REVIEW ARTICLE

Adsorption of DNA at solid–water interfaces and DNA–surfactant binding interaction in aqueous media[#]

D. K. Chattoraj[1,*] and A. Mitra[2]

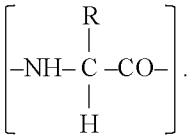
[1]Department of Food Technology and Biochemical Engineering, Jadavpur University, Kolkata 700 032, India
[2]Department of Chemistry, Sree Chaitanya College, Habra 743 268, India

Deoxyribonucleic acid or DNA is unable to accumulate at the air–water interface for structural reasons. However, use of analytical techniques, negatively charged DNA molecule in native and denatured states is observed to be adsorbed on different types of powdered rigid and soft particle under various physicochemical conditions. The thermodynamic affinities for DNA–particle interactions have been evaluated for different systems. From the kinetic studies of the adsorption processes, in the systems, different mechanisms of adsorption process have been suggested. Use of equilibrium dialysis and electrometric techniques extents of binding of cationic, neutral and anionic surfactants in equilibrium and non-equilibrium states have been determined and thermodynamic treatments of the data have been made. Recent extensive developments of these subjects made in the last two decades have been reviewed and possible applications of the topics for industrial applications and understanding of biological processes have been discussed in brief.

Keywords: Adsorbed DNA microelectrophoresis, adsorption kinetics, DNA–polymer interaction, DNA–surfactant binding.

LIVING cells are made of biomacromolecules like proteins, nucleic acids and polysaccharides of various types. The globular proteins remain mainly dissolved in the cytoplasmic fluid of the cell containing inorganic salts and organic solutes. The membranes of living cells are mainly made of lipid bilayers and insoluble proteins. The lipids are of various types. In many types of lipids, the two hydroxyl groups of glycerol are esterified with long-chain fatty acids whereas the third hydroxyl group may combine with a phosphoric acid derivative (e.g. phospholecithin). Long-chain fatty acids containing large number of $-CH_2-$ groups are practically insoluble in aqueous phase but they can spread on the air–water interface in forming monolayers. Lipids are, in general, insoluble in water but they can form monolayer, bilayer, liposomes at an interface. The relatively short-chain fatty acids are slightly soluble in aqueous solvent, and at low bulk concentrations lower the surface tension of water. These acids may form colloidal micelles when the bulk concentration of the acid exceeds a critical value termed as critical micelle concentration (cmc).

The proteins are made of polypeptide chains formed due to linear polymerization of peptide residues



Here R stands for side-chain groups. There are 20 different types of such R groups which may be divided into hydrophobic, hydrophilic and ionic groups. Soluble proteins are regarded as surface-active bioamphiphiles[1]. Proteins may lower the surface tension of water slowly with time. They can also spread on the aqueous surface forming spread monolayer[1]. The molecular weights of different proteins may vary from 10^4 to 10^6 or more. The polypeptide chains may assume a folded or elongated structure due to electrostatic, hydrophobic and other types of interactions[2,3].

Deoxyribonucleic acid (DNA) generally occurring in the central region of the living cell (termed as nucleus) apparently exists in gel or soluble states by extensive hydration and it is anticipated that they have no apparent interaction with cellular lipid surface or endoplasmic lipids dispersed in cytoplasmic fluid[2,4]. DNA does not lower the surface tension of water[5]. The polynucleotide chain[2,3] of DNA contains four organic bases: adenine (A) guanine (G), cytosine (C) and thymine (T). Each of these bases is attached to a deoxyribose ring (Figure 1) with elimination of one molecule of water. Deoxyribose ring bound with a base is also attached with hydroxyl group of phosphate anion by elimination of water with the formation of nucleotide monomer (Figure 1). There are four types of nucleotides containing four bases. Linear polymerization of these monomers will form a single-stranded polynucleo-

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*For correspondence. (e-mail: dkchattoraj@hotmail.com)

tide chain[2,3]. Two single-stranded DNA form a double-helix structure[6] with the attachment of two and three interchain hydrogen bonds between A and T, and G and C bases respectively (Figure 1). Double-helical DNA molecule thus becomes rod-shaped in aqueous media. Central portion of this rod may behave as hydrophobic region whereas outside region covered by ionic phosphate groups is highly hydrophilic in nature[7]. At the air–water interface, rod-shaped DNA is not able to orient its hydrophobic part in air and hydrophilic region towards water so that it is unable to lower the surface tension of water[7]. The present review reflects on the results of our research on studies of affinities of DNA for various types of solid–liquid interfaces. It also indicates that at solid–liquid interfaces, DNA is surface active due to its preferential adsorption from solution to different hydrophilic and hydrophobic, inorganic and organic solid surfaces depending upon physicochemical conditions. Although our work led to several publications since 1965, the different chemical and biological aspects of DNA–surface interactions have been studied after 1985 by other workers and useful applications of such studies have been published by them only in recent years.

In this review article, we shall first present our research on the adsorption of DNA on various solid–liquid surfaces using microelectrophoretic and analytical techniques. We shall describe our own work on binding interaction of surfactants and proteins with DNA, and thermodynamic implications for such interactions. We shall further review in brief more recent work by others on DNA adsorption and binding of surfactants to DNA published mainly from 1990 onwards and their material uses and biological implications.

Electrophoresis of deoxynucleic acid in solution

Due to the possession of ionic phosphate groups, DNA macromolecule becomes negatively charged. By electrometric titration of DNA, the amount of this charge can be estimated[8,9]. With the increase in pH, the negative charge of DNA in solution is observed to increase. This indicates increase in the ionization of DNA with increase in pH. By the application of Tiseleus moving boundary method, the electrophoretic mobility and charge of dissolved DNA in the presence of various neutral salts have been measured by Davidson and co-workers[10] and Ross *et al.*[11]. By appropriate application of electrophoretic theory, extent of binding of the counterions (e.g. Li^+, Na^+, K^+, Rb^+, Cs^+) to DNA has also been estimated by them.

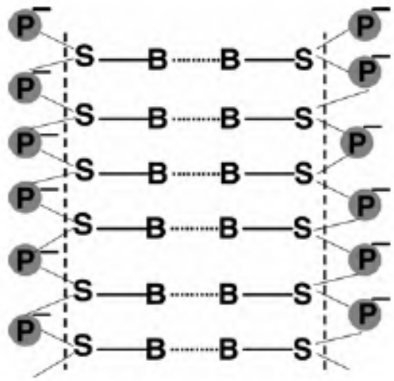

Figure 1. DNA double helix. S, stands for deoxyribose, P, phosphate anion; B, organic bases A, T, G, C; [B–S–P^-], nucleotide monomer; B…B, Hydrogen bonded base in DNA double helix.

