Применение МУРН для исследования морфологии и внутренней структуры органогелей

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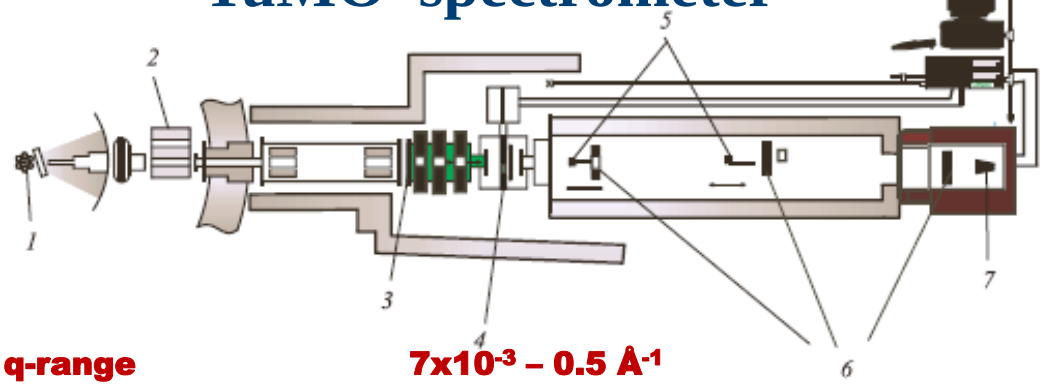
SMALL ANGLE NEUTRON SCATTERING

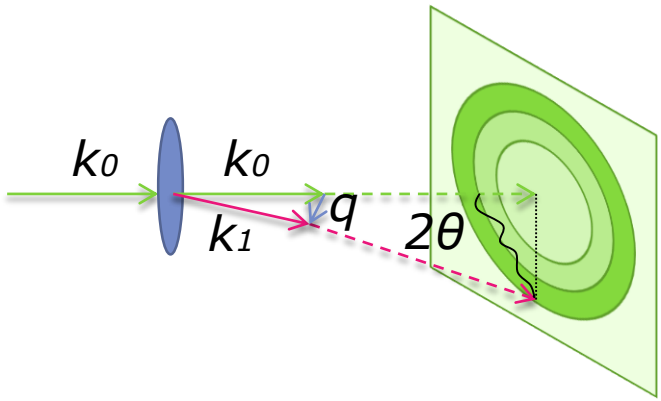
YuMO spectrometer



1 – IBR-2 reactor;
2 – first collimator;
3 – second collimator;
4 – sample;
5 – Vn-standard;
6 – ring-wire detector;
7 –direct beam detector.

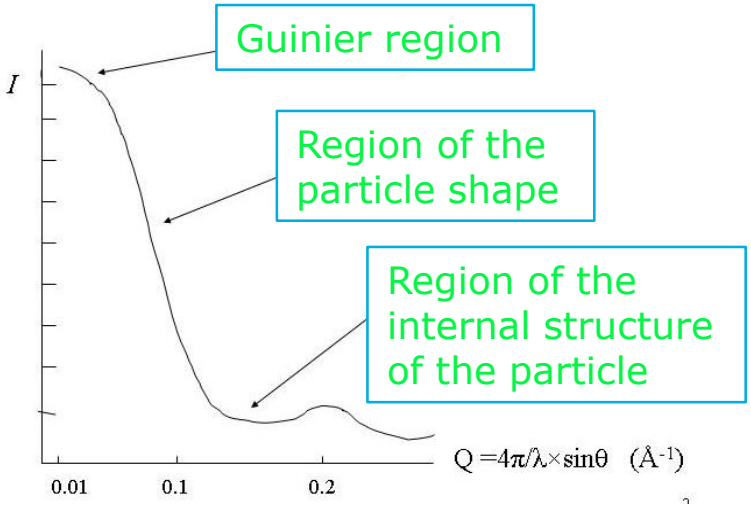
q-range **7×10^{-3} – 0.5 Å^{-1}**

size range of object **500 – 10 Å (for estimation)**
200 Å (max radii of giration)



wave vector $K_0 = 2\,\Pi / \lambda$

scattering vector $q = K_0 - k_1$



small-angle scattering curve (general view)

CHALENGE OF INVESTIGATION

Creation new

SUPRAMOLECULAR ORGANOGELS

gels with a hydrocarbon dispersion medium

smart functional nanoscale materials with high potential for a wide range of ***advanced applications***

