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Mild hydration of didecyldimethylammonium chloride modified DNA by 1H-nuclear magnetic resonance and by sorption isotherm

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The gaseous phase hydration of deoxyribonucleic acid and didecyldimethylammonium chloride ($C_{19}H_{42}ClN$) complexes (DNA-DDCA) was observed using hydration kinetics, sorption isotherm, and high power nuclear magnetic resonance. Three bound water fractions were distinguished: (i) a very tightly bound water not removed by incubation over silica gel, (ii) a tightly bound water saturating with the hydration time $t_1^h = (0.59 \pm 0.04)$ h, and a loosely bound water fraction, (iii) with the hydration time $t_2^h = (20.9 \pm 1.3)$ h. Proton free induction decay was decomposed into the signal associated with the solid matrix of DNA-DDCA complex ($T_{2S}^* \approx 30\,\mu s$) and two liquid signal components coming from tightly bound ($T_{2L_1}^* \approx 100\,\mu s$) and from loosely bound water fraction ($T_{2L_2}^* \approx 1000\,\mu s$). © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4789011]

I. INTRODUCTION

The ultimate bottom-up approach for the manufacturing of nanoscale systems needs controlled arrangements of molecules in 3D. One of suitable materials is DNA (deoxyribonucleic acid), known for its fundamental role in biology. It can self-assemble into complex networks and is therefore sometimes regarded as the "silicon of nano-world." The outstanding properties of DNA result from its unique double-helix structure[1] and today have not been reproduced in man made polymers. A single DNA strand can be considered as a polymer chain built of elementary building blocks referred to as nucleotides, consisting of deoxyribose sugar, a phosphate, and one of four bases [adenine (A), guanine (G), cytosine (C), thymine (T)]. Solid sate DNA is a highly transparent material with absorption edge located at 300 nm, what is crucial for many optoelectronic applications.

The backbone of DNA is strongly hydrophilic because the hydroxyl groups of the sugar residues form hydrogen bonds with water. The pristine DNA easily hydrates and can be dissolved only in water.[2,3] Regrettably, water is not a recommended solvent for spin-coating technique—a standard deposition method in the domain of organic photonics and electronics. A remedy to this limitation is based on the exchange reaction of the sodium cations with cationic surfactants as previously reported.[4] The resulting DNA-cationic surfactant complexes precipitate in water and become soluble in the range of common organic solvents such as alcohols and some halogenated solvents.

So far the best quality films were fabricated from DNA complexed with cetyltrimethyl-ammonium (CTMA). DNA-CTMA has large band gap of 4.7 eV. This is crucial for being efficient electron blocking layer (EBL) and improving light emission in organic light-emitting diodes (OLEDs). Relatively large dielectric constant of 7.8 for DNA–CTMA combined with very smooth surface of thin films make it a promising material for applications in FET transistor structures.[5] There were already reported panoplies of other devices employing DNA-CTMA complex, like devices using second and third order nonlinear optical effects,[6] low loss optical waveguides,[7] and organic photovoltaics.[8] DNA is also an efficient matrix for dispersing other molecular compounds. There are reports on lumophore-doped DNA and laser emission from solid state thin films of DNA.[9]

Because of these facts, DNA-CTMA is considered one of the most promising materials in DNA-based photonics and molecular electronics. Nevertheless, the quest for new, more efficient surfactants continues. It is accompanied by extensive studies aimed at a better understanding of the processes governing the formation of the structure and the properties of DNA-surfactant complexes in the solid state.

Hydration properties are still rather poorly understood for DNA-surfactant complexes. Water content in "dry" product may alter significantly its electronic properties. For example, in the case of pure DNA it was shown that the conductance of molecular assembly, having intermolecular contacts among them, may be strongly affected by the relative humidity.[10]

Native form of solid DNA molecule requires up to 40 wt. % of water. The relative humidity governs the structure adopted by rehydrated DNA lyophilisate, and variation in the hydration level usually results in further conformational changes.[11] The DNA helical structure is defined by the average number of water molecules associated with the nucleotides. These water molecules form the primary and the

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secondary hydration shells.[12] At reduced water vapor pressure, form B the most common for DNA alters to the more compact A form. This effect occurs at a water activity of approximately 0.80, which corresponds to about 20 water molecules per base pair.[13] It was established that if the sample is dehydrated once, the hydration shell never recovers.[14] Also it has been shown that some water molecules per base pair may remain even in extensively dried samples.[15] For example, Leal *et al.*[16] reported a residual water activity despite 24 h drying under high vacuum.

Molecular simulations suggest a quasi-2D percolation transition of water at the surface of the DNA double helix, at which the population of small clusters merges into an infinite network.[17]

Properties of DNA-lipid aggregates differ substantially from the starting DNA. During the swelling, the water uptake in the complex is consistently below that observed for pure DNA.[16] By means of diffraction techniques a peculiar molecular arrangement composed of alternating layers of cationic lipid membranes and tightly packed liquid-crystalline DNA strands was observed.[18] In other experiments, hexagonal phases were found.[19]

In this paper, we discuss the hydration properties of solid DNA complex with didecyldimethylammonium chloride (DDCA), an alternative surfactant to commonly used CTMA.