Microelectrophoretic studies of adsorbed nucleic acids

In the microelectrophoretic method, first used by Chattoraj *et al.*[12,13], powdered particles of glass, dowex resin and alumina particles are suspended in solutions containing nucleic acid (DNA or RNA) at different pH and ionic strength 0.05. The systems are mildly shaken for 20 h for allowing complete adsorption of DNA on the surfaces of these particles. The electrophoretic mobilities of these particles have been measured in a microelectrophoretic cell attached to a microscope[1] and the applied potential gradients have been obtained from the measurement of conductance and electric current passing through the solution during electrophoretic movement. The mobility–pH curves of DNA adsorbed on these particles have been plotted in Figure 2. The mobilities of DNA-adsorbed particles are all found to be negative and pH–mobility curves

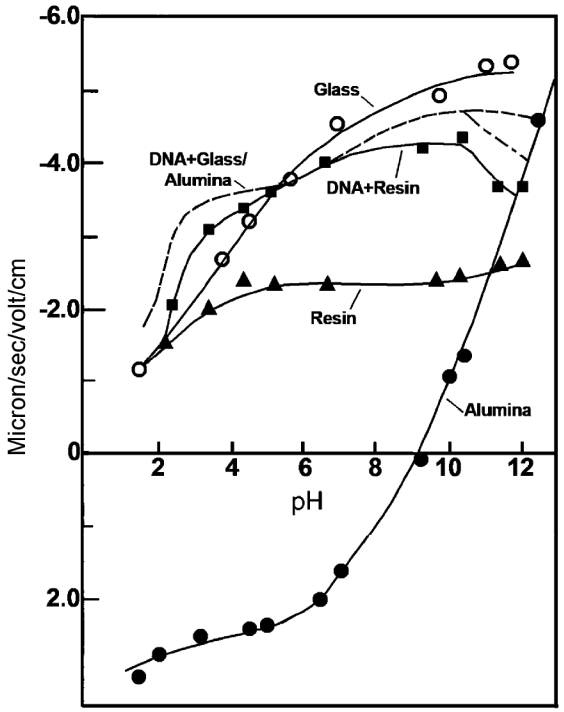

Figure 2. Electrophoretic mobilities[12] of powdered solid particles as function of pH at ionic strength 0.05. (○) Bare glass particles at 27°C, (●) bare alumina particles at 27°C, (▲) Resin particle at 30°C, (-----) DNA adsorbed glass and alumina particles at 27°C, (■) DNA adsorbed resin particles 30°C.

are close to each other. Side by side, pH–mobility curves of bare alumina, glass and resins in the absence of DNA have been included in Figure 2. Comparison of the two types of curves in the absence and presence of DNA clearly indicates that DNA is adsorbed extensively on positively charged alumina and negatively charged glass and resin surfaces so that in all cases, the charges of the particles become negative and values of mobilities are all close to each other. This for the first time has proved that DNA can be adsorbed at solid–liquid interfaces although the macromolecule does not adsorb at the air–water interface. In a subsequent paper, Chattoraj *et al.*[13] have shown that yeast ribonucleic acid containing single-stranded RNA may be adsorbed on all these solid surfaces. DNA and RNA denatured by heat, acid or alkali addition are also found to be adsorbed on these three types of solid–liquid interfaces[12,13]. In the chromosome of eukaryote cell, negatively charged DNA is attached to positively charged protein histone forming nucleohistone. In Figure 3, plot of mobility vs pH of nucleohistone adsorbed on these three types of solid–liquid interfaces is found to be positively charged[14] above isoelectric pH 3.3 and negatively charged below this pH.

Adsorption of DNA at solid–liquid interfaces

As early as 1968, Upadhyay and Chattoraj[15] have investigated direct adsorption of DNA from the solution to the powdered surface of alumina using conventional analytical technique. Here, a series of DNA solutions of known concentrations (C_2^t) in buffer at a given pH have been prepared. To each of these solutions at constant volume, a definite amount of alumina powder has been added. The mixtures have been shaken for 20 h mildly in stoppered bottles and then allowed to stand for 8 h when solid powder has settled down at the bottom. The DNA concentration C_2 of the supernatant has been estimated at 260 nm using a standard curve obtained by measuring adsorbance of a series of solutions of known DNA concentrations by spectrophotometric method. Values of the extent of adsorption Γ_2^1 per kg of DNA (or per mole of nucleotide) can be calculated using the equation

$$\Gamma_2^1 = \frac{V^t}{1000}(C_2' - C_2). \quad (1)$$

Here V^t stands for volume of the solution per kg of DNA (or per mole of nucleotide). The average value of molecular weight of nucleotide was taken as 330 in this calculation[7].

In Figure 4, Γ_2^1 values for DNA (and RNA) have been plotted against different values of C_2 at fixed values of pH. Γ_2^1 is observed to increase with increase of C_2 until its value attains fixed average value Γ_2^m. Each curve is found to fit Langmuir equation in linear form. The adsorption isotherms of denatured and native DNA by alumina particles are found to be widely different from each other[15].

Gani *et al.*[7] have measured adsorption of DNA on different solid powders (Figure 5) as functions of mole fraction X_2 (equal to $C_2/55.5$) of nucleotide at fixed values of pH, ionic strength, and native and denatured states of DNA respectively. Γ_2^1 as usual increases with the increase of X_2 until a fixed maximum value of adsorption (Γ_2^m) is reached at a critical value of X_2^m. The adsorption isotherms of DNA on charcoal powder in the presence of neutral salts such as LiCl, NaCl, KCl, CsCl, KBr, $CaCl_2$ and Na_2SO_4 are observed to be different from each other due to the difference in the extent of DNA hydration in the presence of these salts[7]. In the presence of sodium dodecyl sulphate (SDS) and Triton X-100, the adsorption of DNA on charcoal has been observed to be affected[7]. The adsorption isotherms of native and various forms of denatured DNA are significantly different from each other. Role of different solid powders, e.g. charcoal, silica,

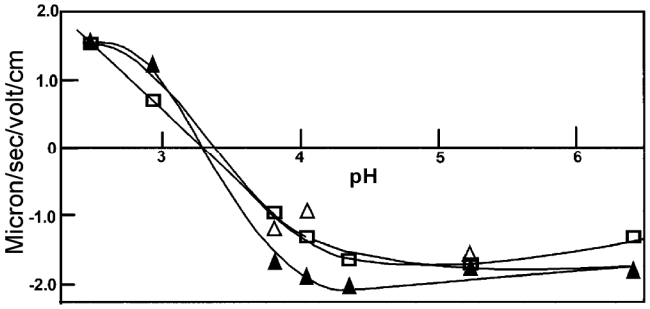

Figure 3. Electrophoretic mobilities of adsorbed nucleo-histone[14] at 25°C on alumina particles as a function of pH at ionic strengths (Δ), 0.00; (□), 0.05 and (▲), 0.10.

