

Confinement of Structural Isomers in MCM-41-SIL Matrix as Seen by Extrinsic Probes via PALS and ESR: *n*-BuOH vs. *t*-BuOH

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Introduction and Motivation

The structural-dynamic state of **organic compounds** in the **bulk** and **confined** states is usually characterized by two basic kinds of **experimental techniques**:

- conventional (standard) **macroscopic thermodynamic techniques**, such as DSC via enthalpy or/and using **diffraction, scattering, resonance and relaxation** ones based on microscopic **intrinsic probes**, such as static and dynamic density fluctuation, magnetic and electric dipole reorientation of compound's constituents
- non-standard **microscopic techniques**, such as **positron annihilation lifetime** or/and **spectroscopy (PALS)**, **electron spin resonance (ESR)** utilizing appropriate **microscopic atomic- or/and molecular-sized extrinsic probes**.

Structural isomerie is the well-known aspect of **organic compounds** consisting often in dramatic changes of physical and chemical properties of a series of **organics** having the **same summary chemical formula** and the **different structural formulae**.

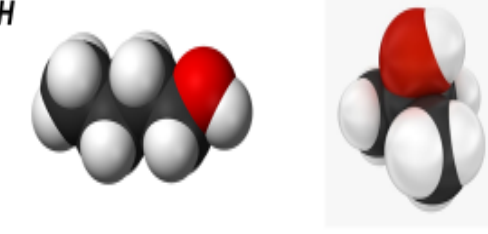
In our contribution, a combined **extrinsic probe** approach is used to characterize selected group of two from the four structural isomers of **butanol**, namely, ***n*-butanol** and ***tert*-butanol** in the **bulk** and **confined** physical states as seen by the above-mentioned microscopic **PALS** and **ESR** techniques as well as to reveal their mutual relationships suggesting the similar or distinct underlying processes.

Model components:

confined organic media:

two limiting structural isomers of polar protic **butanol** $C_4H_{10}O$

***n*(normal)-butanol** $CH_3CH_2CH_2CH_2OH$
***t*(tertiary)-butanol** $(CH_3)_3COH$



- potential effects of **molecular form**, i.e., linear vs. globular molecular shape and related **molecular aggregation**, i.e., chain-like vs. micelle-like clusters and related **hydrophilicity vs. hydrophobicity** character of these clusters

confining inorganic hard-type matrix:

MCM-41-SIL

- native **silica matrix** with i) ordered array of parallel, i.e., non-crossed cylindrical pores of $D_{pore} = 40 \text{ \AA}$
- hydrophilic **silanol groups -Si-OH**

Internal and external physico-chemical factors in the bulk vs. confinement problem by **intrinsic** vs. **extrinsic** techniques

In general, the **confinement** topic is the multi-parameter one depending on:

- physico-geometric factor** i.e. geometrical hindrance on medium by pore of matrix



- physico-chemical factor** i.e. physico-chemical properties of pore surface and interface of medium / matrix system



In the case of **extrinsic** techniques, one additional factor, i.e., relative strength of interaction between **organic medium** and **inorganic matrix** vs. that between **extrinsic probe** and **organic medium** vs. **inorganic matrix** are of important relevance.

Experimental techniques:

- atomistic** i.e. **ortho-positronium, (o-Ps) - positron annihilation lifetime spectroscopy (PALS)**

$$R_{o-Ps} = 0.53 \text{ \AA}$$

- molecular** i.e. **stable free radicals**, the so-called **spin probes** - **electron spin resonance (ESR)**

$$R_{TEMPO} = 3.5 \text{ \AA}$$



bulk vs. confined medium and confined matrix: chemical composition, physical micro-structure, static and dynamic fluctuations

o-Ps probe: size, quantum-mechanical nature

spin probe: size, shape, polarity => potential interaction with medium, matrix

DSC data: standard cooling/heating scans with Φ_c and $\Phi_h = -10/+10 \text{ K/min}$

bulk *n*-BuOH vs. confined *n*-BuOH

Bulk states:

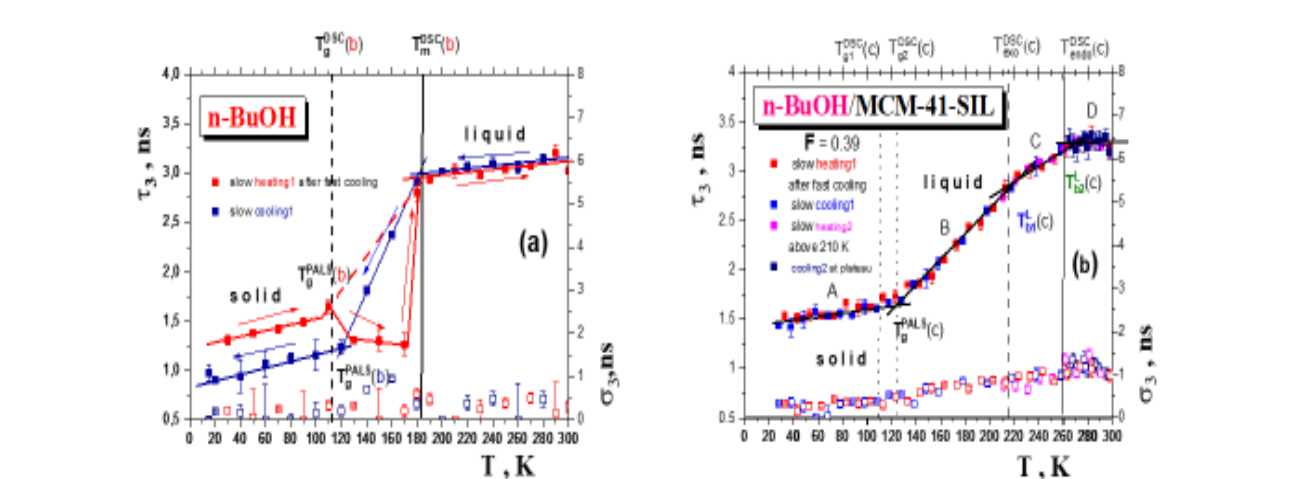
- absence of evident T_g transition during **cooling** and **heating** in ***n*-BuOH** contrary to ***t*-BuOH**, but its presence during **subsequent heating** in ***n*-BuOH**
- presence of 2 exo- due to crystallization and endo-events due to melting in ***n*-BuOH** and even 3 endo-events due to T_{DSC} , T_m and T_g in ***t*-BuOH** due to distinct **crystallization** and **H-bonding abilities** depending on **molecular shape:** linear vs. globular

bulk *t*-BuOH vs. confined *t*-BuOH

Confined states:

- apparently without any pronounced thermo-events, i.e. very spreaded T_g and the absence of T_{DSC} and T_m events
- differences: after enlargement: 2 T_g effects in **confined *n*-BuOH** - see later

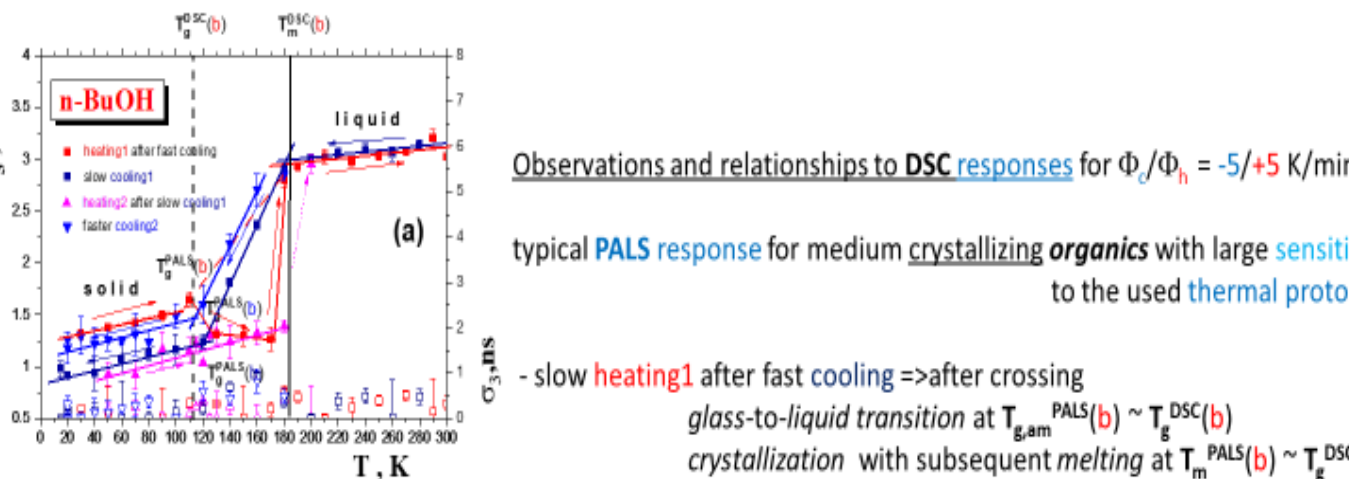
PALS — mutual comparison of bulk *n*-BuOH vs. confined *n*-BuOH/MCM-41-SIL systems



Empirical findings:

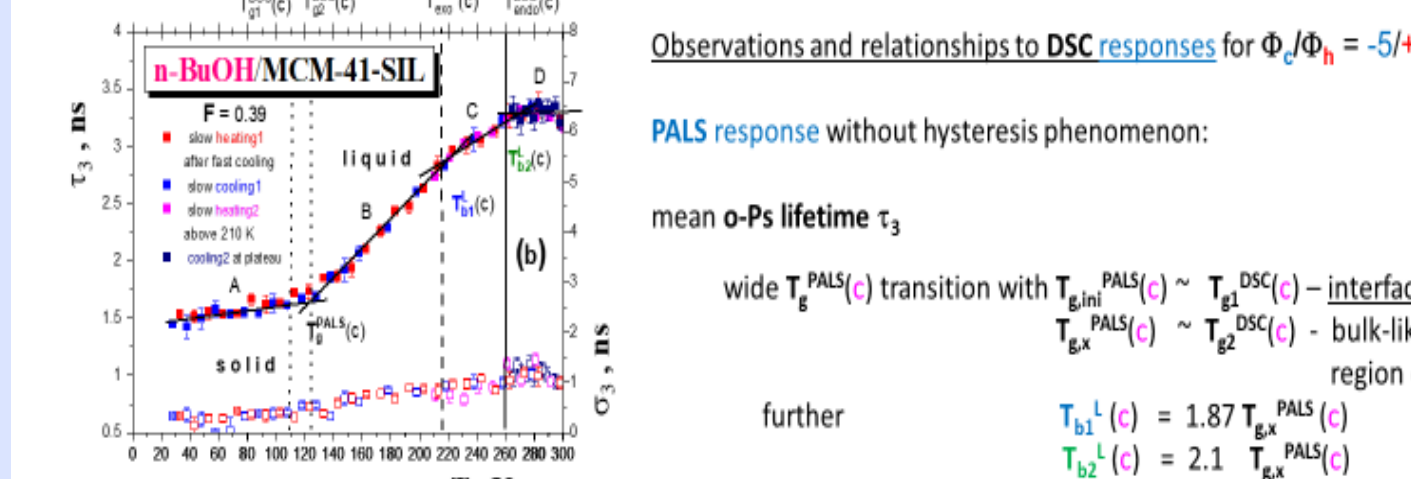
- amorphization** and **heterogenization** of crystallizing linear ***n*-BuOH** medium with larger mean **free volume size** and broader **free volume hole size distribution** in **confined *n*-BuOH/MCM-41-SIL** system

PALS data: bulk *n*-BuOH



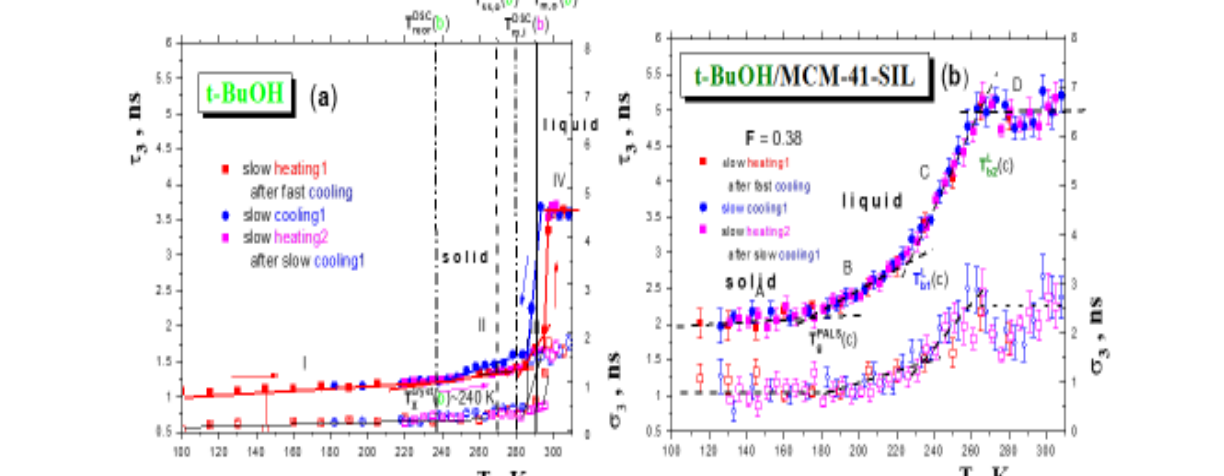
- Observations and relationships to **DSC** responses for $\Phi_c/\Phi_h = -5/+5 \text{ K/min}$: typical PALS response for medium **crystallizing organics** with large sensitivity to the used **thermal protocol**:
 - **slow heating** after fast cooling => after crossing **glass-to-liquid transition** at $T_{g,slow}^{PALS}(b) \sim T_{DSC}(b)$ crystallization with subsequent **melting** at $T_m^{PALS}(b) \sim T_{DSC}(b)$
 - **slow cooling** => crystallization over wide T range with $T_{DSC,slow\ cool}^{PALS}(b) > T_{DSC}(b)$
 - **heating** after very slow cooling => melting at $T_m^{PALS}(b) \sim T_{DSC}(b)$
 - **faster cooling** => shift for crystallization with $T_{DSC,fast\ cool}^{PALS}(b) > T_{DSC}(b) > T_{DSC}(b)$