drug delivery

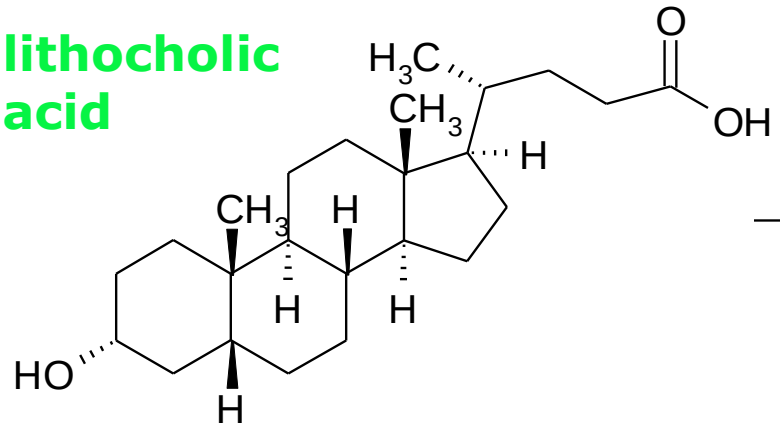
tissue engineering

light-harvesting systems

optoelectronics

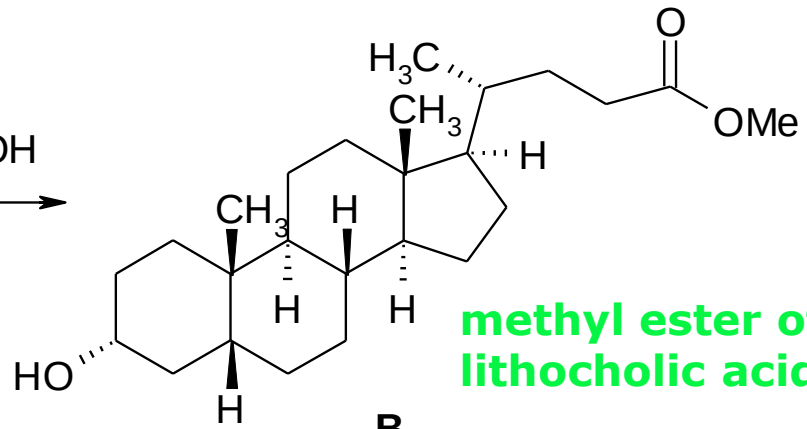
7OPhOLCA: SCHEME OF SYNTHESIS

lithocholic acid



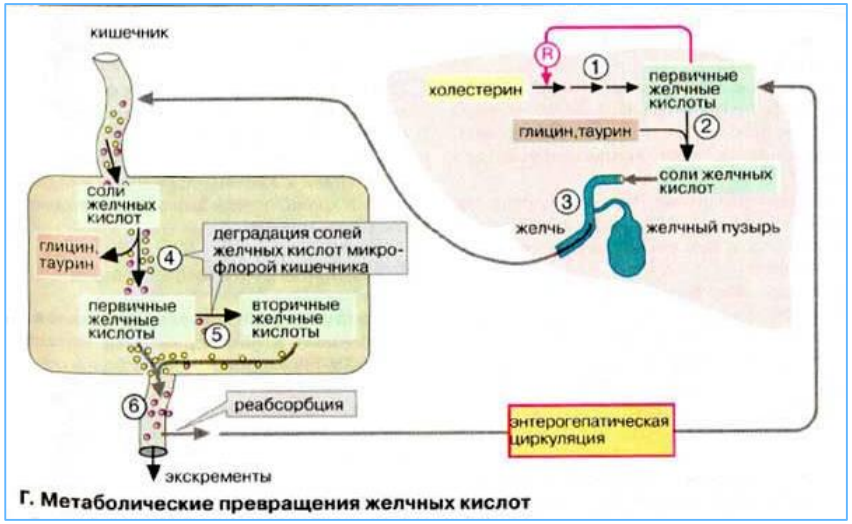
A

CH_3OH →

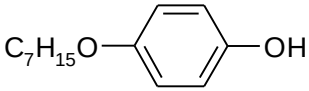


B

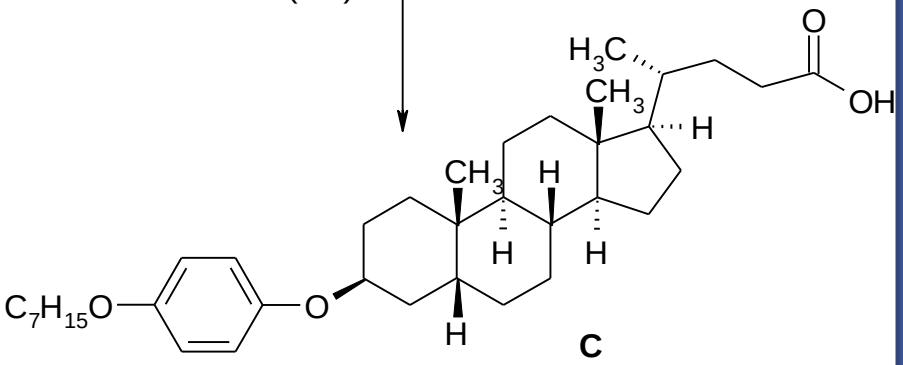
methyl ester of lithocholic acid



Г. Метаболические превращения желчных кислот

1. 

2. water/methanol (1:1)



C

4-heptyloxyphenylo-lithocholic acid ether (Acronym 7OPhOLCA)

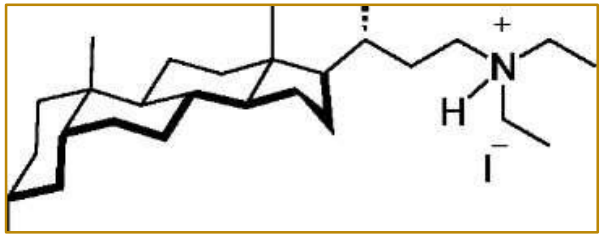
easy form a hydrogen bonds with the proton acceptor molecules

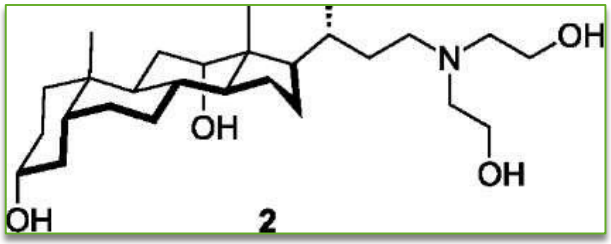
GEL FORMATION

	1	2
Chloroform	S	S
Mesitylene	S	P
1,2-Dichlorobenzene	TG (CGC 2 mM)	TG (W)
Chlorobenzene	TG (CGC 2 mM)	GP
Benzene	I	P
Toluene	I	GP
Isopropanol	S	S
DMSO/water	P	**TG** (CGC 5 mM)
DMF/water	S	**TG**
MeOH/water	P	S
Acetone/water	S	GP
AcOH/water	S	GP
Dioxane/water	S	TLG
CH_3CN/water	S	OG

TG - ***transparent gel***; TLG - translucent gel; GP - gelatinous precipitate; S - solution; I - insoluble; P - precipitate; OG - opaque gel; W – weak

for two compounds:
1 – ionic; 2 – non ionic





<u>do not form gel</u> with bile acids the solvents with high molecular weight or without proton donor-acceptor groups

<u>form gel</u> in mixtures of DMSO (dimethyl sulfoxide)**/water (1:2 to 3:2),**
DMF (dimetyloformamid)**/water (2:3 to 3:2), 1,4-dioxane/water (1:4)**

[Maitra, J. Org. Chem. 2011].

DMSO – organic solvent have proton acceptor group. Gel systems are formed by hydrogen bonds.

SULFOXIDES: PROPERTIES AND APLICATIONS

DMSO

CRYOPROTECTOR

PROPERTY

The ability to bind free radicals

Reducing damage of biological objects

APLICATION

Cell biology

Cryobiology

Medicine

Agriculture

SOLVENT

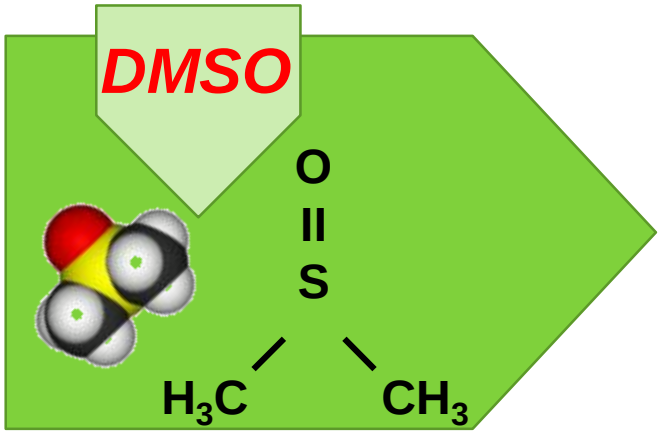
PROPERTY

High permeability through biological membranes

APLICATION

Medicine

Pharmacology



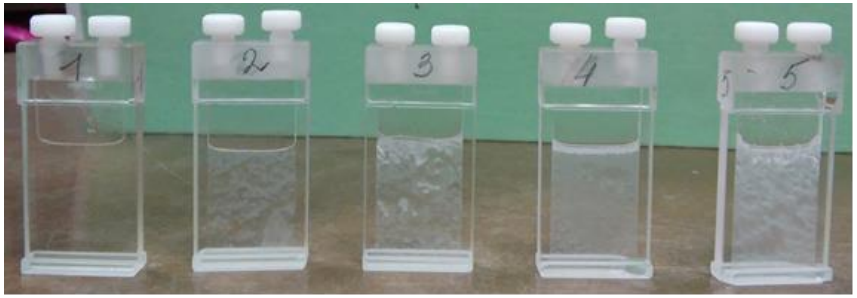
hydrophobic interactions play a crucial role in the interaction