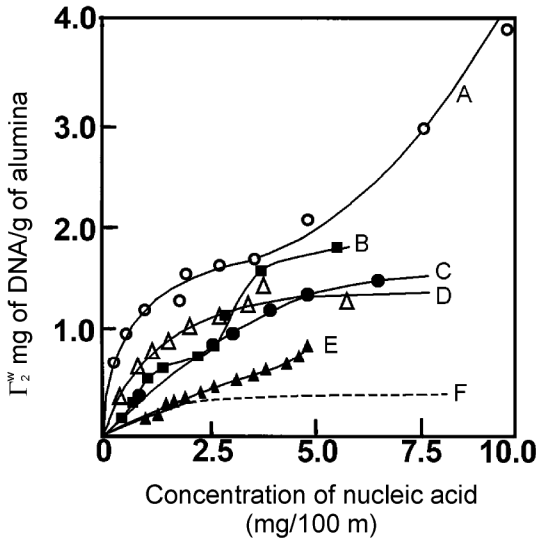

Figure 4. Adsorption[15] of native and denatured DNA and RNA onto alumina powder at 25°C, pH 6.5 and ionic strength 0.05 with NaCl. A, heat-denatured DNA; B, Heat-denatured RNA; C, acid denatured DNA; D, alkali denatured DNA; E, native RNA; F, native DNA.

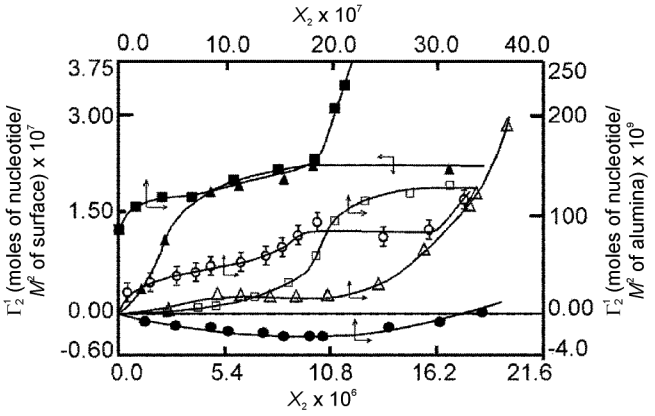

Figure 5. Plot of Γ_2^1 against X_2 for the adsorption of native DNA on different solid surfaces[7] at 28°C, pH 6.5 and ionic strength 0.05. (○) silica; (□) chromium; (●), sephadex; (Δ) Cl^- resin; (■) charcoal, (▲) alumina.

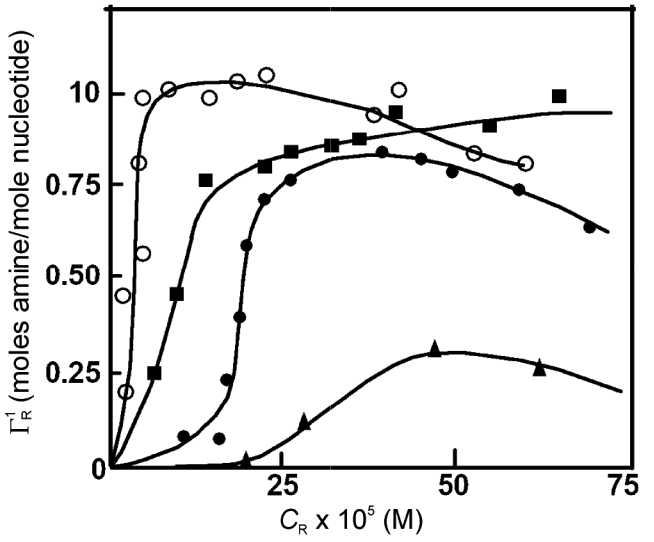

Figure 6. Γ_R^1 vs C_R plot of DNA, phosphate buffer[20], ionic strength 0.0625 and 30°C for (○), CTAB; (■), CPCl; (●), MTAB; (▲), DTAB.

chromium, resin, sephadex, alumina on DNA adsorption under the same physicochemical conditions is found to be significantly different from each other[7]. In many cases, Γ_2^1 increases further from Γ_2^m when $X_2 >> X_2^m$ due to the formation of multilayers of DNA formed at the interface. Standard free energies of adsorption, $\Delta G°$ for the various adsorption isotherms of DNA have been calculated using the integrated forms of the Gibbs adsorption equation[16]. From further thermodynamic analysis, standard enthalpy changes for adsorption of DNA have been observed to be compensated by the change in entropy of different systems undergoing adsorption process.

Gani *et al.*[17] have measured extents of adsorption (Γ_2^1) of DNA on the surface of casein (a milk protein) as function of pH, temperature and ionic strength of the medium and using various types of salts and denaturants. In all cases, Γ_2^1 increases with increase in DNA concentration until the maximum value Γ_2^m is attained. DNA in native state is not able to accumulate at the casein surface in the presence of NaCl. But with the addition of $CaCl_2$ and $AlCl_3$, the extent of adsorption at this soft surface increases to a significant amount. The mechanism for the role of adsorbed water in controlling the adsorption process has been discussed qualitatively by them[17].

Halder *et al.*[18] have shown that the adsorption isotherm of DNA on the hydrophilic surface of cellulose at acid pH 4.0 at different ionic strengths, temperatures and in the presence of high concentrations of LiCl, NaCl, KCl and Na_2SO_4 respectively are widely different from each other. They have compared maximum values of adsorption Γ_2^m for all these systems with critical explanations. Halder *et al.*[18] have surprisingly noted that at pH 6.0 and 8.0, values of Γ_2^1 for DNA are all significantly negative due to the excess positive hydration of cellulose at these pH values. They have further noted that in the presence of urea even at pH 4.0. Γ_2^1 becomes negative for the same reason. However, at this acid pH, values of Γ_2^1 for DNA denatured by heat, acid and alkali are positive but their magnitudes are widely different from each other.

