The CdCl$_2$ effects on synthetic DNAs encaged in the nanodomains of a cationic water-in-oil microemulsion

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Electronic Supplementary Information

Microstructure of the hosting quaternary microemulsion in the presence of NaCl and polyAT

The structure of the quaternary system CTAB|pentanol|water|hexane covering a wide part of its phase diagram has been the subject of deep investigations by the authors and reported in several papers.[1,2,3]

In order to check if the solubilization in the inner water compartment of the reverse micellar aggregates of NaCl and high molecular weight polyAT (MW= 900÷1900 kDa) affected the microstructure of the hosting system, proton self diffusion NMR (SD-NMR) experiments and conductivity measurements have been performed also varying the temperature, according to a well assessed protocol.[1]

Microemulsions at W_0=15 (W_0= [H$_2$O]/[CTAB]), P_0= 8.5 (P_0= [pentanol]/[CTAB]) at an overall concentration of CTAB of 0.100M, have been prepared in the presence of NaCl 0.35 and 0.75M with or without polyAT ([polyAT]= $4.76 \cdot 10^{-5}$ M) in the presence of 1mM tris buffer (pH= 8). As a comparison, the behaviour of a matched polyAT containing microemulsion without NaCl has been also prepared.

In the following table the results coming from SD-NMR experiments performed at 298 K are collected.

[NaCl] (M)	PolyAT[a)]	$D°_{CTAB}$ (m²/s)	D_{OH} (m²/s)	R_h (Å)[b)]	P_{free}
0	(-)	$1.83 \cdot 10^{-10}$	$2.60 \cdot 10^{-10}$	37.0	0.04
0	(+)	$1.87 \cdot 10^{-10}$	$3.22 \cdot 10^{-10}$	36.2	0.06
0.35	(-)	$1.90 \cdot 10^{-10}$	$2.50 \cdot 10^{-10}$	35.7	0.03
0.35	(+)	$1.94 \cdot 10^{-10}$	$2.71 \cdot 10^{-10}$	34.9	0.04
0.75	(-)	$1.91 \cdot 10^{-10}$	$2.46 \cdot 10^{-10}$	35.5	0.03
0.75	(+)	$1.93 \cdot 10^{-10}$	$2.51 \cdot 10^{-10}$	35.1	0.03

[a)] (-): absence of polyAT; (+): presence of polyAT ([polyAT]= $4.76 \cdot 10^{-5}$ M)
[b)] calculated according to Stokes-Einstein relationship, using $\eta = 3.22 \cdot 10^{-4}$ Pa·s [1]

Due to the total solubility of CTAB at the interface, the self diffusion coefficient determined by the decay of the trimethylammonium signal of the surfactant can be safely assumed to coincide with the self diffusion coefficient of the whole aggregates, *i.e.*: $D_{mic} = D_{CTAB}$. Taking into consideration that this microemulsion is made of discrete aggregates behaving like non interacting hard spheres[1], from the experimental self diffusion coefficient, the corresponding value at infinite dilution ($D°_{mic}$) can be easily calculated according to the virial expansion truncated to the first term[4]: $D°_{mic} = D_{mic}/(1-2\Phi)$, being Φ the volume fraction of the dispersed phase (Φ= (volume of H_2O+ CTAB)/volume of solution). Using the molar volume of 18.053 mL/mol for water[5] and 360.9 mL/mol for CTAB[6], Φ can be easily calculated for each sample, taking into consideration in the case of the NaCl containing samples the effective added volume, obtained by the weighted amount of saline solution through their relative densities.[7]

The data point to a system made of discrete spherical droplets of practically constant hydrodynamic radii even in the presence of NaCl and, eventually, polyAT. The calculated dimensions, moreover, are well in agreement with those already reported in the literature[1-3].

To the NMR signal of the hydroxyl group contribute, in principle, both the water and the n-pentanol at the interface. It has been already demonstrated[1] that the contribution of the cosurfactant to the ^{1}H-NMR OH signal is negligible and therefore the observed D_{OH} is due only to the contribution of the water moving with the aggregates (endomicellar water) and of water molecules moving in the continuous phase (free water), due to its finite solubility in the continuous organic bulk. According to Lindman[8,9], in the case of a fast exchange between two sites it can be written:

$D_{obs} = (1-P_{free})D_{mic} + P_{free}D_{free}$

where D_{obs} is the observed self diffusion coefficient of water in the microemulsion (indicated as D_{OH}, in the preceding Table), P_{free} is the fraction of water freely diffusing in the organic bulk and D_{free} and D_{mic} are the self diffusion coefficients of the water free in the organic bulk

and confined in the core of the reverse micellar aggregates, respectively. Since D_{free} has been already measured[1] for a microemulsion of the same bulk composition ($D_{free}= 2.70 \cdot 10^{-9}$ m^2/s), it is possible to determine the fraction of water dispersed in the organic bulk (last column of the preceding Table). Again, the obtained values are in close agreement with that reported in the literature for the parent system, further confirming the preservation of the microstructure even in the presence of high salt concentrations and high molecular weight polyAT.
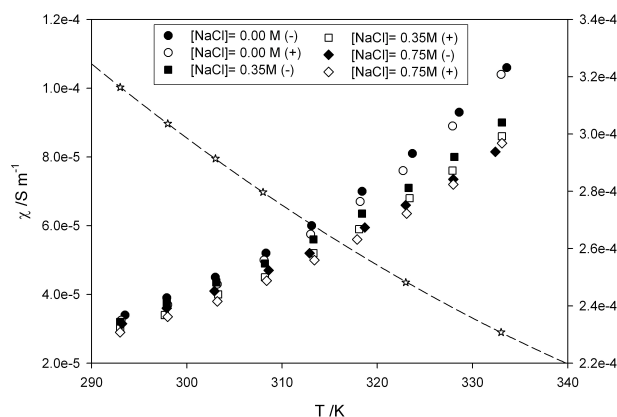
In order to check if the system retains its basic microstructure also upon increasing the temperature, the specific conductivity of the above mentioned microemulsions has been measured in the range 293÷ 333K (Fig. a). Though increasing with temperature, the measured specific conductivity never shows percolative transition to bicontinuous phases, always remaining in the range of values typical of water-in-oil microemulsions ($10^{-6}÷10^{-4}$ S/m). The conductivity behaviour of water in oil microemulsions are quantitatively described by Kallay's equation[11]:

Fig. a: specific conductivity as a function of temperature of the quaternary microemulsion prepared with different NaCl content with (+) and without (-) polyAT. Dynamic viscosity data refer to pure hexane and are from ref. 10 (the dashed line is a mere guide for the eyes).

$$\chi = \frac{KT \epsilon_0 \epsilon}{2 \pi \eta} \frac{r-l}{r^4} \Phi$$

where χ is the specific conductivity, K the Boltzmann constant, T the thermodynamic temperature, ε_0 the permittivity of vacuum, ε the relative permittivity of the medium around the water core of a droplet, η the viscosity of the oil phase, r the hydrodynamic radius of the reverse micelles, l the thickness of the interfacial layer and Φ the volume fraction of the dispersed phase. Clearly, the conductivity data of Fig. a can be rationalized both in terms of the reduced viscosity of the medium and of an increase of the volume fraction of the dispersed phase due to cosurfactant loading of the interface upon increasing the temperature. Probably both effects occur but the data in our possess do not allow their decoupling. The thing that does matter in this instance, however, is that the experimental data available point to a substantially unchanged structure of the polynucleotides hosting system even at temperatures close to the boiling point of the hexane. Moreover, upon cooling down to the starting temperature value, the system shows no hysteresis at all (not shown).

References

1   M. Giustini, G. Palazzo, G. Colafemmina, M. Della Monica, M. Giomini, A. Ceglie, *J. Phys. Chem.* 1996, **100**, 3190.

2   G. Palazzo, F. Lopez, M. Giustini, G. Colafemmina, A. Ceglie, *J. Phys. Chem. B*, 2003, **107**, 1924

3   G. Palazzo, L. Carbone, G. Colafemmina, R. Angelico, A. Ceglie, M. Giustini, *Phys. Chem. Chem. Phys.*, 2004, **6**, 1423

4   T. Ohtsuky, K. Okano, *J. Chem. Phys.*, 1982, **77**, 1443

5   *Handbook of Chemistry and Physics*, 65th edition, CRC Press, Boca Raton, FL, 1984-1985

6   F. Reiss-Husson, V. Luzzati, *J. Phys. Chem.*, 1964, **68**, 3504

7   *Handbook of Chemistry and Physics*, 48th edition, CRC Press, Boca Raton, FL, 1967-1968

8   P.G. Nilsson, B. Lindman, *J. Phys. Chem.*, 1983, **87**, 4756

9   P.G. Nilsson, B. Lindman, *J. Phys. Chem.*, 1984, **88**, 5391

10   M.F. Bolotinov, Y.A. Neruchev, *J. Chem. Eng. Data*, 2003, **48**, 739

11   N. Kallay, A. Chittofrati, *J. Phys. Chem.,* 94, **1990**, 4755