SCIENTIFIC INTEREST

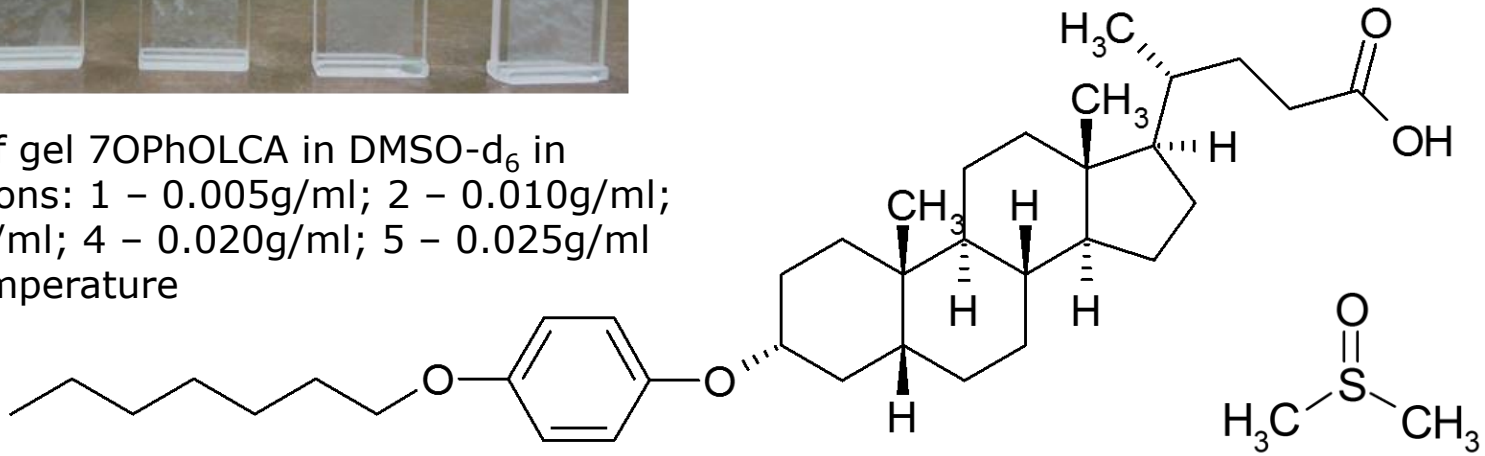
Morphology

Internal structure

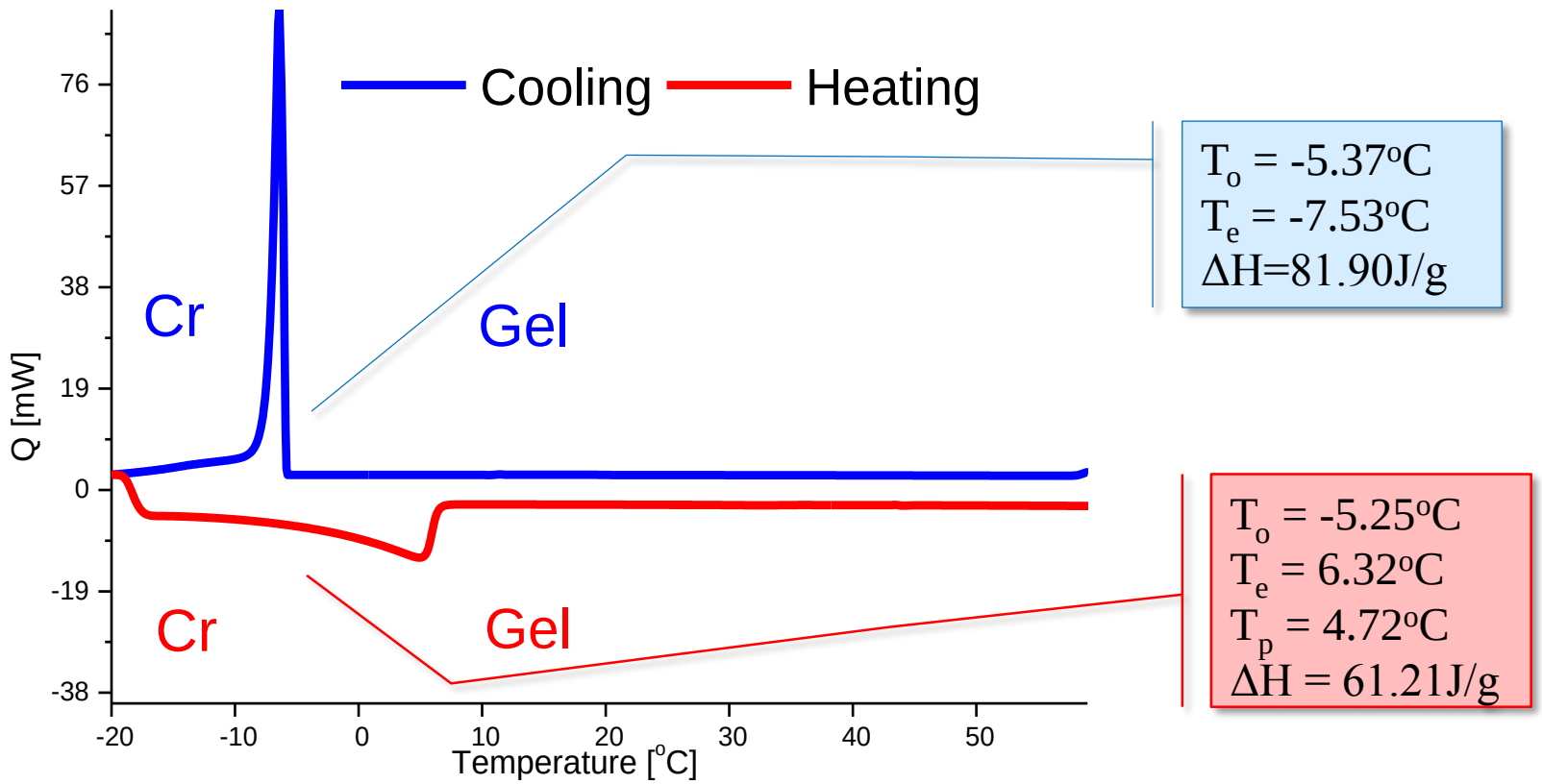
Phase transitions



Solutions of gel 7OPhOLCA in DMSO-d_6 in concentrations: 1 – 0.005g/ml; 2 – 0.010g/ml; 3 – 0.015g/ml; 4 – 0.020g/ml; 5 – 0.025g/ml at room temperature