Mitra *et al.*[19] have investigated the kinetic aspects of DNA adsorption at different hydrophobic and hydrophilic interfaces at several temperatures, pH and ionic strength. The initial rates for DNA adsorption in all these concentrations are controlled by diffusion process. The steady values of the extents of adsorption (Γ_2^e) are attained after nearly six hours. The rates of adsorption in all cases fit the first order rate equations of two different rate constants K_1 and K_2 respectively. Using the Arrhenius equation, the energies of adsorption E_1^* and E_2^* for DNA adsorption have been evaluated. Also using the Eyring equation, the enthalpy and entropy of activation ΔH_0^* and ΔS_0^* respectively have been evaluated by Mitra *et al.*[18] for both the kinetic steps. The adsorption of DNA for charcoal–water and silica–water interfaces is found to be entropy controlled but for $BaSO_4$–water interface, the observed adsorption process is enthalpy controlled.

DNA–surfactant binding

Chatterjee and Chattoraj[20] as early as in 1979 determined the binding ratio Γ_2^1 for several long-chain amines to calf thymus DNA as functions of the ligand concentration C_2 using the equilibrium dialysis method. DNA solution prepared in appropriate buffer has been taken in a dialysis casing and the tightly bound casing has been placed in the solution of surfactant prepared in the same buffer. The system containing casing and surfactant solution is then mildly shaken for 20 h until dialysis equilibrium is attained. The concentration C_2 of the dialysate has been analysed by spectrophotometric methods[21,22]. Different amines used in their experiments are cetyl trimethyl ammonium bromide (CTAB), myristyl trimethyl ammonium

bromide (MTAB), dodecyl trimethyl ammonium bromide (DTAB) and cetyl pyridinium chloride (CPCl). The isotherms for binding these surfactants to DNA have been obtained from experimental data[20]. The formation and dissociation of the saturated DNA–amine complexes are observed to be reversible. With the increase of ionic strength of the medium, the initial slope representing electrostatic contribution to binding isotherm increases indicating association of the ligands on the DNA bound region. Γ_2^1 increases with increase of C_2 until a maximum value Γ_2^m is obtained at a critical value C_2^{cri} of the ligand. Both Γ_2^m and Γ_2^1 are observed to increase significantly with the increase in chain length of the surfactant due to hydrophobic interaction. The standard free energy change for binding ligand to DNA has been evaluated using derived thermodynamic relation, and the standard states for binding process have been clearly defined[16,20]. The binding of MTAB and CPCl has been observed to increase with increase in temperature. Using these binding data, enthalpy and entropy values ΔH° and ΔS° have been evaluated. Binding is thus observed to be controlled by entropy effect related to hydrophobic interaction. The binding isotherms are also found to depend upon nature of different neutral salts like KCl, NaCl, LiCl, Na_2SO_4 and $MgCl_2$ present in the bulk solutions possibly due to hydration effect.

Chatterjee *et al.*[23] also have observed that the binding ratio Γ_2^1 for the anionic ligand SDS to DNA is negligibly small irrespective of the ligand concentrations below cmc and the ionic strength 0.05 at 30°C. At 30°C, the isotherms for binding neutral surfactant Triton X-100, hexanoic and octanoic acids respectively to DNA exhibit signs of cooperative interactions. Temperature effect to binding indicates that the hydrophobic effect contribution to binding process is negligible. Standard free energy change for binding of Triton X-100 and fatty acids to DNA have been calculated using appropriate thermodynamic equations.

Chatterjee and Chattoraj[24] have also studied the thermal stabilities of DNA in the presence of CTAB, MTAB, DTAB and CPCl. Thermal stability of DNA helix decreases considerably at the pre-cooperative state of ligand binding concentration in the presence of low concentrations of amines. At a higher ligand concentration, the melting profile of saturated DNA–amine complex has close similarities with that of pure DNA in the aqueous medium. It was proposed that due to DNA–amine binding interaction, the strain in the helix structure of DNA is released so that more compact folded structure of the DNA–amine complex may result.

Gani *et al.*[25] have studied extent of binding of SDS to the binary complex formed between calf thymus DNA and CTAB as function of SDS concentration by using equilibrium dialysis technique at different temperatures and pH. The most interesting aspect to be noted in this experiment is that the water insoluble DNA–CTAB binary complex gets solubilized in the ternary mixture in the presence of SDS (Figure 7). When DNA is thermally denatured, the ternary system DNA–CTAB–SDS remains insoluble. Significant change in the extent of binding has been noted with the variation of the relative composition of DNA and CTAB in their binary mixture. In the absence of CTAB, SDS does not bind to DNA as shown earlier[23]. ΔG° values for all these systems have been calculated using integrated form of the Gibbs adsorption equation[16]. Gani *et al.*[26] have measured binding of CTAB to calf thymus DNA, BSA, and to their binary mixtures respectively as functions of bulk concentrations of each surfactant using equi-librium dialysis technique. They have also measured Γ_2^1 for CTAB to collagen, gelatin, DNA–collagen and DNA–gelatin mixtures respectively. The conformational structures of different biopolymers are observed to play significant role in macromolecular interaction between protein and DNA in the presence of CTAB. Using the additivity rule, the ideal values (Γ_2^1) of protein–DNA mixtures have been estimated. Deviations of ideal values from experimental values have been explained by them in terms of interactions between biopolymers and CTAB forming DNA–protein–CTAB complex in the system.

Maulik *et al.*[27] have measured equilibrium binding of CTAB with DNA by an electrometric method using surfactant reversible electrode as functions of pH and ionic strength. The strong binding interaction between DNA and CTAB has been shown by them to be reversible. The free energies of binding[27,28] found by them are distinctly of two categories. The low and high free energies of interaction correspond to normal and co-operative binding processes.

Using the same electrometric technique with ion-selective membrane electrode, kinetics of binding CTAB

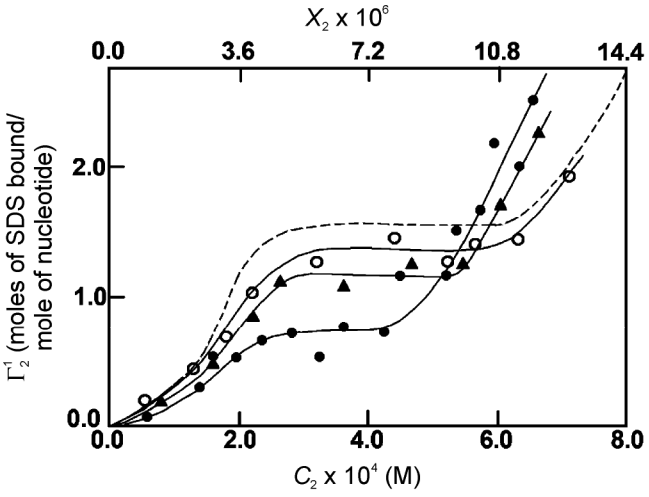

Figure 7. Parameters for SDS binding[25] to DNA–CTAB complex[20] (Ratio of nucleotide : CTAB, 1 : 1) at $\mu = 0.05$. Plot of Γ_2^1 (moles SDS bound per mole nucleotide) against bulk SDS concentration C_2 at 28°C (-----) DNA = CTAB complex, pH 5.0 (○), pH 7.2, (Δ) pH 9.0, heat denatured DNA–CTAB complex (●), pH 5.0.

to DNA has been studied by Maulik *et al.*[29]. The binding follows first order kinetics and occurs in three stages for native DNA. Denatured DNA indicates two stage first order kinetics. The activation energies were low but entropies of activation are high. Also, entropy–enthalpy compensation effect is observed for all systems studied.

