

Interproton distances changes during phase transitions in some heataccumulating/emitting organic materials studied by NMR

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Investigations on direct electric energy production using phase transition (PT) heat accumulation/emission is of great technology relevance. Solution of the problem gives an opportunity to use sustainable temperature changes during 24 hours. Phase transitions in materials named thermal energy storage (TES) systems, can be used for power generation - transformation of heat of fusion/crystallization in electric current power through thermoelectric Seebeck effect during the process of PT at cooling [1,2].

For phase transitions study was used isoparaffin $i\text{-C}_{22}\text{H}_{46}$ (docozan) of density $\rho = 774,9 \text{ kg/m}^3$, molecular weight $M = 310.6$, temperature of melting $T_m = 44^\circ\text{C}$, temperature and heat of allotropy transformation $T_A = 43^\circ\text{C}$, temperature of crystallization $T_{cr} = 30,4^\circ\text{C}$ with heat of $\Delta H_C = 11,7 \text{ kcal/mol}$. For measurements of NMR-relaxation structure-dynamical parameters (SDP) - spin-lattice T_{1i} , spin-spin T_{2i} relaxation times - the NMR relaxometer NMR-10/PC was used. It has resonance frequency $\nu_0 = 9,2 \text{ MHz}$ and is described in our paper [3]. Temperature of samples was maintained with accuracy $\pm 0,2^\circ$ by thermo stabilization unit of our patent [4]. Spin-lattice T_{1i} relaxation times were determined using spin-echo recovery sequence $90^\circ\text{-}\tau\text{-}90^\circ\text{-}\tau_0\text{-}180^\circ$. For spin-spin T_{2i} relaxation times measurements $90^\circ\text{-}\tau\text{-}(180^\circ\text{-}2\tau\text{-})_N$ sequence was used. Experimental error of measurements was: for relaxation times $\pm 3\div 4\%$, for NMR-signal amplitudes recurrence $\pm 2\%$, and could be reduced $(n)^{1/2}$ times using n accumulations.

It was established, that solidification processes for $i\text{-C}_{22}\text{H}_{46}$ two proton phases end not only at different temperatures T_K , but also at different times t_k (fig.2) which depends from molecular motions restrictions. For proton phase B they are $T_K = 34^\circ\text{C}$ and $t_k = 76 \text{ min}$, for A they are $T_K = 22^\circ\text{C}$ and $t_k = 156 \text{ min}$. with the end of phase transition of paraffin $i\text{-C}_{22}\text{H}_{46}$ to crystal state. It was considered, that in high-temperature approximation relaxation rate $(T_{1,2})^{-1}$ have two types of contributions: - intramolecular $(T_{1,2})^{-1}_{\text{int}}$, which characterize relaxation from reorientations of CH_3 groups and cis-trans configuration motion of $\dots\text{-CH}_2\text{-CH}_2\text{-CH}_2\dots$ chains:

$$(T_{1,2})_{\text{int}}^{-1} = 3\gamma^4 h^2 \tau_R / 8\pi^2 R_{ij}^6 \quad (1)$$

and intermolecular $(T_{1,2})^{-1}_{\text{tr}}$ from translational forms of motions in melt of $i\text{-C}_{22}\text{H}_{46}$ [8]:

$$(T_{1,2})_{\text{tr}}^{-1} = \pi\gamma^4 h^2 N_{\text{TD}}(1 + 2a_0/5D\tau_D)/4a_0^3 \quad (2)$$

where $\gamma/2\pi = 4256/\text{sec}\cdot\text{gauss}$ – gyromagnetic ratio for protons, $h = 6,626\cdot 10^{-34}\text{J/s}$ – Plank constant, $N_1 = 6,75\cdot 10^{28}\text{ m}^{-3}$ – number of spins in cm^3 , a_0 – average molecular diameter, R_{ij} – average distance between protons (nm), τ_R and τ_D – correlation times of rotational and translational motions ($\tau_D = a_0/12D$), D – self diffusion coefficient. In colloid systems $(T_{2i})_{\text{int}}^{-1}$ is sufficiently greater, than $(T_{2i})_{\text{tr}}^{-1}$, for instance even for compact benzol molecule (interproton distance $R_{ij} = 0.257\text{ nm}$) is equal to 4,5% from the full relaxation rate, so eq(4) can be rewritten:

$$T_{1,2B}^{-1} = (3\gamma^4 h^2 / 4\pi^2 R_{ij}^6) \tau_0 \exp(E_A/RT) \quad (3)$$

where E_A – activation energy, from which inter-proton distances R_{ij} can be calculated, which changed from $R_{ij} = 0.26\text{ nm}$ to $R_{ij} = 0.23\text{ nm}$ at phase transition of crystallization.

1. Weaver S.G., Weaver D., Weaver S.P. (2010) Power generation using thermal gradients maintained by phase transitions. Patent of USA № US 7.810.330 B1.
2. Zalba B., Marin J.M., Cabeza L.F., Mehling H. (2003) *Applied Thermal Engineering* **23**, 251.
3. Kashaev R.S.-H., Idiatullin Z.Sh., Temnikov A.N. Device for sample thermostabilization in in relaxometer NMR (2006) Patent of Russian Federation on invention # 2319138.
4. Kashaev R.S., Faschiev N.R. (2011) *Applied Magnetic Resonance*, **41**, i.1, 31-43.