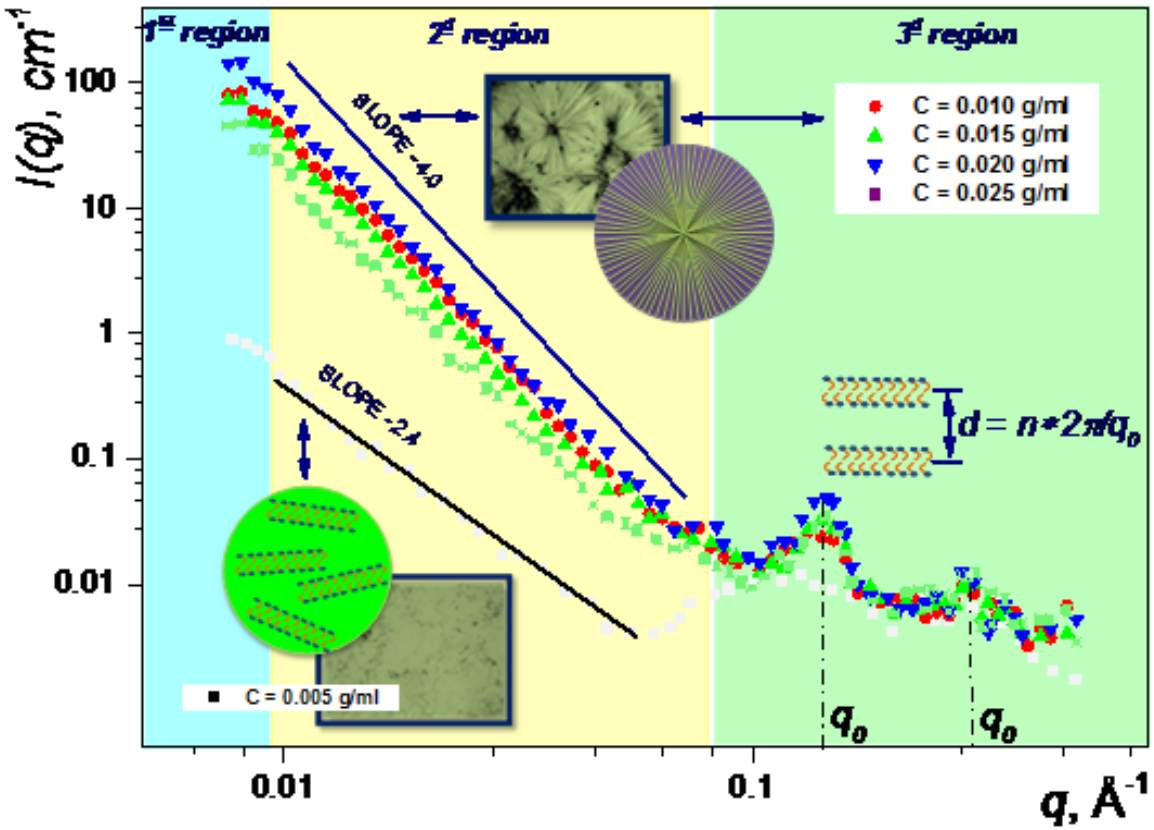
DSC METHOD



Thermograms of full cycle heating and cooling for 7OPhOLCA in DMSO-d_6 (0.015g/ml), in the range of -20°C to 60°C with rate of 5deg/min for sample with mass 14.02mg

SANS METHOD: Effect of concentration

Guinier region | Morphology | Internal structure

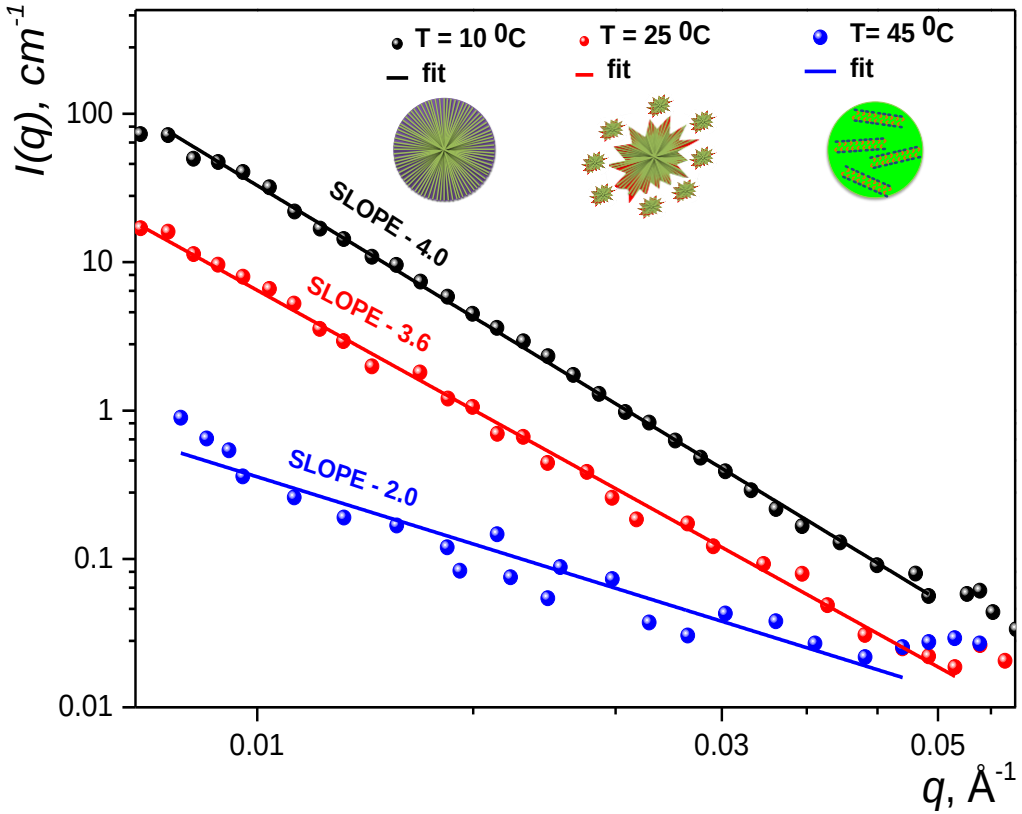


SANS curves for 7OPhOLCA in DMSO-d_6 at concentrations C = 0.005, 0.010, 0.015, 0.020 and 0.025g/ml at T = 10ºC

The scattering intensity is determined by a power law: $I(q) \sim q^{-m}$, where m is a power-law exponent related to a fractal dimension as D = 6 – m. The gradient gives information about the morphology of the sample.

The scattering on the individual lamellas with d = 43.4 ± 0.1Å

SANS METHOD: Temperature effect



SANS curves for 7OPhOLCA in DMSO-d_6 with C = 0.015g/ml at T = 10, 25 and 45ºC

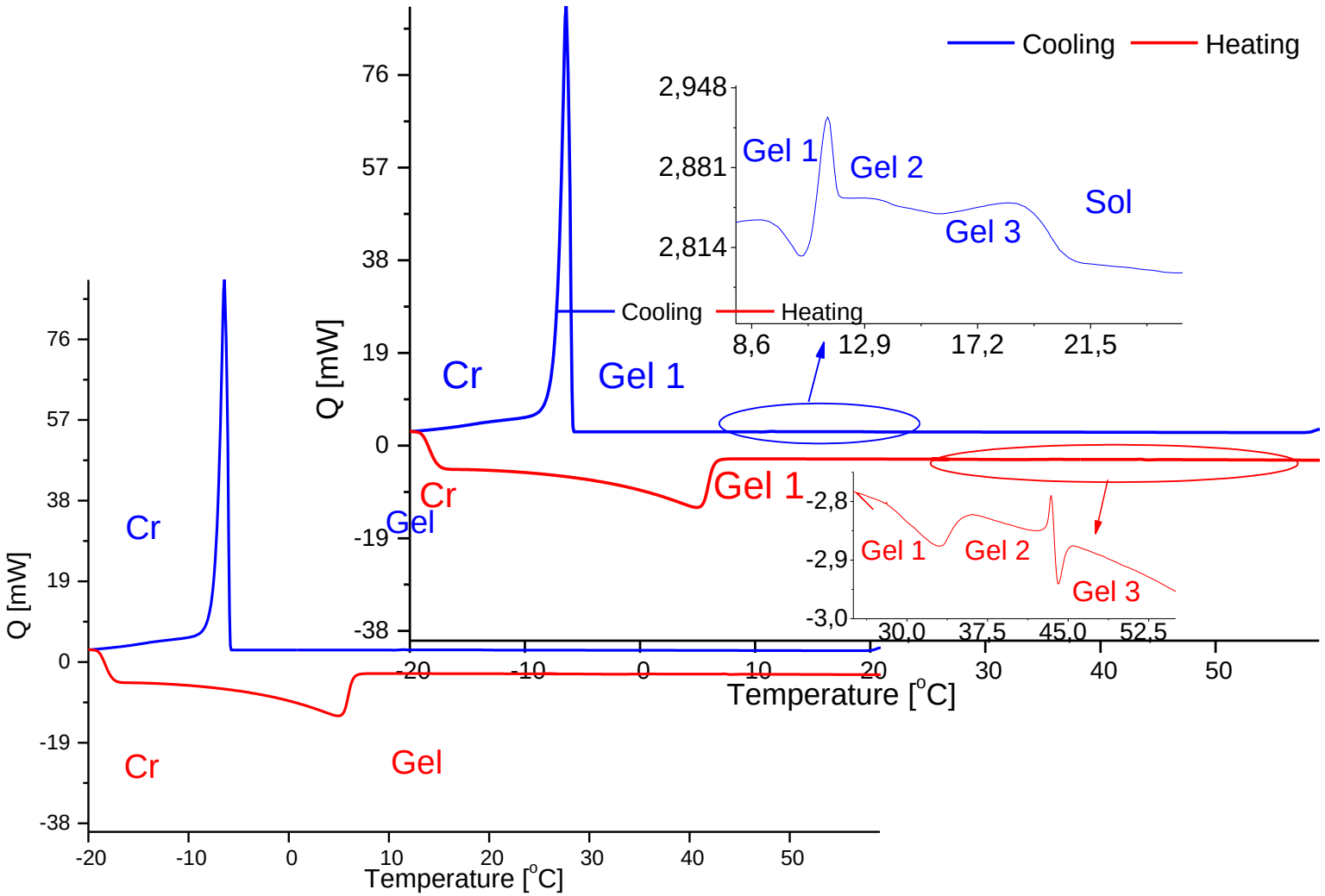
m = -4.0 ± 0.2 – objects with a smooth surface,