Recently it has been shown by Shani[30] that DNA is able to bind on different hydrophilic soft surfaces at pH 6.5. Γ_2^m for these systems stand in the following order: stearic acid > milk fat > phosphatidyl choline > choline > cholesterol > palmitic acid. The adsorption isotherm of DNA on phosphatidyl choline at 28°C and pH 6.5 indicates that at higher values of nucleotide concentrations, DNA undergoes multilayer adsorption.

Similar to binding of cationic surfactant to DNA, histone, a cationic protein has been found to bind DNA at different physicochemical conditions as shown by Chattoraj *et al.*[31] using interfacial tension technique. The same technique has been used recently by Mitra *et al.*[32] who have shown that many globular proteins like BSA, β-lactoglobulin, α-lactalbumin and lysozyme will bind to DNA at intermediate range of pH due to the formation of nucleic acid–protein complex. Using isopiestic vapour pressure measurement technique, Chattoraj and Bull[33] have measured absolute binding of inorganic salts and water to DNA.

We also note from all these discussions that from 1965 to 1985, besides our publications on DNA adsorption and surfactant binding interaction, there were no significant publications in this area of research. Only in the last 10–20 years, other workers became interested in this emergent area of research and came up with many interesting new observations using novel experimental techniques.

Current research by other workers

Very recently, Tang *et al.*[34] have reported the stereoselective adsorption of DNA molecules on the N-isobutyryl-L(D)-cysteine (NIBC) enantiomer modified gold surfaces. They have examined the state and morphological change of the adsorbed DNA molecules on L and D chiral surface by atomic force microscopy (AFM) and DNA adsorption quantity on these two surfaces using the quartz crystal microbalance (QCM) method. Their results have shown that DNA molecules have a much stronger interaction with the L surface than the corresponding D surface. According to these authors, this kind of stereospecific interaction between DNA and chiral surfaces might be interesting to understand the stereospecific cell/substrate interaction and the origin of the chiral preference in nature.

Hook *et al.*[35] have investigated the interaction of double-stranded plasmid DNA with the allylamine plasma polymer (ALAPP) and polyethylene glycol (PEG) coated surfaces. These two coatings are commonly used for the control of protein and cell–surface interactions on biomedical devices. Large adsorptions of DNA on such modified surfaces create a scope to produce two-dimensionally controlled DNA adsorption on spatially patterned ALAPP and PEG chemistry.

Cai *et al.*[36] reported the adsorption, desorption and degradation of DNA by DNaseI on montmorillonite and different hydroxyaluminum–montmorillonite complexes ($Al(OH)_x$–montmorillonite) at different physicochemical conditions like pH and presence of calcium ions. Their results showed that OH–Al loading on montmorillonite and $A1(OH)_x$–M complexes provide protection for DNA against degradation by DNaseI.

Mateo-Marti *et al.*[37] have studied the adsorption of single-stranded peptide nucleic acid (ssPNA) on a natural pyrite surface, as well as the further adsorption of ssDNA on a PNA-modified pyrite surface by means of reflection absorption infrared spectroscopy (RAIRS), AFM and X-ray photoemission spectroscopy (XPS) techniques. The results of their experimental techniques confirmed that PNA adsorbs on pyrite surface, interacting through nitrogen-containing groups of the nucleobases and the iron atoms of the surface and the strong PNA/pyrite interaction inhibits further hybridization of PNA with complementary ssDNA.

Recently, Nguyen and Elimelech[38] have studied adsorption rates of various forms of plasmid DNA on organic matter coated silica using a quartz crystal microbalance. Resulting structure of adsorbed DNA layers has been examined by dynamic light scattering technique under different physicochemical conditions. The adsorption has been observed to be irreversible. Reflection anisotropy spectroscopy has been used by Consuelo *et al.*[39] for study of single and double-stranded DNA adsorbed on a plate placed in electrochemical cell. Pastre *et al.*[40] have studied adsorption of DNA molecules on negatively charged mica mediated by divalent and trivalent cations using AFM. They compared the images of adsorbed DNA molecules in terms of different salts present in solution. Li *et al.*[41] have demonostrated that electrophoresis on a flat silica surface is an effective method for separation of adsorbed DNA molecules of various configurations. Gromelski *et al.*[42] have shown that in the presence of divalent cations, DNA can undergo adsorption interaction on zwitterionic lipids and this observation is useful in gene therapy. Zao *et al.*[43] have shown that using ellipsometric technique, bioactive DNA can be mobilized on polyethylene amine coated silicon oxide–water interface. According to these authors, the study may be useful for fabrication of biosensors and gene chips via interfacial adsorption.

Frantescu *et al.*[44] have shown that efficiency of electrophoretic transfer of gene DNA into tissue cells by electric pulses depends crucially on the adsorption of the gene DNA to the plasma cell membrane in presence of calcium ions.

DNA compaction by alkyl trimethyl ammonium and other surfactant ions at hydrophobic silica surfaces has been studied by Cardenas and co-workers[45,46] using null-ellipsometry technique. Mc Loughlin *et al.*[47] have studied surface complexation of DNA with a cationic surfactant DTAB using dynamic surface tension, ellipsometry and Brewster angle microscopy. Horinaka *et al.*[48] have studied the adsorption process of DNA from solution to the surface of polyethylenimine using circular dichroism including time-resolved measurements to elucidate the conformation of DNA at the solid–liquid interface.

Yang *et al.*[49] have imaged and studied self-assembled double-stranded DNA adsorbed on gold–solution interface using electrochemical scanning tunnelling microscopy. For the information of storage in DNA-based biochips, Liu *et al.*[50] have made an attempt to construct a reversible exchange interface of DNA. Here a highly reproducible and reversible adsorption–desorption interface of DNA based on nano-size zirconia in different pH aqueous media has been successfully fabricated.