PALS data: confined *n*-BuOH/MCM-41-SIL



- Observations and relationships to **DSC** responses for $\Phi_c/\Phi_h = -5/+5 \text{ K/min}$: **PALS** response without hysteresis phenomenon: mean **o-Ps** lifetime τ_1 wide $T_{g,slow}^{PALS}(c)$ transition with $T_{DSC}(c) \sim T_{DSC}(c)$ - interface region bulk-like "cage" region of pore further $T_{g,slow}^{PALS}(c) = 1.87 T_{DSC}(c)$ $T_{g,slow}^{PALS}(c) = 2.1 T_{DSC}(c)$ being atypical high even for protic polar organics and moreover $T_{g,slow}^{PALS}(c) \sim T_{DSC}(c)$ i.e. some reorganization, i.e. ordering followed by disordering during **heating** or **cooling**
- o-Ps** lifetime dispersion σ_1 wider in comparison with that for **bulk *n*-BuOH** due to the co-existence of **interface** and **"core"** regions in pore

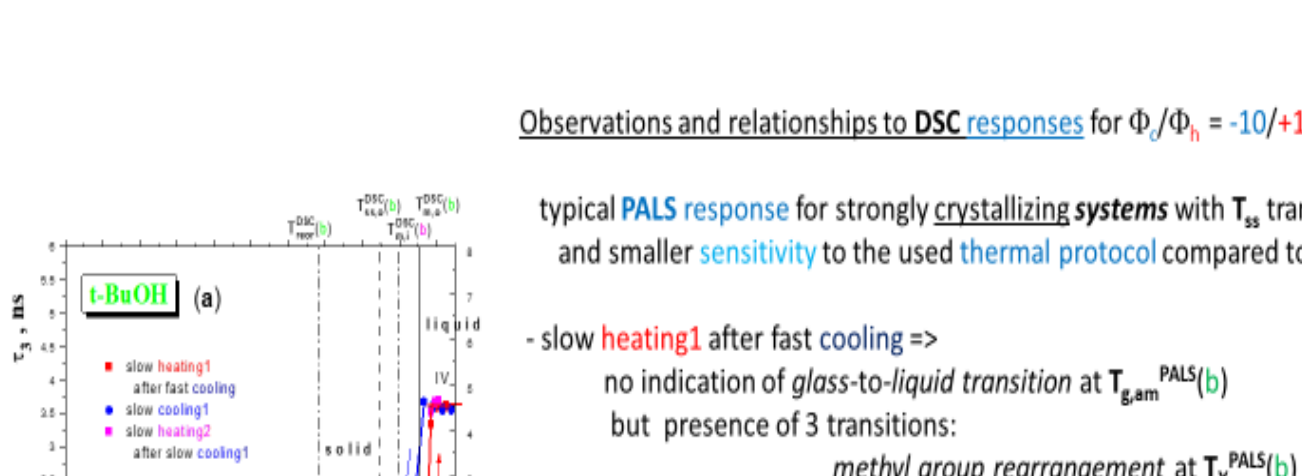
PALS — mutual comparison of bulk *t*-BuOH vs. confined *t*-BuOH/MCM-41-SIL systems



Empirical findings:

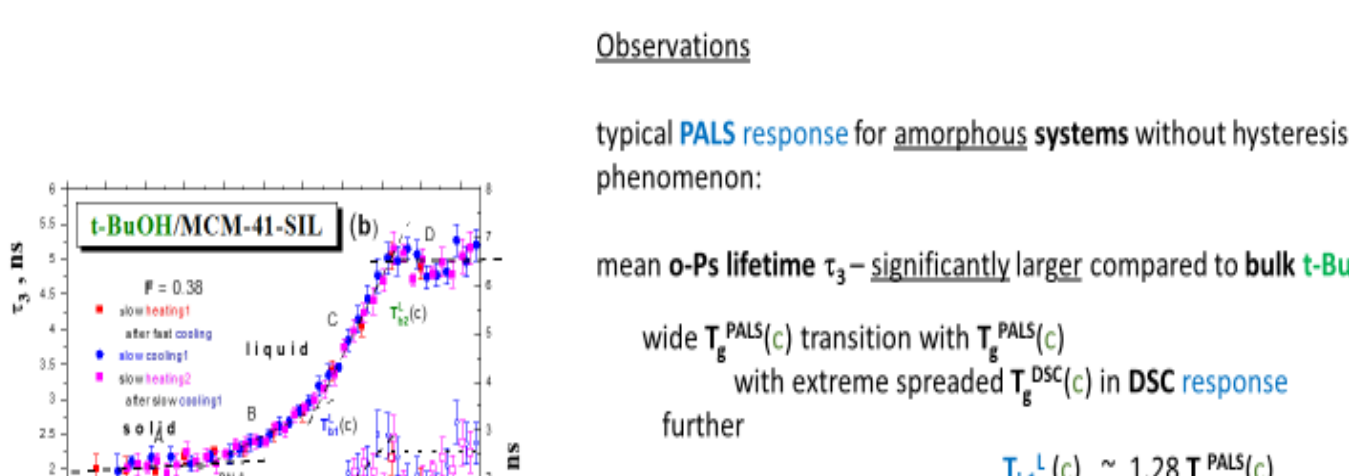
- amorphization** and **heterogenization** of strongly crystallizing globular ***t*-BuOH** medium with significantly larger mean **free volume size** as well as broader **free volume hole size distribution** in **confined *t*-BuOH/MCM-41-SIL** system also in comparison with **confined *n*-BuOH/MCM-41-SIL** system