m = -3.6 ± 0.1 – surface fractal,

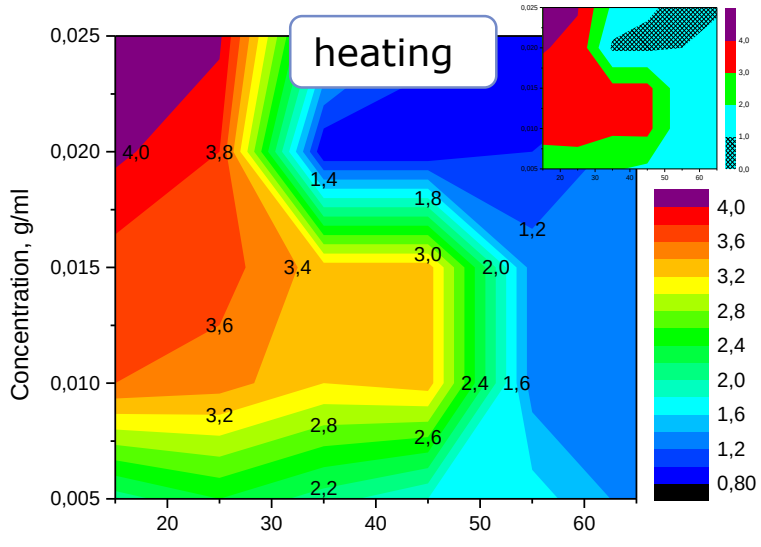
m = -2.0 ± 0.1 – a system consist from the fully separated lamellas

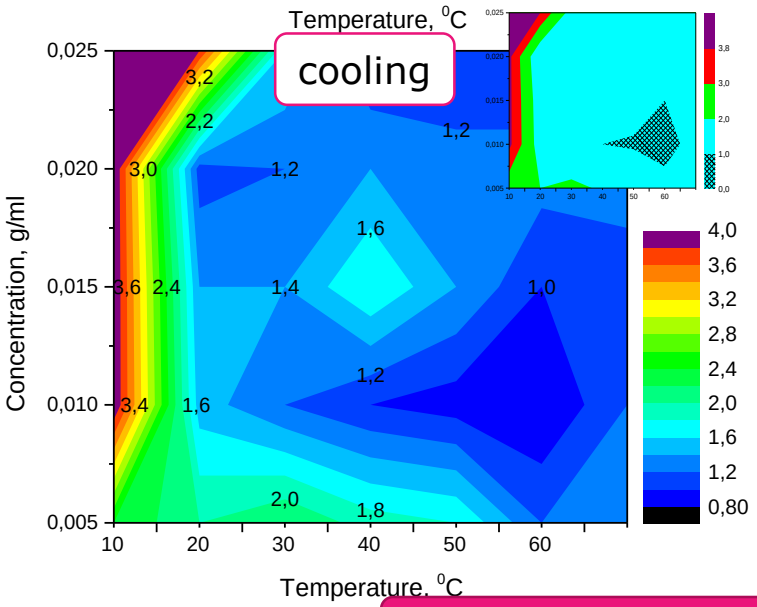
*Increasing of the temperature led to the **morphology transitions Gel 1 → Gel 2 and Gel 2 → Gel 3.***

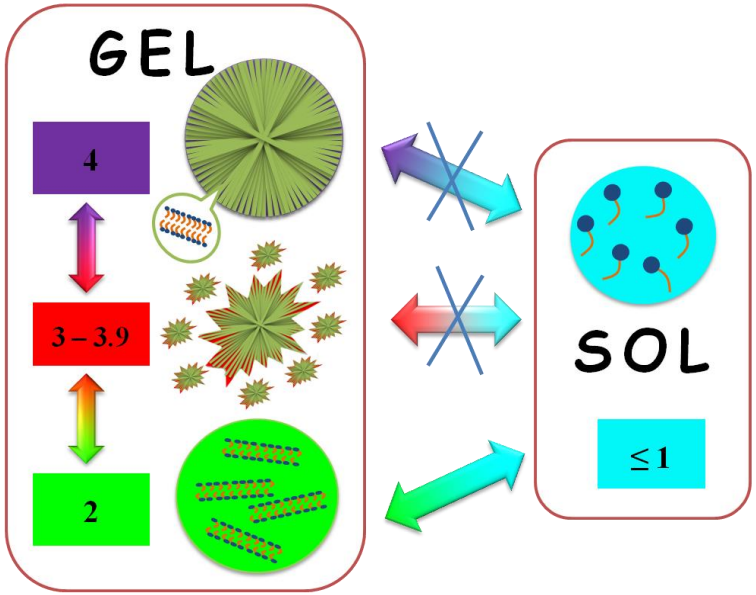
DSC METHOD: *Morphology transition in Gel phase*



SANS METHOD: *Sol – Gel transition*





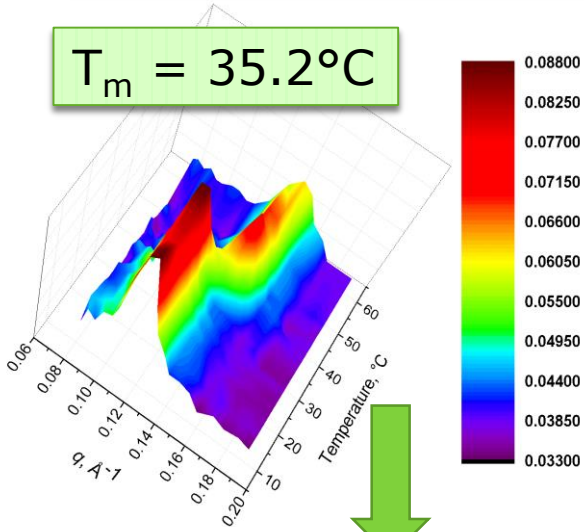


Proposed Sol – Gel transition scheme for the 7OPhOLCA in DMSO-d_6 determined by SANS. The values 4, 3.0 - 3.9, 2 and 1 correspond to the objects with a smooth surface, surface fractal, lamellas in solution and disordered state, respectively