With varied environmental conditions the DNA-DDCA films underwent hydration process from gaseous phase. We analyzed this process in terms of the number and distribution of water binding sites, the sequence and the kinetics of their saturation, and the formation of very tightly, tightly and loosely bound water fractions. We tried to understand the molecular mechanism of structural changes during rehydration from the anhydrous state. We monitored the effect of the structure swelling which occurs for hydration reached for $p/p_0 = 100\%$.

II. MATERIALS AND METHODS

DNA sodium salt, isolated from frozen salmon milt and roe sacs, was purchased from CIST (Chitose Institute of Science and Technology, Japan). It was converted to DNA-DDCA (DDCA: didecyldimethyl-ammonium chloride, Fig. 1), a DNA-surfactant complex according to the procedure already described elsewhere.[20]

For the DNA-DDCA complex the range of the phase stability was tested by calorimetric experiments. DSC measurements were performed using DSC8000 Perkin-Elmer calorimeter. DNA-DDCA samples were placed into the aluminum pans routinely used in this instrument and then hydrated in desiccator at relative humidity, $p/p_0 = 76\%$ for 100 h, which provided nearly saturation hydration level for the sample. After the hydration, the samples were sealed. Measurements were done during heating in the temperature range from 20 °C to 150 °C, at heating rate equal to 10 °C/min.

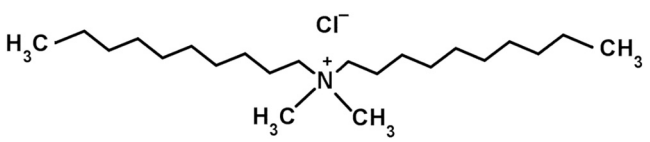

FIG. 1. The didecyldimethylammonium chloride—$C_{22}H_{48}ClN$ (usually abbreviated DDCA).

Prior to hydration courses the air dry samples ($\Delta m/m_0 = 0.172 \pm 0.023$, where m_0 is the dry mass of the sample) were incubated for 240 h over silica gel (i.e., at relative humidity, $p/p_0 = 0\%$). Previous experiences proved such a time sufficient to arrive at a constant mass.[3] The hydration level was $\Delta m/m_0 = 0.0823 \pm 0.0017$. The observed dehydration followed a single exponential decay with time constant $t_1^d = (5.4 \pm 1.1)$ h.

The sample hydration courses were performed from the gaseous phase with controlled humidity, at room temperature ($t = 22$ °C), over the surfaces of saturated solutions of $KC_2H_3O_2$ ($p/p_0 = 23\%$), $CaCl_2$ ($p/p_0 = 32\%$), K_2CO_3 ($p/p_0 = 44\%$), $Na_2Cr_2O_7$ ($p/p_0 = 52\%$), NH_4NO_3 ($p/p_0 = 63\%$), $Na_2S_2O_3$ ($p/p_0 = 76\%$), K_2CrO_3 ($p/p_0 = 88\%$), Na_2SO_4 ($p/p_0 = 93\%$), K_2SO_4 ($p/p_0 = 97\%$), and over a water surface ($p/p_0 = 100\%$).

The dry mass of the samples was determined after heating at 70 °C. After first 30 min of heating, the sample was weighted, then heating was continued. No further decrease in sample mass was recorded for 5 days of drying.

The high power relaxometer WNS HB-65 (Waterloo NMR Spectrometers, Canada) was used to record proton free induction decays (FIDs) of DNA-DDCA complexes. The resonance frequency was 30 MHz (at $B_0 = 0.7$ T); the transmitter power 400 W; the pulse length $\pi/2 = 1.5\ \mu$s; and the spectrometer dead time 10 μs. Data were averaged over 2000 accumulations with repetition time 2 s. The measurements were performed at room temperature ($t = 22$ °C). The obtained data were analyzed applying the one-dimensional, FID analyzing procedure of the two-dimensional (in time domain) nuclear magnetic resonance (NMR) signal-analyzing dedicated software CracSpin.[21]

The swelling was assumed as a threshold process and fitted by the function expressed by Eq. (2) and approximated as $\frac{1}{2}\{1 + \tanh[\alpha(t - t_0)]\}$ with substitution of sufficiently large empirical parameter α.[2,3]

III. RESULTS

A. Thermal properties

Fig. 2 shows a DSC scan recorded for the sample hydrated at $p/p_0 = 76\%$ for 100 h (the hydration level corresponded to $\Delta m/m_0 = 0.1845$ in Fig. 2). Usually discerned for native DNA at about 90 °C denaturation endothermic peak[22] was not observed. An endothermic process starts at ca. 115 °C. It is preceded by a plateau between 70 and 90 °C. The beginning of this region was arbitrarily chosen as the upper limit for sample heating while it was drying to attain constant mass.