PALS data: bulk *t*-BuOH



- Observations and relationships to **DSC** responses for $\Phi_c/\Phi_h = -10/+10 \text{ K/min}$: typical PALS response for strongly crystallizing systems with T_g transition and smaller sensitivity to the used **thermal protocol** compared to ***n*-BuOH**:
 - **slow heating** after fast cooling => no indication of **glass-to-liquid transition** at $T_{g,slow}^{PALS}(b)$ but presence of 3 transitions: methyl group rearrangement at $T_{DSC}(b) \sim T_{DSC}(b)$ solid-to-solid transition at $T_{DSC}(b) \sim T_{DSC}(b)$ and melting at $T_m^{PALS}(b) \sim T_{DSC}(b)$
 - **slow cooling** => crystallization over narrow T range with $T_{DSC,slow\ cool}^{PALS}(b) > T_{DSC}(b)$
 - **heating** after very slow cooling => ss- and melting at $T_m^{PALS}(b)$ and $T_{DSC}(b)$

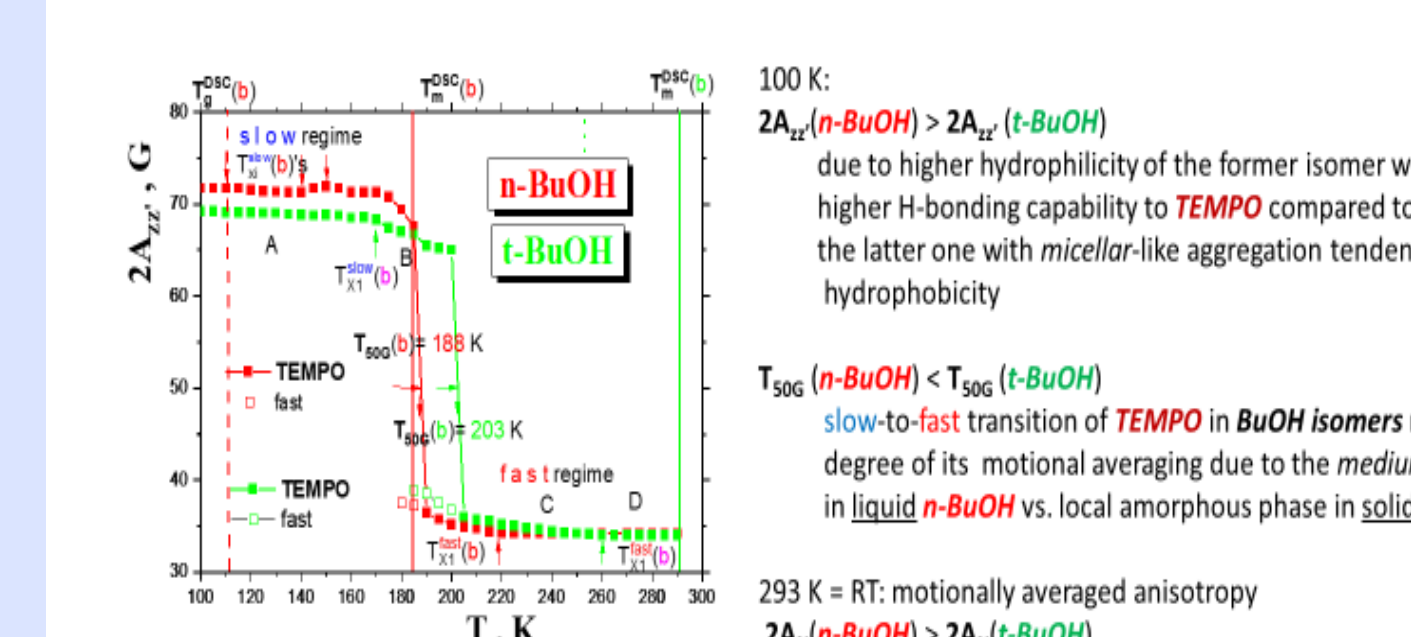
PALS data: confined *t*-BuOH/MCM-41-SIL



- Observations: typical PALS response for **amorphous systems** without hysteresis phenomenon: mean **o-Ps** lifetime τ_1 significantly larger compared to **bulk *t*-BuOH** wide $T_{g,slow}^{PALS}(c)$ transition with $T_{DSC}(c)$ with extreme spreaded $T_{DSC}(c)$ in DSC response further $T_{g,slow}^{PALS}(c) \sim 1.28 T_{DSC}(c)$ $T_{g,slow}^{PALS}(c) \sim 1.47 T_{DSC}(c)$ being typical rather to apolar organics due to the presence of **hydrophobic** clusters
- o-Ps** lifetime dispersion σ_1 significantly broader in comparison with that for **bulk *t*-BuOH** as well as with that for **confined *n*-BuOH/MCM-41-SIL** system due to the co-existence of **interface** and **"core"** regions in pore