Interaction of cationic surfactants with calf thymus DNA has been studied in aqueous media by Chatterjee and Moulik[51] using spectrophotometric, viscometric, tensiometric dynamic light scattering, circular dischroism, fluoroscent microscopic and microcalorimetric techniques. All the surfactants are found to interact fairly with DNA making the biopolymer condensed even to the aggregated globular configuration at higher concentration of the surfactant. Melting temperature and light scattering intensity are increased, whereas viscosity of system is decreased in the presence of surfactants. From calorimetric titration measurement, the binding interaction has been shown to lead to small enthalpy change.

Rosa *et al.*[52] have used circular dichroism, UV adsorption and calorimetry to prove that DNA–surfactant interaction for double-stranded and single-stranded DNA are different from each other. Nakanishi *et al.*[53] have studied the effect of CTAB on aggregated DNA molecules in water. They have shown that CTAB causes changes from loosely packed spherical to rod-like DNA aggregates near cmc. Melnikov *et al.*[54] and also Matulis and co-workers[55] have shown that as a result of co-operative interactions with CTAB the elongated DNA helices condense and end up into compact conformation even to the globular form. The process is called transfection. The complexed product has the potential for introduction into living cells. Various physicochemical techniques have been used for study of DNA–surfactant interaction processes subsequently[56–58].

Besides DNA–surfactant interaction, the complex formation of nucleic acid with natural and synthetic polycationic macromolecules has been studied extensively[59–66]. Among the synthetic macromolecules, poly(amido amine) (PAMAM) dendrimer has a unique mimic property of biological macromolecules, including globular proteins such as histone, haemoglobin, cytochrome C, and haemerythrin, and many other bioassemblies. In recent years, a large number of studies covering many different aspects of DNA–dendrimer interactions have appeared in the literature[67–72]. From AFM images, Mitra and Imae *et al.*[70] explored the morphology of the dried dendrimer/DNA complexes adsorbed on mica surface at different mixing ratio of dendrimer and DNA. Generally, cationic macromolecules protect the DNA from degradation through condensation and also promote the interaction with cell membrane. DNA adsorbed on many polymeric materials has been used for nucleic acid-based drug delivery systems[73,74].

In the near future, there will be more studies on the interactions of DNA with membrane materials of cells *in vitro* and *in vivo*[2]. Different types of cationic lipids may be used to entrap negatively charged DNA for the gene transfer *in vivo*. This approach has been used for the aerosol delivery of DNA to lungs and development of cancer vaccines[75]. In human tissues DNA is delivered using 'gene guns' involving DNA-coated gold particles[75–77]. It has been further demonstrated that DNA immobilization on solid surfaces is a necessary step for preparation of DNA-based biosensors[78], microarrays[79], DNA–hybridization[80] development of bio-films, etc. Also DNA adsorption on soil minerals may protect gene from enzymatic degradation[36] for which more work is necessary.

In all these studies carried out recently, DNA adsorption on solid–liquid interfaces and DNA–surfactant interaction in bulk and at interfaces were used to develop useful DNA technologies for thin-film applications. In the near future, attempts will be made to understand many biological interactions involving DNA, proteins, lipids, metal ions and water present in cells in equilibrium and dynamic states during cell divisions. In this respect, Chatterji and Rajdev[81] have made a critical study on interaction of DNA with protein film formed using Langmuir monolayer and Langmuir–Blodgett techniques. They have used various types of modern instruments in their study of biological interactions of DNA in cell. This field of study will expand soon to further understand biological processes.

1. Bull, H. B., *An Introduction to Physical Biochemistry*, FA Davis, Philadelphia, 1971, 2nd edn.
2. Nelson, D. L. and Cox, M. M., *Lehniger Principles of Biochemistry*, Replica Press, India, 2005, 4th edn.
3. Stryer, L., *Biochemistry*, W. H. Fernman, New York, 1995, pp. 75–77.
4. Roberts, E. D. P. De, Nowinski, W. W. and Saez, F. A., *Cell Biology*, W.B. Saunders Co, Philadelphia, 1970, 5th edn.
5. Chattoraj, D. K., Bull, H. B. and Chalkley, R., Binding of histone to DNA. *Arch. Biochem. Biophys.*, 1972, **152**, 778–785.
6. Watson, J. D. and Crick, F. H. C., Molecular structure of nucleic acids. *Nature*, 1953, **171**, 737–738.
7. Gani, A., Mukherjee, D. C. and Chattoraj, D. K., Adsorption of biopolymer at solid–liquid interfaces. Part 1: Affinities of DNA to hydrophilic and hydrophobic solid surfaces. *Langmuir*, 1999, **15**, 7130–7138.