Gel – Sol transition is reversible with hysteresis on the temperature

PHASE TRANSITION OF PC MEMBRANES IN THE SULFOXIDES PRESENTS

T_m = 35.2°C

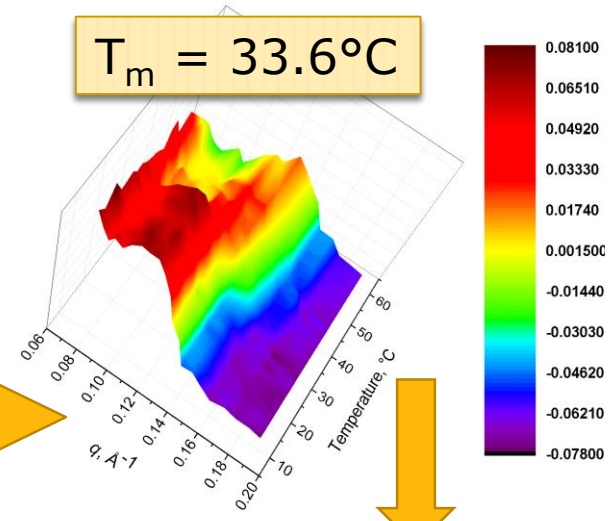


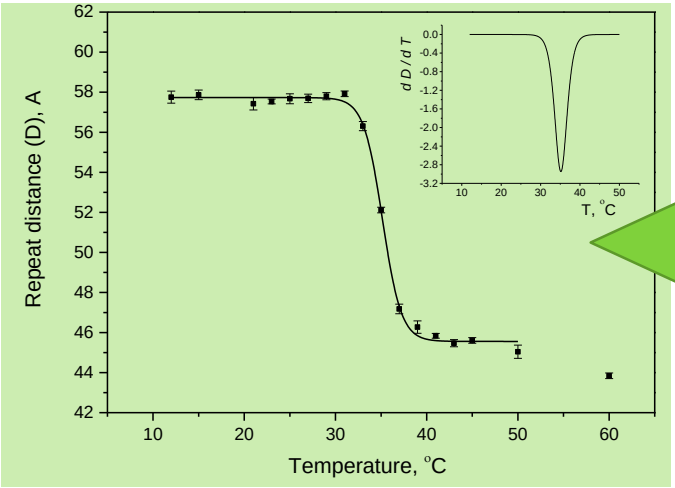
Phase diagrams of the **spontaneous** MLVs DMPC (2 wt %)