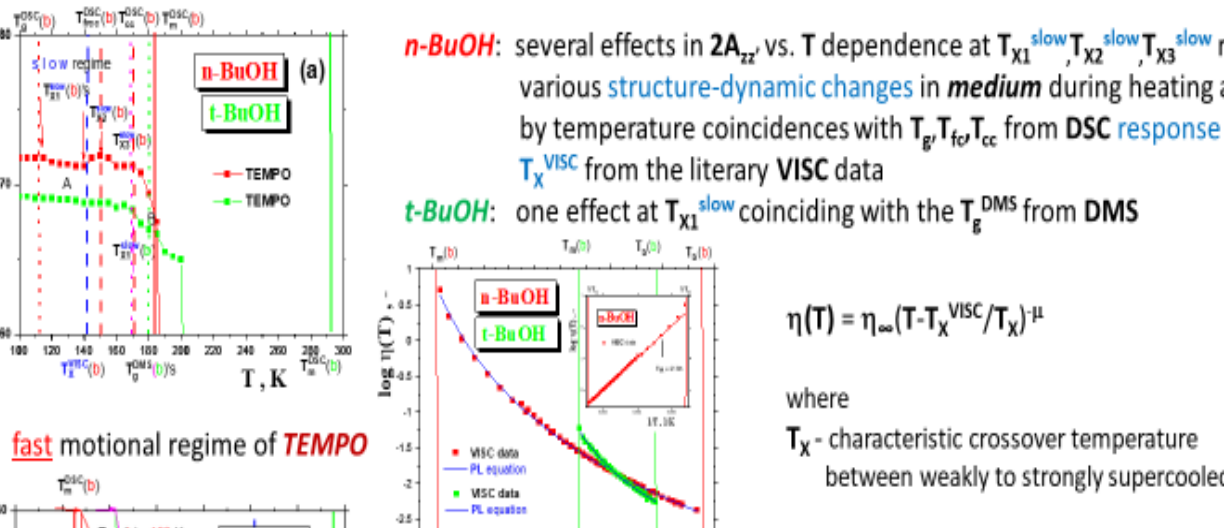
ESR data: mutual comparison of bulk *n*-BuOH/TEMPO vs. *t*-BuOH/TEMPO systems

anisotropic and isotropic hyperfine constants: $2A_{iso}(100K)$ and $A_{is}(RT)$ - measures of **probe - component (medium)** interaction and degree of changes of anisotropy averaging due to mobility of **bulk medium**



- 100 K: $2A_{iso}(n-BuOH) > 2A_{iso}(t-BuOH)$ due to higher hydrophilicity of the former isomer with higher H-bonding capability to **TEMPO** compared to the latter one with micellar-like aggregation tendency causing hydrophobicity
- $T_{DSC}(n-BuOH) < T_{DSC}(t-BuOH)$ slow-to-fast transition of **TEMPO** in **BuOH** isomers reflects degree of its motional averaging due to the medium's mobility in **liquid *n*-BuOH** vs. local amorphous phase in **solid *t*-BuOH**
- 293 K = RT: motional averaged anisotropy $2A_{iso}(n-BuOH) > 2A_{iso}(t-BuOH)$ dtd as for $2A_{iso}$

slow motion regime of TEMPO

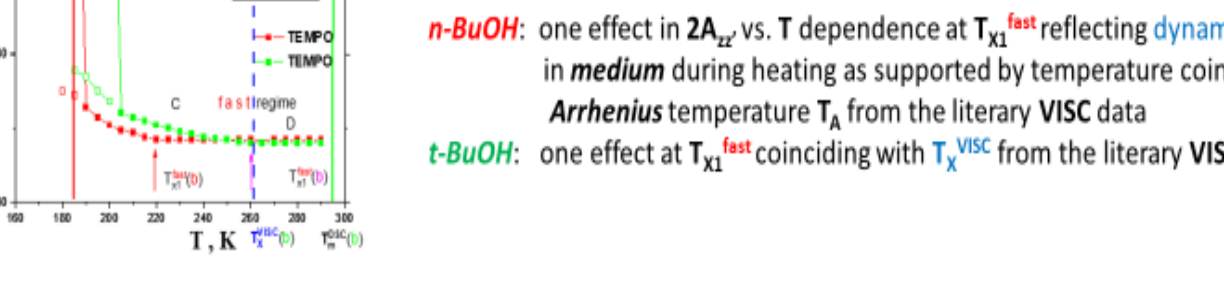


***n*-BuOH:** several effects in $2A_{iso}$ vs. T dependence at T_{DSC}^{slow} , T_{DSC}^{fast} reflecting various **structure-dynamic changes** in **medium** during heating as supported by temperature coincidences with T_g , T_m , T_{DSC} from DSC response as well as with T_{DSC} from the literary VISC data