B. Hydration kinetics

The hydration courses performed from the gaseous phase at $p/p_0 \leq 63\%$ for lyophilized DNA-DDCA complexes are fitted well by single exponential function (Fig. 3),

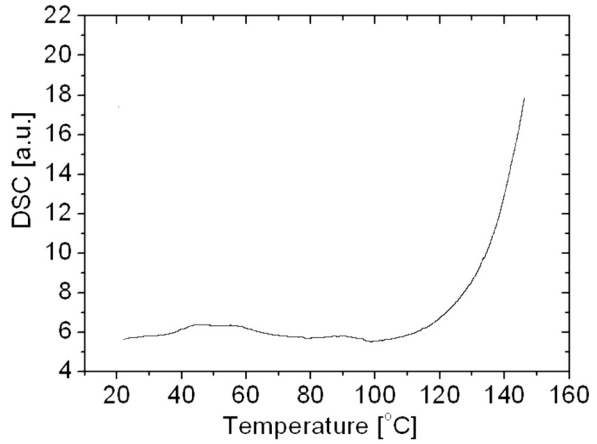

FIG. 2. Calorimetric scan of thermal decomposition of DNA-DDCA complex (recorded at the heating rate 10 °C/min, and at the estimated hydration level $\Delta m/m_0 = 0.1845$).

$$\Delta m(t)/m_0 = A_0^h + A_1^h \cdot [1 - \exp(-t/t_1^h)], \tag{1a}$$

where $\Delta m/m_0$ is the relative mass increase, A_0^h is the saturation level for very tightly bound water fraction (i) not removed by incubation over silica gel ($p/p_0 = 0\%$), A_1^h is the saturation level for the tightly bound water fraction (ii), and t_1^h is the corresponding hydration time constant.

The average, over all final humidity levels reached for specific p/p_0 values, of very tightly bound water component $A_0^h = 0.033 \pm 0.001$. The amplitude of tightly bound water component $A_1^h = 0.06 \pm 0.04$ and its hydration time $t_1^h = (0.59 \pm 0.04)$ h.

For higher hydration levels obtained during the hydration courses performed at p/p_0 between 63% and 100%, the loosely bound water fraction appears and the hydration course is better fitted by the two exponential function,

$$\Delta m(t)/m_0 = A_0^h + A_1^h \cdot [1 - \exp(-t/t_1^h)] + A_2^h \cdot [1 - \exp(-t/t_2^h)], \tag{1b}$$

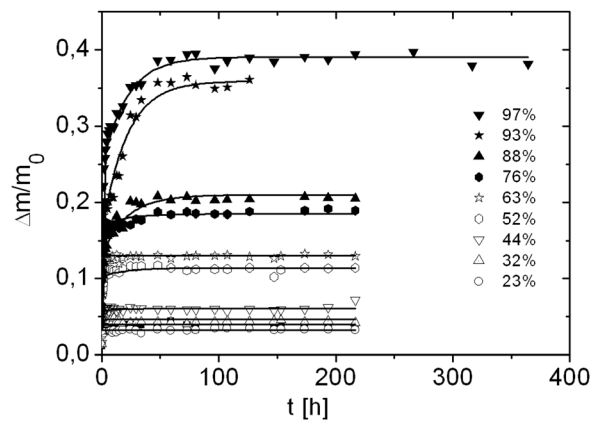

FIG. 3. The hydration kinetics for DNA-DDCA complex recorded as relative mass increase expressed in units of dry mass $\Delta m/m_0$. The hydration was performed from the gaseous phase at different values of relative humidity p/p_0. Targets humidity: $p/p_0 = 23\%$ – open circles, $p/p_0 = 32\%$ – open triangles, $p/p_0 = 44\%$ – open reverse triangles, $p/p_0 = 52\%$ – open diamonds, $p/p_0 = 63\%$ – open starlets, $p/p_0 = 76\%$ – closed diamonds, $p/p_0 = 88\%$ – closed triangles, $p/p_0 = 93\%$ – closed starlets, $p/p_0 = 97\%$ – closed reversed triangles. The error bars are within the plot symbols.

where A_2^h is the saturation level for the loosely bound water fraction (iii), and $t_2^h = (20.9 \pm 1.3)$ h is the corresponding hydration time constant. The constant A_2^h increases gradually with increasing relative humidity of the atmosphere. Third exponential component in hydration kinetics curve was not observed as it was for hydration of salmon sperm crude DNA.[2]

C. Swelling

The DNA-DDCA lyophilized complex, hydrated at $p/p_0 = 100\%$, revealed the delayed hydration process starting at $t_3^h = (150.5 \pm 2.4)$ h (see Fig. 4). The observed sample swelling process was well fitted using the two step function,

$$\Delta m(t)/m_0 = A_0^h + A_1^h \cdot [1 - \exp(-t/t_1^h)] + A_2^h \cdot [1 - \exp(-t/t_2^h)] + \begin{cases} 0 & t < t_0 \\ A_3^h \cdot [1 - \exp(-t/t_3^h)] & t > t_0, \end{cases} \tag{2}$$

where $A_3^h = 0.180 \pm 0.022$ was the swelling amplitude and $t_3^h = (40.6 \pm 1.5)$ h was the swelling time. The level of the swelling was much smaller than it was for salmon sperm DNA and started after significantly shorter incubation at $p/p_0 = 100\%$.[8] This suggests differences in outer surface of the DNA-DDCA lyophilizate grains.

