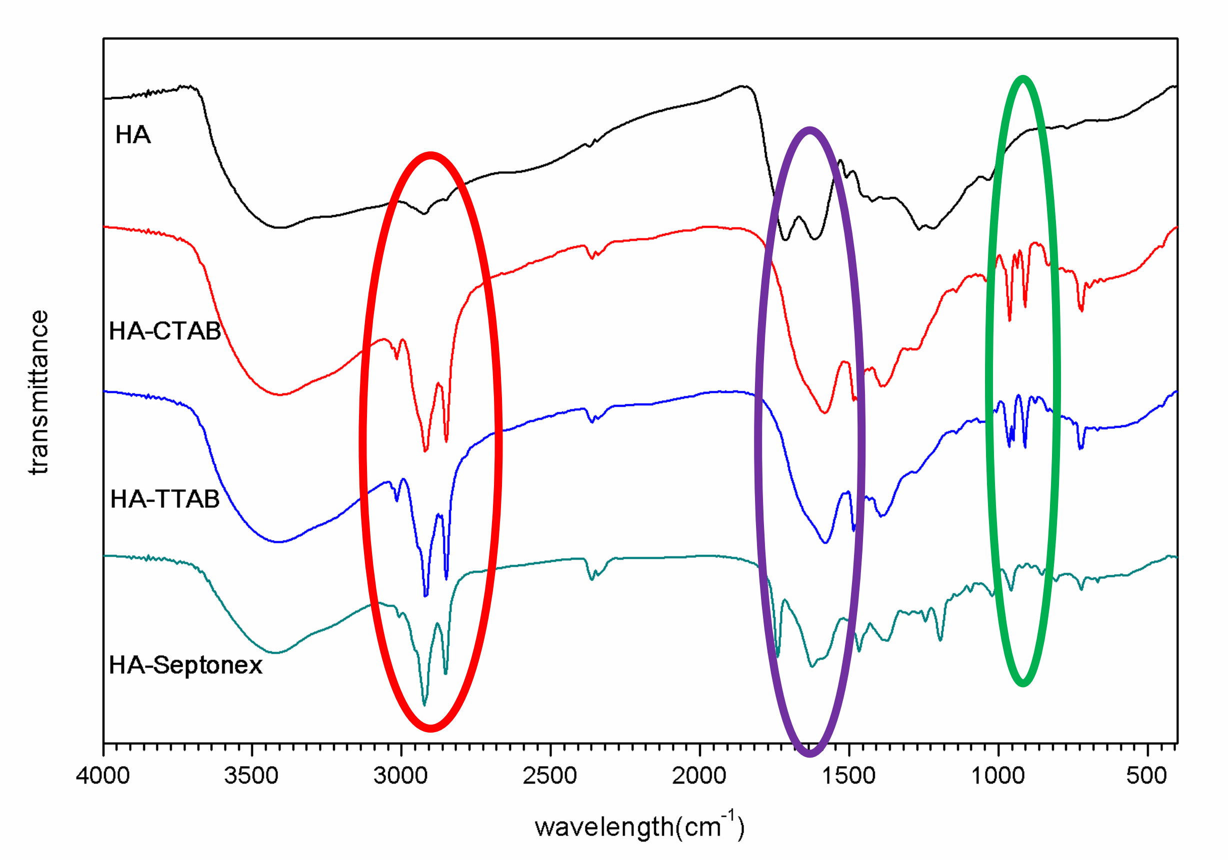




FTIR spectroscopy

FTIR on complexes formed after phase separation of HA

- precipitates only with cationic surfactants
- formed precipitates dialyzed and freeze-dried



3020 cm^{-1} –N–CH_3

2940+2840 cm^{-1} – aliphatics

1720 cm^{-1} – COO^-

1500 cm^{-1} – $N(CH_3)$

1000-900 cm^{-1} – N-C bond

Take-home messages

- colloidal methods (DLS, ELS…) => description aggregation of HA + surfactants
- phase separation observed for cationic surfactants + HA
- interactions confirmed by EA, TGA and FTIR
- non-ionic + anionic => no phase separation observed

- further description of the origin of interactions

  => advanced spectroscopy (FCS, FTIR, dif-UV/VIS)

- part of our IHSS Young investigator grant (2018-2020)

Future perspectives

1. Fundamental research

- utilization of HA with selectively blocked COOH groups
- isothermic titration calorimetry => enthalpy of interaction
- advanced spectroscopy => detailed description of the way of interaction of HA with surfactants (e.g. ionic bond, ...)
- combination with sorption experiments

2. Applied research

- optimization of HA application form
- universal sorbent for surfactants and other harmful species (heavy metals, pesticides etc.)

Acknowledgement

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IHSS NATURAL ORGANIC MATTER RESEARCH

MATERIALS RESEARCH CENTRE

GRANT AGREEMENT	YOUNG INVESTIGATOR RESEARCH GRANT (YIG)
for the	"Interaction of different (methylated) humic acids with organic ionic compounds"
DATE	July 12, 2018
between	
INSTITUTION /	Brno University of Technology, Faculty of Chemistry, Purkynova 464/118 CZ-612 00 Brno, Czech Republic
GRANTEE	Dr. Jiri Smilek
GRANT PERIOD	2 years
(begin and end)	from September 1st 2018 to August 31st 2020
and	International Humic Substances Society (IHSS)

- **coauthors – Dr. Petr Sedlacek, Dr. Jiri Smilek**
- **colleagues – Dr. Jitka Krouska, Dr. Vojtech Enev**
- **involved students – Tomas Duchacek, Sarka Sovova, Aneta Hronova**

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Thank you for your attention!