8. Guland, J. M., Jordan, D. O. and Taylor, H. F. W., Deoxypentose nucleic acids. Part II. Electrometric titration of the acidic and the basic groups of the deoxypentose nucleic acid of calf thymus. *J. Chem. Soc.*, 1947, 1131–1141.
9. Cosgrave, D. J. and Jordan, D. O., Deoxypentose nucleic acids. Part VI. Electrometric titration of the acidic and basic groups of the deoxypentose nucleic acids of lamb thymus and herring sperm. *J. Chem. Soc.*, 1949, 1413–1415.
10. Olivera, B. M., Baine, P. and Davidson, N., Electrophoresis of the nucleic acids. *Biopolymers*, 1964, **2**, 245–257.
11. Ross, P. D. and Shruggs, R. L., Electrophoresis of DNA. III. The effect of several univalent electrolytes on the mobility of DNA. *Biopolymers*, 1964, **2**, 231–236.
12. Chattoraj, D. K., Chowrashi, P. and Chakravarti, K., Electrophoresis of adsorbed DNA. *Biopolymers*, 1967, **5**, 173–184.
13. Chowrashi, P., Chattoraj, D. K. and Chakrabarti, K., Electrophoresis of absorbed RNA. *Biopolymers*, 1968, **6**, 97–104.
14. Upadhyay, S. N. and Chattoraj, D. K., A conformational change of adsorbed nucleo-histone from microelectrophoretic study. *Indian J. Biochem. Biophys.*, 1972, **8**, 12–16.
15. Upadhyay, S. N. and Chattoraj, D. K., Adsorption of calf thymus DNA on the solid–liquid interface. *Biochim. Biophys. Acta*, 1968, **151**, 561–563.
16. Chattoraj, D. K., Biswas, S. C., Mahapatra, P. and Chatterjee, S., Standard free energies of binding of solute to proteins in aqueous medium. Part 2: Analysis of data obtained from equilibrium dialysis and isopiestic experiments. *Biophys. Chem.*, 1999, **77**, 9–25.
17. Gani, A., Mukherjee, D. C. and Chattoraj, D. K., Adsorption of biopolymer at solid–liquid interfaces, Part II: Interaction of BSA and DNA with casein. *Langmuir*, 1999, **15**, 7139–7144.
18. Halder, E., Chattoraj, D. K. and Das, K. P., Adsorption of biopolymers at hydrophilic cellulose–water interface. *Biopolymers*, 2005, **77**, 286–295.
19. Mitra, A., Chakraborty, P. and Chattoraj, D. K., Kinetics of adsorption of DNA at solid–liquid interface. *J. Indian Chem. Soc.*, 2001, **78**, 689–696.
20. Chatterjee, R. and Chattoraj, D. K., Hydrophobic interactions of DNA with long-chain amines. *Biopolymers*, 1979, **18**, 147–166.
21. Mukherjee, P., Use of ionic dyes in analysis of ionic surfactants and other ionic organic compounds. *Analyst. Chem.*, 1956, **28**, 870–873.
22. Biswas, H. K. and Mondal, B. M., Extraction of anions into chloroform by surfactant cations. Relevance to dye extraction method of analysis of long chain amines. *Analyst. Chem.*, 1972, **44**, 1636–1640.
23. Chatterjee, R., Mitra, S. P. and Chattoraj, D. K., Binding of sodium dodecyl sulphate, triton X and short chain fatty acids to DNA. *Indian J. Biochem. Biophys.*, 1979, **16**, 22–27.
24. Chatterjee, R. and Chattoraj, D. K., Thermal transion of DNA in presence of long-chain amines. *Indian J. Biochem. Biophys.*, 1979, **16**, 236–239.
25. Gani, S. A., Chattoraj, D. K. and Mukherjee, D. C., Solubilisation and binding of DNA–CTAB complex with SDS in aqueous media. *Indian J. Biochem. Biophys.*, 1999, **36**, 233–239.
26. Gani, S. A., Chattoraj, D. K. and Mukherjee, D. C., Binding of cationic surfactants to DNA and DNA–protein mixtures. *Indian J. Biochem. Biophys.*, 1999, **36**, 165–176.
27. Maulik, S., Dutta, P., Chattoraj, D. K. and Moulik, S. P., Equilibrium studies on the binding of cetyl trimethyl ammonium bromide and sodium docecyl sulphate with bovine serum albumin, β-lactoglobin, hemoglobin, gelatin, lysozyme and deoxyribonucleic acid. *Colloids Surf., B: Biointerfaces*, 1998, **11**, 57–65.
28. Chattoraj, D. K. and Birdi, K. S., *Adsorption from Solution and the Gibbs Surface Excess*, Plenum Press, New York, 1984.
29. Maulik, S., Chattoraj, D. K. and Moulik, S. P., Binding of cetyltrimethyl ammonium bromide with deoxyribo nucleic acid. *Colloids Surf., B: Biointerfaces*, 1998, **11**, 57–65.
30. Shani, D., Adsorption interaction of milk proteins and other biopolymers on solid–liquid and air–water interfaces. Ph D thesis, Jadavpur University, 2009.
31. Chattoraj, D. K., Bull, H. B. and Chalkley, R., Binding of histone to DNA. *Arch. Biochem. Biophys.*, 1972, **152**, 778–785.
32. Mitra, A., Chattoraj, D. K. and Chakraborty, P., Binding of globular proteins to DNA from surface tension measurement. *J. Biochem. Biophys.*, 2001, **38**, 313–320.
33. Chattoraj, D. K. and Bull, W. B., Water and solute binding to DNA. *Arch. Biochem. Biophys.*, 1971, **142**, 363–370.
34. Tang, K., Gan, H., Li, Y., Chi, L., Sun, T. and Fuchs, H., Stereoselective interaction between DNA and chiral surfaces. *J. Am. Chem. Soc.*, 2008, **130**, 11284–11285.
35. Hook, A. L., Thissen, H., Quinton, J. and Voelcker, N. H., Comparison of the binding mode of plasmid DNA to allylamine plasma polymer and poly(ethylene glycol) surfaces. *Surface Sci.*, 2008, **602**, 1883–1891.
36. Cai, P., Huang, Q., Li, M. and Liang, W., Binding and degradation of DNA on montmorillonite coated by hydroxyl aluminum species. *Colloids Surf., B: Biointerfaces*, 2008, **62**, 299–306.
37. Mateo-Marti, E., Briones, C., Rogero, C., Gomez-Navarro, C., Methivier, Ch., Pradier, C. M. and Martin-Gago, J. A., Nucleic acid interactions with pyrite surfaces. *Chem. Phys.*, 2008, **352**, 11–18.
38. Nguyen, T. H. and Elimelech, M., Adsorption of plasmid DNA to a natural organic matter-coated silica surface: kinetics, conformation, and reversibility. *Langmuir*, 2007, **23**, 3273–3279.
39. Consueol, M., Smith, C. I., Fenig, D. G., Edenwards, C. and Weightman, P., Adsorption of calf thymus DNA on Au(110) studied by reflection anisotropy spectroscopy. *Langmuir*, 2007, **23**, 2078–2082.
40. Pastre, D. *et al.*, Anionic polyelectrolyte adsorption on mica mediated by multivalent cations: a solution to DNA imaging by atomic force microscopy under high ionic strengths. *Langmuir*, 2006, **22**, 6651–6660.
41. Li, B. *et al.*, Separation of DNA with different configurations on flat and nanopatterned surfaces. *Anal. Chem.*, 2006, **78**, 4743–4751.
42. Gromelski, S. and Brezesinski, G., DNA condensation and interaction with zwitterionic phospholipids mediated by divalent cations. *Langmuir*, 2006, **22**, 6293–6301.
43. Zhao, X., Fang, P. and Lu, J. R., Adsorption of polyethyleneimine characterized by spectroscopic ellipsometry. *Prog. Nat. Sci.*, 2005, **15**, 56–59.
44. Frantescu, A., Tonsing, K. and Neuman, E., Interfacial ternary complex DNA/Ca/lipids at anionic vesicle surfaces. *Bioelectrochemistry*, 2006, **68**, 158–170.
45. Cardenas, M., Nylander, T., Thomas, R. K. and Lindman, B., DNA compaction onto hydrophobic surfaces by different cationic surfactants. *Langmuir*, 2005, **21**, 6495–6502.
46. Cardenas, M., Campos-Teran, J., Nylander, T. and Lindman, B., DNA and cationic surfactant complexes at hydrophilic surfaces. An ellipsometry and surface force study. *Langmuir*, 2004, **20**, 8597–8603.
47. McLoughlin, D. and Langevin, D., Surface complexation of DNA with a cationic surfactant. *Colloids Surf. A*, 2004, **250**, 79–87.
48. Horinaka, J., Nakura, H. and Maeda, S., *In situ* measurement of circular dichroism of DNA adsorbing onto a solid. *J. Biochem. Biophys. Meth.*, 2004, **61**, 349–357.
49. Yang, G. Z., Ling, L. S., Wan, L. J., Fang, X. H. and Bai, C. L., Electrochemical scanning tunnelling microscope imaging of self-assembled monolayer of double-stranded DNA on Au(111). *J. Nanosci. Nanotechnol.*, 2004, **4**, 561–564.
50. Liu, S. Q., Xu, J. J. and Cher, H. Y., A reversible adsorption-desorption interface of DNA based on nano-sized zirconia and its application. *Colloids Surf. B*, 2004, **36**, 155–159.
51. Chatterjee, A. and Moulik, S. P., Studies on surfactant biopolymer interaction. II. Interaction of cetyl trimethyl ammonium-, cetyl