***t*-BuOH:** one effect at T_{DSC}^{slow} coinciding with the T_{DSC}^{slow} from DMS

$\tau(T) = \tau_{\infty} [1 - T_{DSC}^{slow}/T]^p$ where T_{DSC}^{slow} characteristic crossover temperature between weakly to strongly supercooled liquid

fast motional regime of TEMPO



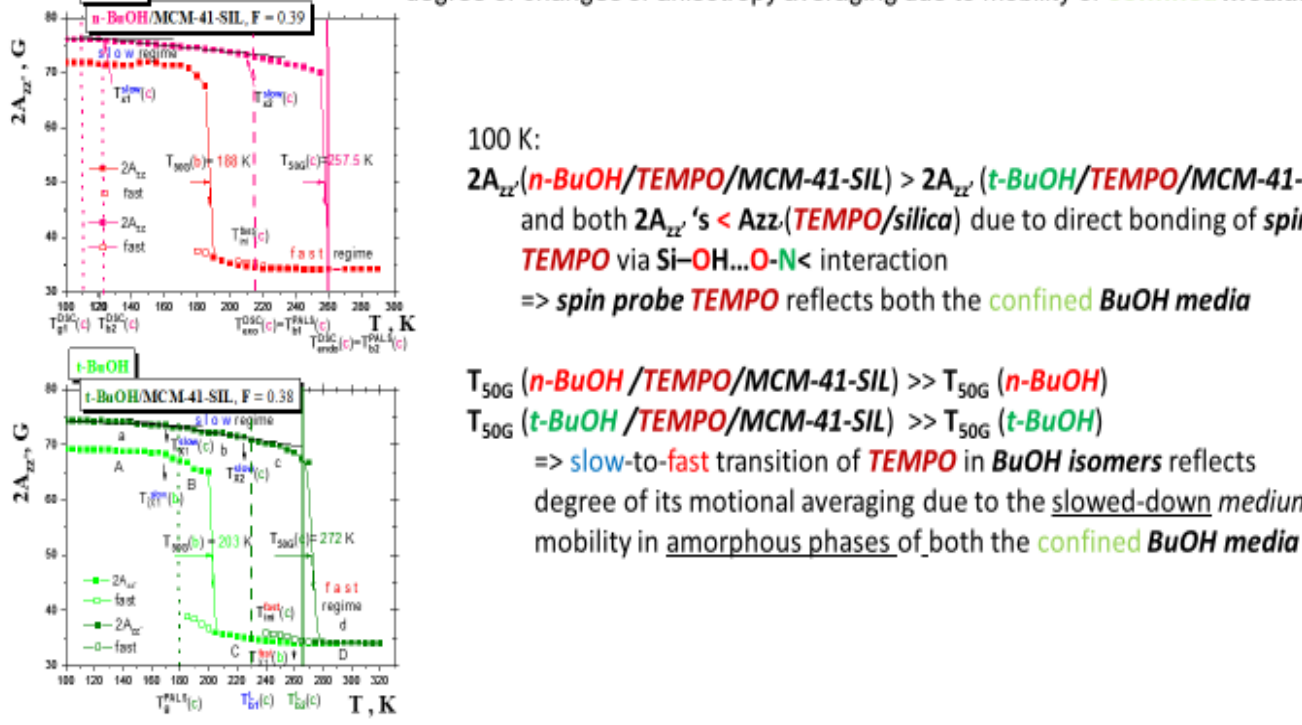
***n*-BuOH:** one effect in $2A_{iso}$ vs. T dependence at T_{DSC}^{fast} reflecting **dynamic change** in **medium** during heating as supported by temperature coincidence with **Arrhenius** temperature T_A from the literary VISC data

***t*-BuOH:** one effect at T_{DSC}^{fast} coinciding with T_{DSC}^{fast} from the literary VISC data

ESR data:

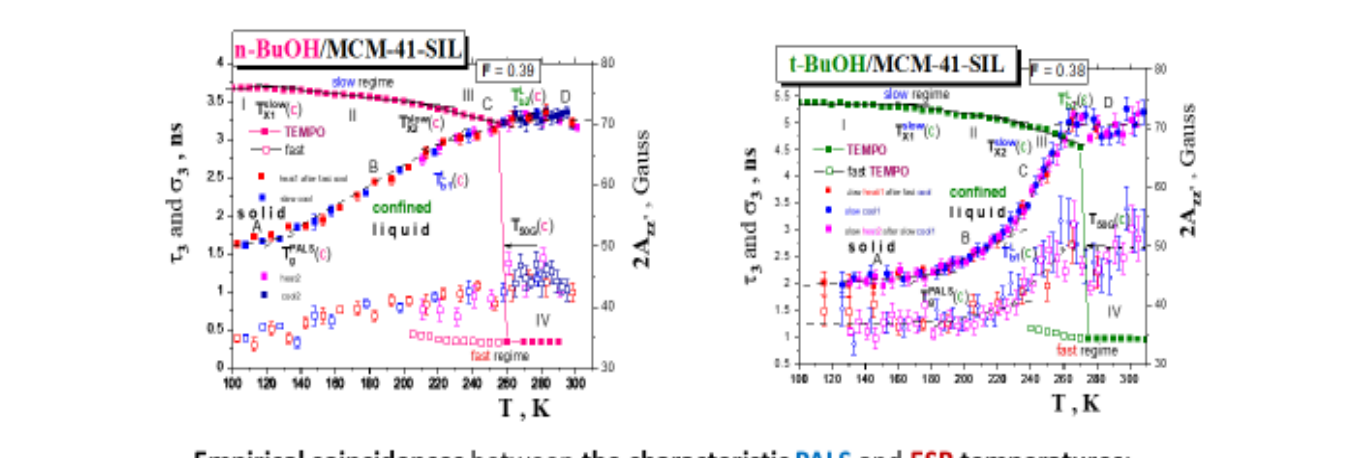
mutual comparison of confined *n*-BuOH/TEMPO/MCM-41-SIL vs. *t*-BuOH/TEMPO/MCM-41-SIL systems

anisotropic and isotropic hyperfine constants: $2A_{iso}(100K)$ and $A_{is}(RT)$ - measures of **probe - component (confined medium and/or confining matrix)** interaction and degree of changes of anisotropy averaging due to mobility of **confined medium**



- 100 K: $2A_{iso}(n-BuOH/TEMPO/MCM-41-SIL) > 2A_{iso}(t-BuOH/TEMPO/MCM-41-SIL)$ and both $2A_{iso} \propto \Delta z(\text{TEMPO}/\text{silica})$ due to direct bonding of **spin probe TEMPO** via **Si-OH...O-N** interaction => **spin probe TEMPO** reflects both the **confined BuOH media**
- $T_{DSC}(n-BuOH/TEMPO/MCM-41-SIL) > T_{DSC}(t-BuOH/TEMPO/MCM-41-SIL) > T_{DSC}(t-BuOH)$ => **slow-to-fast** transition of **TEMPO** in **BuOH** isomers reflects degree of its motional averaging due to the **slowed-down** medium's mobility in **amorphous phases** of both the **confined BuOH media**

Mutual comparison of PALS and ESR responses for both the confined BuOH/MCM-41-SIL systems



- Empirical coincidences between the characteristic **PALS** and **ESR** temperatures: 100-310K: four corresponding regions A-C @ I-IV **three characteristic PALS and ESR** temperatures: $T_{DSC}^{slow}(c) \sim T_{DSC}^{slow}(c)$ $T_{DSC}^{fast}(c) \sim T_{DSC}^{fast}(c)$ $T_{DSC}^{slow}(c) \sim T_{DSC}^{slow}(c)$
- => the similar or the same underlying processes controlling the respective changes in free volume expansion and spin probe mobility

Summary and Conclusions

A combined investigation of the effect of **structural isomerie** represented by the two limiting isomers of **butanol**, namely, ***n*-BuOH** and ***t*-BuOH** using extrinsic probe **PALS** and **ESR** techniques together with standard **DSC** one was performed.

- The main empirical findings are as follows:
 - in the **bulk** state the structural isomer effect in **BuOH's** on their **PALS** and **ESR** response is determined dominantly by molecular shape and related **hydrophilicity** of the constituents, i.e. molecules or/and their clusters
 - in the **confined** state in the mesoporous native **MCM-41-SIL** matrix, both the **structural isomers** exhibit similar **global PALS** behavior consisting in amorphization and strong heterogenization of the confined **BuOH media**, i.e., enlargement of mean **free volume** and drastic increase of **free volume distribution** with specific differences in the related parameters
 - in the **confined** state in the mesoporous **MCM-41-SIL** matrix, both the **structural isomers** exhibit similar **global ESR** behavior consisting in increase of the **constituent-spin probe TEMPO** interaction and very strong slowing down of the **spin probe TEMPO** mobility in the **confined BuOH media** with the mutual coincidences between the characteristic **PALS** and **ESR** temperatures of the respective changes in the **free volume expansion** and the **spin probe TEMPO** mobility in spite of the fact that the increased free volume parameters lead to the decreased **spin probe TEMPO** dynamics