D. Sorption isotherm

For DNA-DDCA complexes the total saturation hydration level, C^h, was calculated as a sum of all hydration curve components,

$$C^h = \sum_{i=0}^{n} A_i, \tag{3}$$

where n equals 1 or 2 depending on hydration level (see Eqs. (1a) and (1b)), and the obtained numbers were taken for the construction of sorption isotherm.

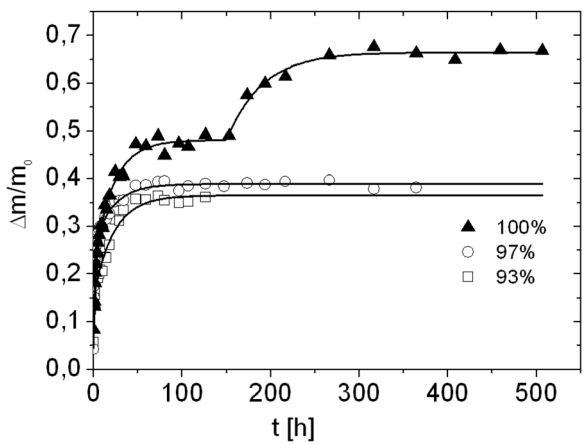

FIG. 4. The swelling process observed at gaseous phase hydration of DNA-DDCA complex. The presented hydration courses were performed at $p/p_0 = 93\%$ (open squares), at $p/p_0 = 97\%$ (open circles), and at $p/p_0 = 100\%$ (closed triangles).

The obtained sorption isotherm reveals approximately sigmoidal form (Fig. 5), and is well fitted by the sorption models concerning two types of water binding sites, namely, (i) stronger "primary" water binding sites (directly bound to the sorbent surface) and (ii) weaker "secondary" water binding sites (bound to the already bound water molecules, or to the sorbent surface).

Either for BET[23] model or for Dent[24] model the sorption isotherm is fitted by the sigmoidal function,

$$C^h(h) = \frac{\Delta M}{m_0}\frac{b_1 h}{(1-bh)\cdot(1+b_1 h - bh)}, \tag{4}$$

where h is relative humidity, p/p_0, expressed in absolute units, and $\Delta M/m_0$ is the mass of water saturating primary water binding sites. If the number of primary water binding sites covered by i water molecules equals S_i, and the contribution of empty water primary binding sites is S_0, the parameter $1/b_1$ is defined as $S_0/S_1|_{h=1} = 1/b_1$.

Both considered models of sorption isotherm differently approximate the population of subsequent layers of secondary bound water, $S_n/S_{n-1}|_{h=1}$. BET model takes $b = S_n/S_{n-1}|_{h=1} = 1$, whereas in Dent model this number may be varied between 0 and 1.

To test the relevance of the sorption isotherm model used, the sorption data are usually presented in a parabolic form (see Fig. 6), which for BET model is expressed as

$$\frac{h}{\Delta m/m_0} = A + Bh - (A+B)h^2, \tag{5a}$$

whereas for Dent model as

$$\frac{h}{\Delta m/m_0} = A + Bh - Ch^2, \tag{5b}$$

where parameters $\frac{\Delta M}{m_0}$, b, b_1 are expressed in terms of A, B, C as

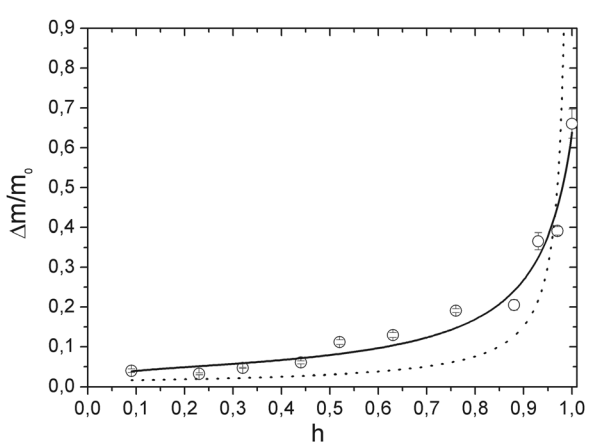

FIG. 5. The sorption isotherm for DDCA/DNA complexes. Abscissas of experimental points represent relative humidity h ($=p/p_0$) and ordinates relative mass increase. The symbol $\Delta m/m_0$ denotes here values of C^h parameter, calculated according to Eq. (3). Open circles – measured points, solid line – Dent model, dotted line – BET model.