in DMSO/$D_2$0
X_{DMSO} = 0.2

in DESO/$D_2$0
X_{DESO} = 0.2

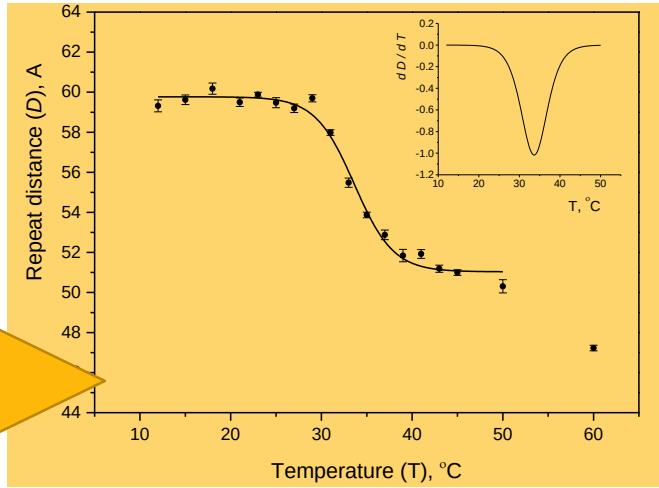
T_m = 33.6°C



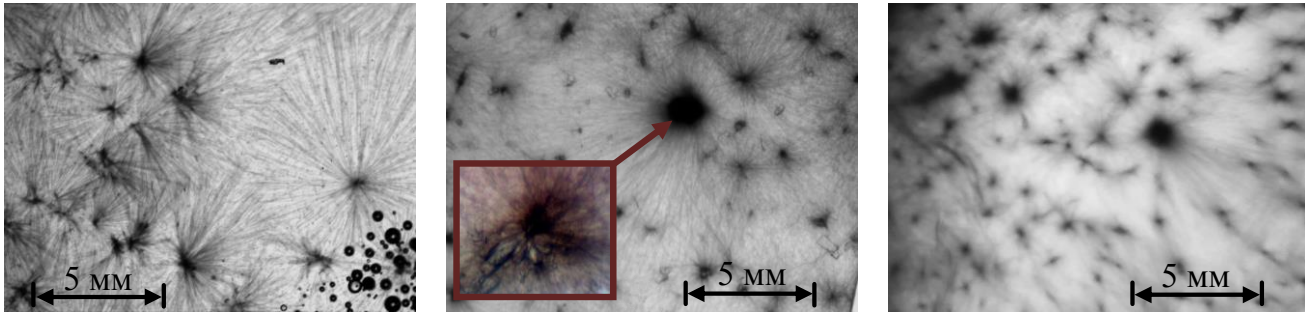


Transition
$L_{\beta'} \rightarrow L_{\alpha}$

Transitions
$L_{\beta'} \rightarrow P_{\beta'} \rightarrow L_{\alpha}$

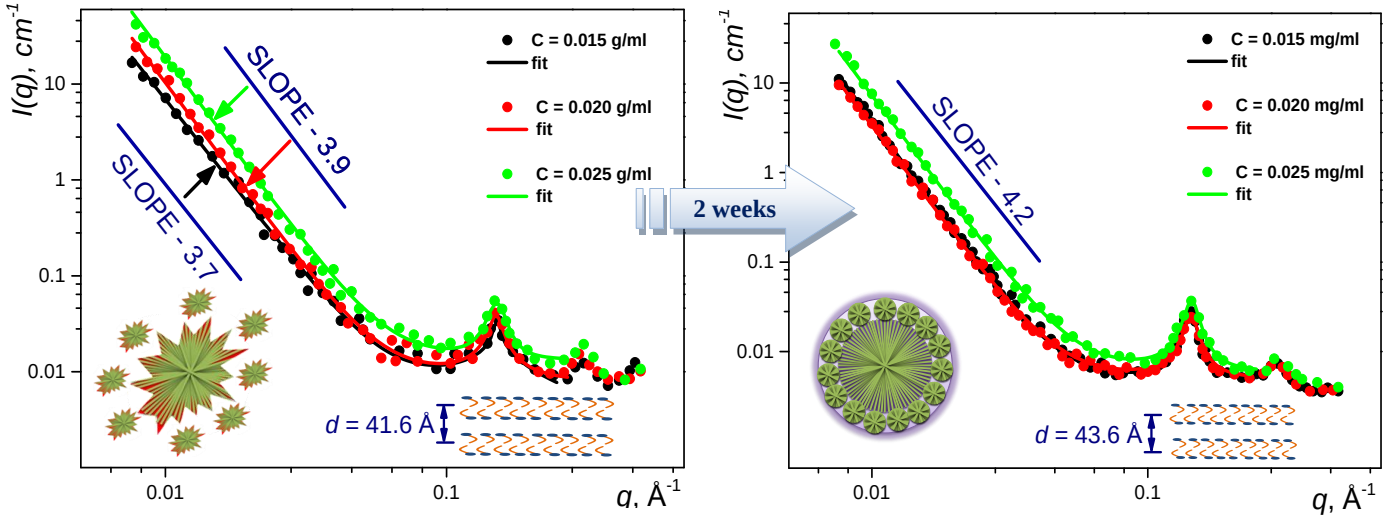


SANS METHOD: Time effect



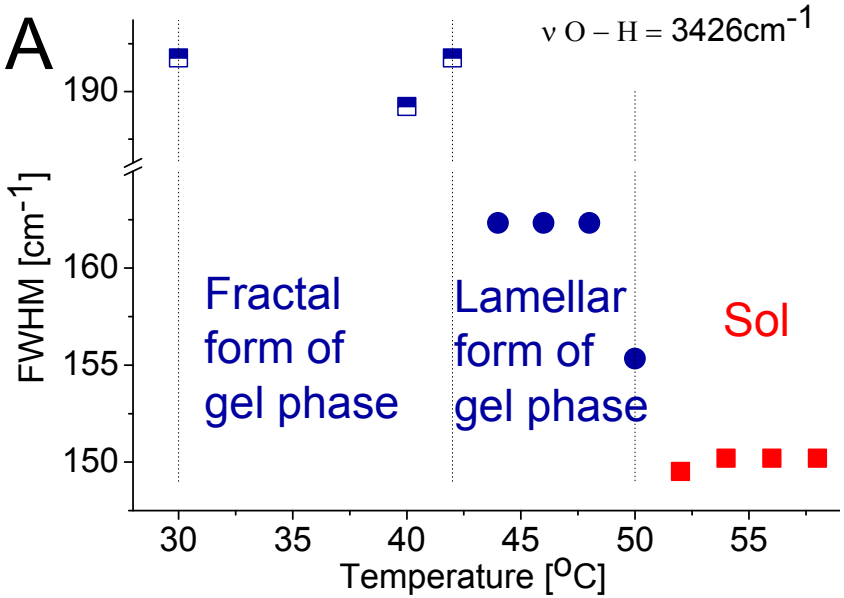
A ***B*** ***C***

Optical microscopy image for 7OPhOLCA in DMSO-d_6 at concentration C = 0.025 g/ml (***A***) after preparation, (***B***) after 4 days with max magnification 6.3x of the crystallization center and (***C***) after 14 days



SANS curves for 7OPhOLCA in DMSO-d_6 with C = 0.015, 0.020 and 0.025g/ml at T=20°C after preparation (***left***) and after 14 days (***right***)

INFRARED SPECTROSCOPY (FT - IR)



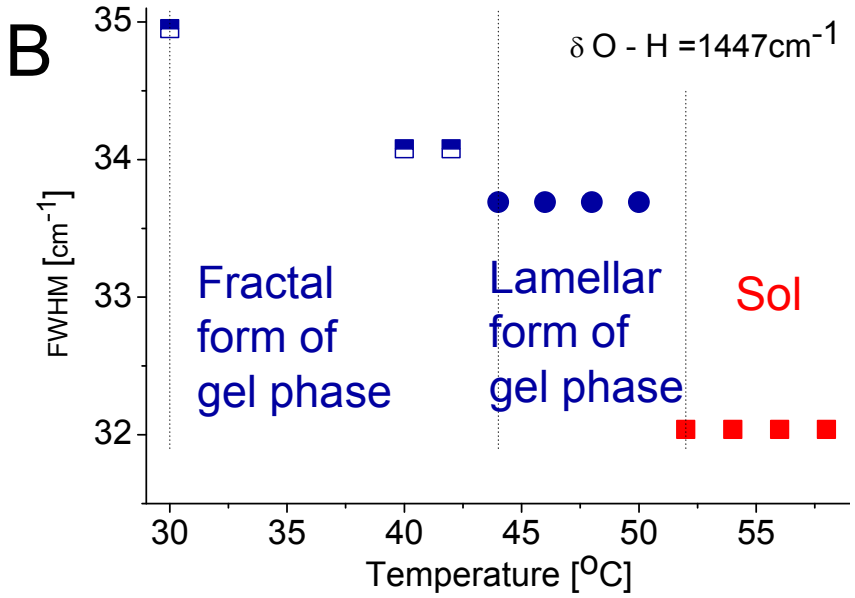


Figure of full-width at half-maximum (FWHM) in function of temperature of hydroxyl group, during heating. A – stretching vibrations (vOH); B – deformation vibrations (δOH) in the range of temperature from 30°C to 60°C for sample ”3”.

SUMMARY

Type of transition		HEATING CYCLE					
		0.015g/ml				0.025g/ml	
		DSC 5deg/min 14.02mg	SANS	FTIR		DSC 2deg/min 26.21mg	SANS
Cr - Gel	T_p	4.72	X	X		4.37	X
	ΔH	61.21				52.99	
	ΔS	0.22028				0.19094	
Gel - Fractal form of gel	T_p	32.92	X	X		X	25
	ΔH	0.20				X	
	ΔS	0.00065				X	
Fractal form of gel - Lamellar form of gel	T_p	42.25	45	42		X	28
	ΔH	0.03				X	
	ΔS	0.00010				X	
Lamellar form of gel - Sol	T_p	X	52	50		33.60	35
	ΔH	X				1.29	
	ΔS	X				0.00421	

		COOLING CYCLE					
Type of transition		0.015g/ml				0.025g/ml	
		DSC 5deg/min 14.02mg	SANS	FTIR		DSC 2deg/min 26.21mg	SANS
Sol - Lamellar form of gel	T_p	18.58	18	X		X	29
	ΔH	0.21				X	
	ΔS	0.00072				X	
Lamellar form of gel – Fractal form of gel	T_p	14.99	15	X		X	21
	ΔH	0.08				X	
	ΔS	0.00028				X	
Fractal form of gel - Gel	T_p	11.46	11	X		15.29	18
	ΔH	0.09				1.18	
	ΔS	0.000316				0.00409	
Gel – Cr	T_p	-6.41	X	X		-4.95	X
	ΔH	81.90				69.64	
	ΔS	0.29296				0.25041	

USER POLICY IN FLNP JINR

IBR-2 Spectrometers:

Diffraction: HRFD, DN-2, DN-12, DN-6, SKAT-EPSILON, FSD

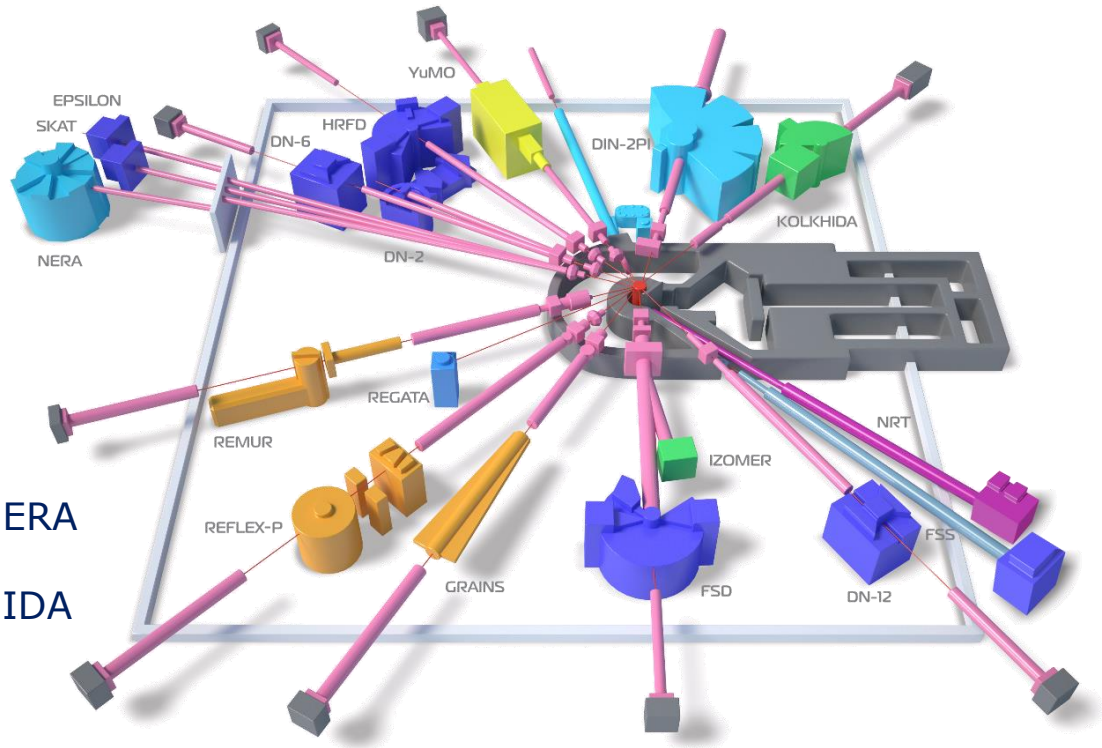
Small-angle scattering: YuMO

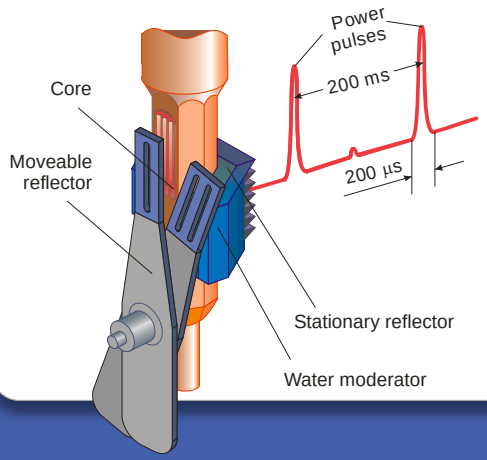
Reflectometry: REMUR, REFLEX, GRAINS

Inelastic scattering: DIN-2PI, NERA

Nuclear Physics: ISOMER, KOLHIDA

Irradiation Facility





Period for proposal submission
September 1 - October 15
March 1 - April 15

http://ibr-2.jinr.ru

Conferences on Condensed Matter Research at IBR-2 reactor

Thank you for your attention!

Up to new meetings in Dubna

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Yu. Gorshkova
FLNP JINR

WHAT WE CAN LEARN USING SANS: OBJECTS AND PARAMETERS

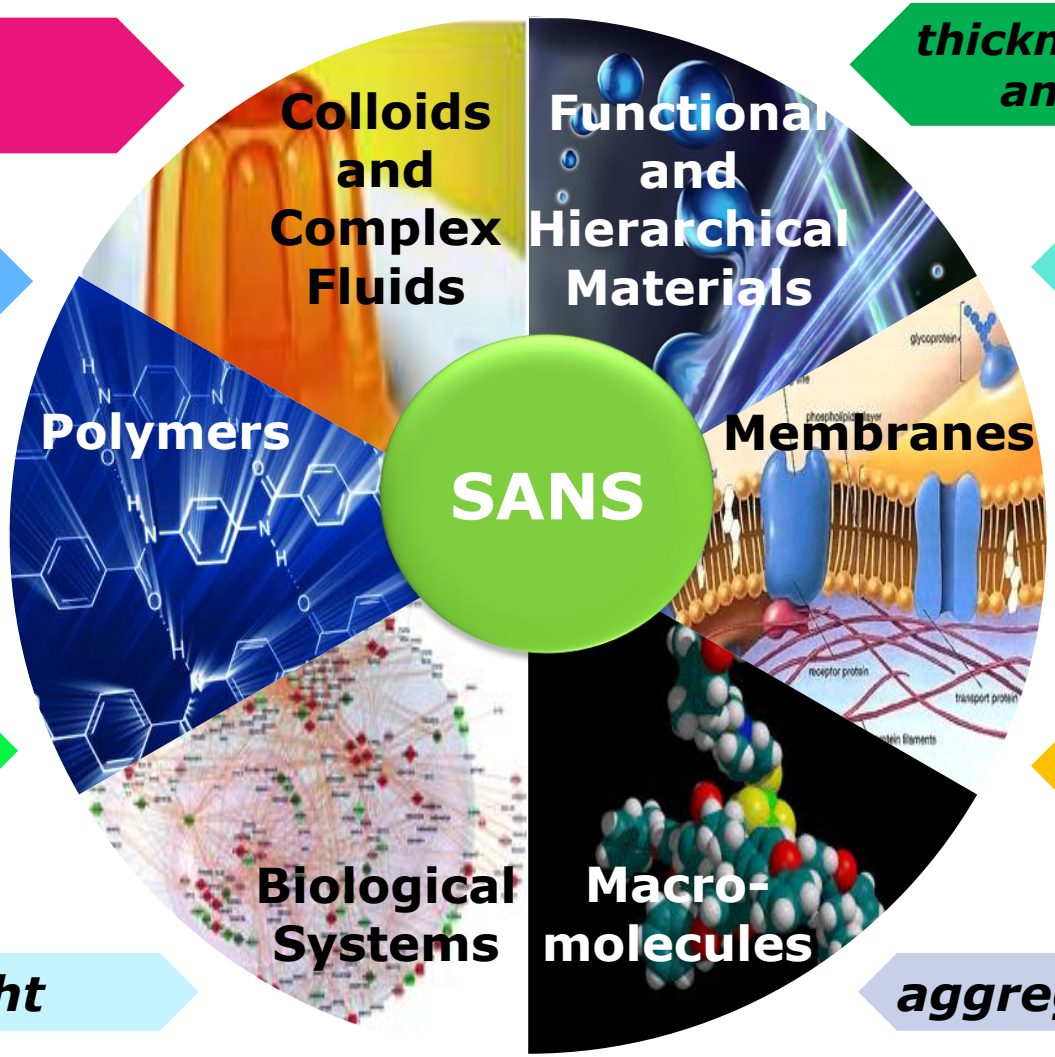
shape and size of particles

structure

volume fraction

size distribution

molecular weight



thickness of the layers and repeat spacing

particles density

mosaicity

fractal dimension

aggregation number

Main parameters of YuMO instrument

Parameters	Value
Flux on the sample (thermal neutrons)	$10^7 – 4x10^7$ n/(s cm^2) [1]
Used wavelength	0.5 Å to 8 Å #
Q-range	$7x10^{-3} – 0.5$ Å^{-1}
Dynamic Q-range	q_{max}/q_{min} up to 100
Specific features	Two detectors system [2,3], central hole detectors
Size range of object *	500 – 10 Å
Intensity (absolute units -minimal levels)	0.01 cm^{-1}
Calibration standard	Vanadium during the experiment [4]
Size of beam on the sample	8 – 22 mm^2 @
Collimation system	Axial
Detectors	He^3 -fulfiled, home made preparation, 8 independent wires [5]
Detector (direct beam)	^{6}Li-convertor (home made preparation)
Condition of sample	In special box in air
Q-resolution	low, 5-20%
Temperature range	-50°C -+130°C ^ (Lauda)
Temperature range	700 °C ** (Evrotherm)
Number of computer controlled samples	14 ***
Background level	0.03 – 0.2 cm^{-1}
Mean time of measurements for one sample	1 h +
Frequency of pulse repetition	5 Hz
Electronic system	VME
The instrument control software complex	**SONIX** [6]

WHAT WE CAN LEARN USING SANS: SIZE RANGE