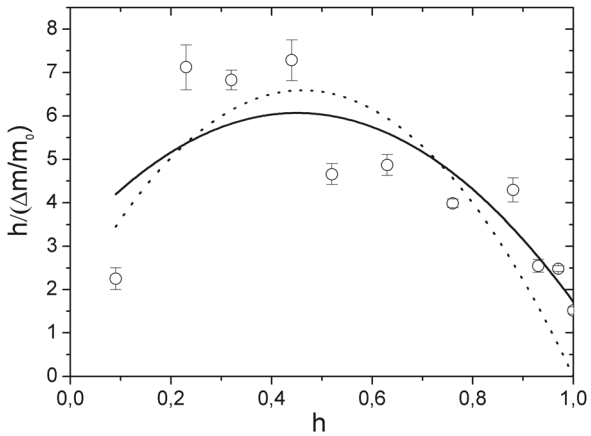

FIG. 6. Parabolic form of Dent and BET model of the sorption isotherm for DNA-DDCA complexes [open circles – experimental data, solid line – fitted Dent model (Eq. (5b)), dotted line – fitted BET model (Eq. (5a))].

$$b = \frac{\sqrt{B^2+4AC}-B}{2A}\ (\text{a}),\ b_1 = \frac{B}{A} + 2b\ (\text{b}),\ \frac{\Delta M}{m_0} = \frac{1}{Ab_1}\ (\text{c}). \tag{6}$$

At h = 1 the parabolic form for the sorption isotherm function for BET model is required to equal 0, so that the discrepancy from 0 at h = 1 is a measure of the Dent model applicability.

For DNA-DDCA complexes the sorption isotherm is significantly better fitted by Dent model ($b = 0.932 \pm 0.010$) than by BET model. This value is close to that obtained for lyophilized photosynthetic membranes. For native, fully developed photosynthetic membrane lyophilizates b = 0.863,[25] whereas for native developing membranes b = 0.896, and for EDTA-washed ones (b = 0.929).[26]

The mass of water saturating primary water binding sites was $\Delta M/m_0 = 0.043 \pm 0.006$, which is close to the corresponding value obtained from hydration kinetics for very tightly bound water pool.

The unoccupied binding sites portion at $h = 1$ for DNA–DDCA complex equals $1/b_1 = 2.4\%$. This is a reasonable value for a bio-derived material. It is similar to $1/b_1$ values found, for example, in the case of mature and developing photosynthetic membranes.[25,26]

E. Proton free induction decays

Proton free induction decays (FIDs) for DNA-DDCA complexes, at low hydration levels ($\Delta m/m_0 \leq 0.125$), are well fitted by the superposition of one Gaussian component, with the amplitude S, coming from immobilized protons, and one exponential component, L_1, coming from water tightly bound on the surfaces of the structure (Eq. (7a)),

$$FID(t) = S\cdot\exp\left(-\left(\frac{t}{T_{2S}^*}\right)^2\right) + L_1\cdot\exp\left(-\frac{t}{T_{2L_1}^*}\right), \tag{7a}$$

where $T_{2S}^* \approx 25\,\mu$s is proton relaxation time (taken as the time required for the Gaussian signal to decay to 1/e of its initial amplitude) of the solid signal component, and $T_{2L_1}^*$ is the relaxation time of proton liquid fraction L_1.

For the hydration levels ($0.125 \leq \Delta m/m_0 \leq 0.25$) the second exponential component of FID signal, L_2, appears, coming from loosely bound water on the surfaces of the structure (Fig. 7(b)),

$$\mathrm{FID(t)} = \mathrm{S}\cdot\exp\left(-\left(\frac{\mathrm{t}}{\mathrm{T}^*_{2\mathrm{S}}}\right)^2\right) + \mathrm{L}_1\cdot\exp\left(-\frac{\mathrm{t}}{\mathrm{T}^*_{2\mathrm{L}_1}}\right) + \mathrm{L}_2\cdot\exp\left(-\frac{\mathrm{t}}{\mathrm{T}^*_{2\mathrm{L}_2}}\right), \quad (7b)$$

where L_2 is the amplitude and $T^*_{2L_2}$ is the relaxation time of loosely bound water fraction.

For still higher hydration levels a signal coming from tightly bound water protons is no longer observed and only the signal from the solid and from free water fraction appears (Eq. (7c)).

$$FID(t) = S\cdot\exp\left(-\left(\frac{t}{T^*_{2S}}\right)^2\right) + L_2\cdot\exp\left(-\frac{t}{T^*_{2L_2}}\right). \quad (7c)$$

The hydration dependence of the proton relaxation times for DNA-DDCA complexes is presented in Fig. 7.

For the proton fraction L_1 the value of the decay time does not depend much on the hydration level and equals $T^*_{2L_1} \approx 80\ \mu s$. As a consequence the L_1 component is not fitted at higher hydration levels as the L_2 component increases in size progressively with hydration level. The relaxation time for the L_1 fraction resembles that for the signal of protons of the immobilized (tightly bound) water in many other, very dry microheterogeneous biological subcellular structures, tissues or whole living organisms at cryptobiosis. At complete dehydration, photosynthetic membranes,[27] bark and bast,[30] wheat seed,[31] thallus of lichenized fungus,[27,28,32] dentine and dental enamel,[33] or controlled pore glasses[34] resemble more a model porous solid than a living entity.

The L_2 signal component, with long T_2, is detected in the whole range of hydration levels investigated and relaxation time $T^*_{2L_2} \approx 1000\ \mu s$. The L_2 signal, expressed in units of solid signal, L_2/S, increases in intensity with increasing hydration level (Fig. 8, open circles), suggesting that this component comes from water loosely bound or free water in the system. This component is an average of components of some proton subsystems undergoing exchange that is in the fast exchange regime.[35] The spin-spin relaxation times $T^*_{2L_2}$ measured in FID experiment are shortened by B_0 inhomogeneities,[36]

$$\frac{1}{T^*_2} = \frac{1}{T_2} + \frac{\gamma\Delta B_0}{2}, \quad (7d)$$

where T_2 is spin-spin relaxation time in the absence of B_0 inhomogeneities, γ is the gyromagnetic ratio, and ΔB_0 is a change of magnetic field B_0 within the sample. For the solid component and short T_2 exponential component $T_2 \ll \gamma\Delta B_0$ so that T_2 values obtained from the FID experiment are the inherent T_2. At higher hydration levels $T_{2L_2} > \gamma\Delta B_0$ and the measured T_2 will be dominated by the field inhomogeneity contribution. That is why $T^*_{2L_2}$ no longer increases with increasing hydration at the higher hydration levels.

Total liquid signal expressed in units of solid, $(L_1+L_2)/S$, linearly depends on hydration level of the sample and can be fitted by the linear function (see Fig. 8, full squares),

$$\frac{(L_1+L_2)}{S}(\Delta m/m_0) = (83.1\pm4.9)\cdot\Delta m/m_0 - (5.37\pm0.57). \quad (8)$$

However, below hydration level $\Delta m/m_0 \approx 0.09$, L_2 component is not observed. The liquid signal, L_1, is constant and equals 1.868 ± 0.036 (Eq. (4)) which corresponds to the mass of water, $\Delta m/m_0 \approx 0.02$, as it is for saturated very tightly bound water layer beyond the hydration range of NMR experimental points.

The L_2 signal, expressed in units of solid, L_2/S, linearly increases with increasing hydration level and varies according to the dependence,

$$\frac{L_2}{S}(\Delta m/m_0) = (83.8\pm5.8)\cdot\Delta m/m_0 - (9.4\pm1.2). \quad (9)$$

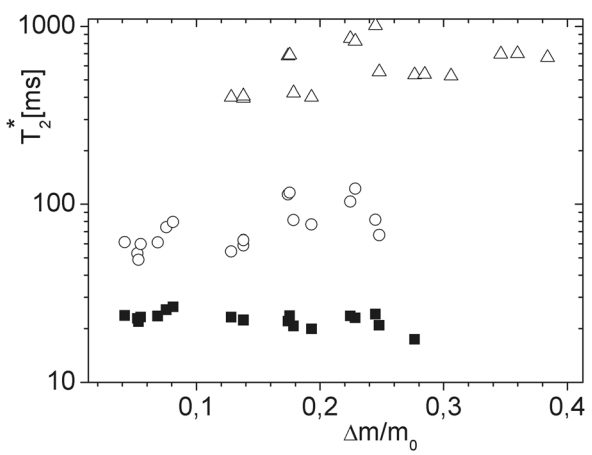

FIG. 7. The hydration dependence of proton FID relaxation times for DNA-DDCA complexes. Solid signal component, S (closed squares), tightly bound water component, L_1 (open spheres), and loosely bound water, L_2 (open triangles), component.

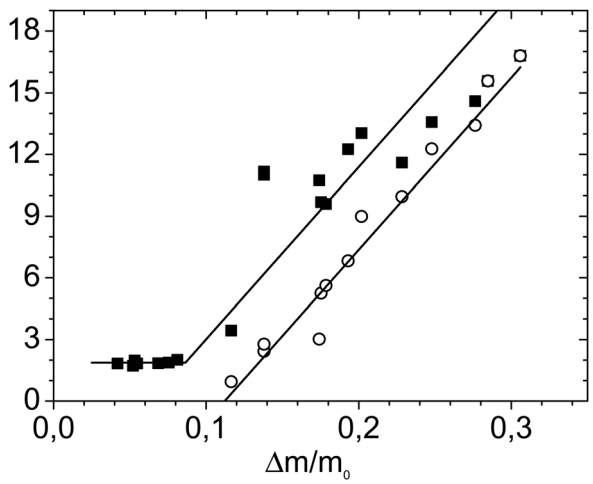

FIG. 8. The $(L_1+L_2)/S$ and L_2/S hydration dependencies for rehydrated DNA-DDCA complexes (full squares and open circles). The solid line was fitted according to Eqs. (8) and (9), respectively.

The estimated (Eq. (9)) value of hydration level at which the loosely bound water fraction appears is equal $\Delta m/m_0 = 0.112 \pm 0.016$. This value is close to the sum of fraction of water saturating very tightly and tightly water binding sites in gravimetric experiments $\Delta M/m_0 = 0.095 \pm 0.044$.

IV. DISCUSSION

Typically, the presence of water soluble fraction in the sample results in a particular dependence of liquid-to-solid signal amplitude on hydration level. This dependence is nonlinear and can be well modeled by a rational function[27,28,32] at low hydration levels, when water soluble fraction is not completely dissolved. Such feature was not observed in the analyzed data. It proves absence of low molecular mass compounds, which usually appear in result of DNA degradation.

Sorption kinetics and isotherm distinguish the fraction of water bound to primary water binding sites (very tightly bound water fraction) in terms of binding strengths, whereas NMR defines water fractions by their mobility. This means that the first water monolayer may be formed by very tightly bound water (bound to primary water binding sites) as well as by tightly bound water. Assuming that the whole immobilized water fraction ($\Delta m/m_0 = 0.112 \pm 0.016$) binds to the inner surfaces of DNA-DDCA complexes, one can approximate the total water-accessible surface of solid DNA-DDCA complex. The obtained value equals of 335 m^2/g of dry mass from NMR, or 285 m^2/g of dry mass taken from the gravimetric data.[29]

The lengths of fully extended (all-trans) hydrocarbon chains of DDCA may be estimated as $l = 1.415$ nm.[37] However, for the temperatures above main lipid phase transition[38,39] the effective lengths of hydrocarbon chain should be taken as $0.75\,l$.[40] This makes 2.12 nm as an effective diameter of the bilayer formed by DDCA (2.83 nm in all trans conformation). This value is little less than the DNA molecule size in native conformation, suggesting that DNA molecule is partially exposed to aqueous medium if the DNA-DDCA micelle is formed at rehydration. The total water-accessible surface consists of not only lipid bilayer surface, but also of exposed outside parts of DNA molecules.

V. CONCLUSION

This paper shows that solid DNA-DDCA complex hydrates to lower level than crude DNA[2] as well as DNA-CTMA[3] solid complex. This effect is likely be connected with the presence of two long didecyl chains in DDCA instead of one long single chain (hexadecyl) in CTMA.

It is well established that the double helical DNA cannot exist without hydration layer.[41] Dehydration induces conformational transition of B form of DNA to more compact A form. There exist several reports claiming electrical conductance of DNA strongly depended on hydration level. Even small relative humidities ($p/p_0 < 17\%$) of the atmosphere may be significant for observed conductivity increase.[42] Water content is one of the factors responsible for DNA dielectric constant.[43] Water effect on these two properties is still under debate. It cannot be excluded, that the presence of water molecules varies electrical properties of DNA lipid complexes in a similar way. As electric properties change with hydration level, it decreases the quality of various technical devices, e.g., FETs, where DNA-CTMA complex was applied as the gate dielectric. Its restricted hydrophilicity may help to solve this problem.

As shown in the current report, DNA-DDCA solid complex can be an interesting alternative to the commonly used DNA-CTMA complex.

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[1]A. J. Steckl, Nat. Photonics **1**, 3 (2007).
[2]H. Harańczyk, J. Czak, P. Nowak, and J. Nizioł, Acta Phys. Pol. A **117**, 397 (2010).
[3]H. Harańczyk, J. Kobierski, D. Zalitacz, P. Nowak, A. Romanowicz, M. Marzec, J. Nizioł, E. Hebda, and J. Pielichowski, Acta Phys. Pol. A **121**, 485 (2012).
[4]L. Wang, J. Yoshida, and N. Ogata, Chem. Mater. **13**, 1273–1281 (2001).
[5]C. Yumusak, T. B. Singh, N. S. Sariciftci, and J. G. Grote, Appl. Phys. Lett.**95**, 263304, (2009).
[6]O. Krupka, A. El-Ghayoury, I. Rau, B. Sahraoui, J. G. Grote, and F. Kajzar, Thin Solid Films **516**, 8932 (2008).
[7]J. G. Grote, J. A. Hagen, J. S. Zetts, R. L. Nelson, D. E. Diggs, M. O. Stone, P. P. Yaney, E. Heckman, C. Zhang, W. H. Steier, A. K. Y. Jen, L. R. Dalton, N. Ogata, M. J. Curley, S. J. Clarson, and F. K. Hopkins, J. Phys. Chem. B **108**, 8584 (2004).
[8]P. Dutta and S. K. Mandal, J. Phys. D **37**, 2908 (2004).
[9]Y. Kawabe, L. Wang, T. Nakamura, and N. Ogata, Appl. Phys. Lett. **81**, 1372 (2002).
[10]D. H. Ha, H. Nham, K.-H. Yoo, H.-m. So, H.-Y. Lee, and T. Kawai, Chem. Phys. Lett. **355**, 405 (2002).
[11]W. Saenger, W. N. Hunter, and O. Kennard, Nature **324**, 385 (1986).
[12]M. Harmouchi, G. Albiser, and S. Premilat, Eur. Biophys. J. **19**, 87 (1990).
[13]W. Saenger, *Principles of Nucleic Acid Structure* (Springer, 1983).
[14]H. Matsui, M. Nagatori, H. Sakamoto, K. Mizoguchi, and N. Toyota, J. Phys. Chem. Solids **71**, 440 (2010).
[15]G. Lewen, S. M. Lindsay, N. J. Tao, T. Weidlich, R. J. Graham, and A. Rupprecht, Biopolymers **25**, 765 (1986).
[16]C. Leal, L. Wadso, G. Olofsson, M. Miguel, and H. Wennerstrom, J. Phys. Chem. B **108**, 3044 (2004).
[17]I. Brovchenko, A. Krukau, A. Oleinikova, and A. K. Mazur, Phys. Rev. Lett. **97**, 137801 (2006)
[18]I. Koltover, T. Salditt, J. O. Rädler, and C. R. Safinya, Science **281**, 78 (1998).
[19]J. O. Rädler, I. Koltover, T. Salditt, and C. R. Safinya, Science **275**, 810 (1997).
[20]J. Nizioł, M. Śniechowski, E. Hebda, M. Jancia, and J. Pielichowski, Chem. Chem. Technol. **5**, 397 (2011).
[21]W. P. Węglarz and H. Harańczyk, J. Phys. D **33**, 1909 (2000).
[22]S. L. Lee, P. G. Debenedetti, J. R. Errington, B. A. Pethica, and D. J. Moore, J. Phys. Chem. B **108**, 3098 (2004).
[23]P. Brunauer, H. Emmett, and E. Teller, J. Am. Chem. Soc. **60**, 309 (1938).
[24]R. W. Dent, Text. Res. J. **47**, 145 (1977).
[25]H. Harańczyk, A. Leja, M. Jemioła-Rzemińska, and K. Strzałka, Acta Phys. Pol. A **115**, 526 (2009).
[26]H. Harańczyk, A. Leja, and K. Strzałka, Acta Phys. Pol. A **109**, 389 (2006).
[27]H. Harańczyk, A. Pietrzyk, A. Leja, and M. A. Olech, Acta Phys. Pol. A **109**, 411 (2006).
[28]H. Harańczyk, M. Bacior, and M. A. Olech, Antarct. Sci. **20**, 527 (2008).

[29]H. Harańczyk, *On Water in Extremely Dry Biological Systems* (WUJ, Krakow, 2003).
[30]H. Harańczyk, W. P. Węglarz, and Z. Sojka, Holzforschung **53**, 299 (1999).
[31]H. Harańczyk, K. Strzałka, G. Jasiński, and K. Mosna-Bojarska, Colloids Surf., A **115**, 47 (1996).
[32]H. Harańczyk, M. Bacior, P. Jastrzebska, and M. A. Olech, Acta Phys. Pol. A **115**, 516 (2009).
[33]N. Funduk, G. Lahajnar, L. Miljkovic, S. Skocajic, D. W. Kydon, L. J. Schrener, and M. M. Pintar, Zobozdrav Vestn. **41**(Suppl.1), 139 (1986).
[34]H. Harańczyk, K. G. Soga, R. J. Rumm, and M. M. Pintar, Magn. Reson. Imaging **9**, 723 (1991).
[35]J. R. Zimmerman and W. E. Brittin, J. Phys. Chem. **61**, 1328 (1957).
[36]A. Timur, J. Petrol. Technol. **21**, 775 (1969).
[37]S. Y. Lee, W. J. Cho, P. S. Hahn, M. Lee, Y. B. Lee, and K. J. Kim, Appl. Clay Sci. **30**, 174 (2005).
[38]A. Wishnia, J. Phys. Chem. **67**, 2079 (1963).
[39]C. McAuliffe, J. Phys. Chem. **70**, 1267 (1966).
[40]C. Tanford, *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*, 2nd ed. (Wiley, 1980).
[41]W. Saenger, W. N. Hunter, and O. Kennard, Nature **324**, 385 (1986).
[42]Y. Matsuo, K. Sugita, and S. Ikehata, Synth. Met. **154**, 13 (2005).
[43]V. Ando and E. Fukada, J. Polym. Sci., Polym. Phys. Ed. **14**, 63(1976).