ethanolyl dimethyl ammonium-, cetyl diethanolyl methyl ammonium-, and cetyl triphenyl phosphonium bromides and cetyl pyridinium chloride with calf thymus DNA. *Indian J. Biochem. Biophys.*, 2005, **42**, 205–215.
52. Rosa, M., Dias, R., Grac, M., Miguel, A. and Lindman, B., DNA–cationic surfactant interactions are different for double- and single-stranded DNA. *Biomacromolecules*, 2005, **6**, 2164–2171.
53. Nakanishi, W., Tsuchiya, K., Okubo, T., Sakai, H. and Abe, M., Cationic surfactant changes the morphology of DNA molecules. *Langmuir*, 2007, **23**, 345–347.
54. Melnikov, S. M., Sergeyev, V. G. and Yoshikawa, K., Transition of double-stranded DNA chains between random coil and compact globule states induced by cooperative binding of cationic surfactant. *J. Am. Chem. Soc.*, 1995, **117**, 9951–9956.
55. Matulis, D., Rouzina, I. and Bloomfield, V. A., Thermodynamics of cationic lipid binding to DNA and DNA condensation: roles of electrostatics and hydrophobicity. *J. Am. Chem. Soc.*, 2002, **124**, 7331–7342.
56. Spink, C. H. and Chaires, J. B., Thermodynamics of the binding of a cationic lipid to DNA. *J. Am. Chem. Soc.*, 1997, **119**, 10920–10928.
57. Kennedy, M. T., Pozhasski, E. V., Rakhmanova, V. and MacDonnald, R. C., Factors governing the assembly of cationic phosphorlipid–DNA complexes. *Biophys. J.*, 2000, **78**, 1620–1633.
58. Bloomfield, V., Condensation of DNA by multivalent cations: considerations on mechanism. *Biopolymers*, 1991, **31**, 1471–1481.
59. Yoksan, R. and Akashi, M., Low molecular weight chitosan-g-l-phenylalanine: Preparation, characterization, and complex formation with DNA. *Carbohydrate Polymers*, 2009, **75**, 95–103.
60. Gawęda, S., Morán, M. C., Pais, A. A. C. C., Dias, R. S., Schillén, K., Lindman, B. and Miguel, M. G., Cationic agents for DNA compaction. *J. Colloid Inter. Sci.*, 2008, **323**, 75–83.
61. Farber, Y. and Domb, A. J., Cationic polysaccharides for gene delivery. *Mater. Sci. Eng. C*, 2007, **27**, 595–598.
62. Masotti, A. *et al.*, Physicochemical and biological study of selected hydrophobic polyethylenimine-based polycationic liposomes and their complexes with DNA. *Bioorg. Med. Chem.*, 2007, **15**, 1504–1515.
63. Alvarez-Lorenzo, C., Barreiro-Iglesias, R. and Iourtchenko, A. C., Bromberg, V. A., Temchenko, M., Deshmukh, S. and Alan Hatton, T., Biophysical characterization of complexation of DNA with block copolymers of poly(2-dimethylaminoethyl) methacrylate, poly(ethylene oxide), and poly(propylene oxide). *Langmuir*, 2005, **21**, 5142–5148.
64. Wu, C. M., Liou, W., Chen, H. L., Lin, T. L. and Jeng, U. S., Self-assembled structure of the binary complex of DNA with cationic lipid. *Macromolecules*, 2004, **37**, 4974–4980.
65. Wolfert, M. A. *et al.*, Polyelectrolyte vectors for gene delivery: influence of cationic polymer on biophysical properties of complexes formed with DNA. *Bioconjugate Chem.*, 1999, **10**, 993–1004.
66. Rädler, J. O., Koltover, I., Jamieson, A., Salditt, T. and Safinya, C. R., Structure and interfacial aspects of self-assembled cationic lipid–DNA gene carrier complexes. *Langmuir*, 1998, **14**, 4272–4283.
67. Fant, K., Esbjörner, E. K., Lincoln, P. and Nordén, B., DNA condensation by PAMAM dendrimers: self-assembly characteristics and effect on transcription. *Biochemistry*, 2008, **47**, 1732–1740.
68. Örberg, M. L., Schillén, K. and Nylander, T., Dynamic light scattering and fluorescence study of the interaction between double-stranded DNA and poly(amido amine) dendrimers. *Biomacromolecules*, 2007, **8**, 1557–1563.
69. Maiti, P. K. and Bagchi, B., Structure and dynamics of DNA–dendrimer complexation: role of counterions, water and base pair sequence. *Nano Lett.*, 2006, **6**, 2478–2485.
70. Mitra, A. and Imae, T., Nanogel formation consisting of DNA and poly(amido amine) dendrimer studied by static light scattering and atomic force microscopy. *Biomacromolecules*, 2004, **5**, 69–73.
71. Ottaviani, M. F., Furini, F., Casini, A., Turro, N. J., Jockusch, S., Tomalia, D. A. and Messori, L., Formation of supramolecular structures between DNA and starburst dendrimers studied by EPR, CD, UV, and melting profiles. *Macromolecules*, 2000, **33**, 7842–7851.
72. Bielinska, A. U., Chen, C., Johnson, J. and Baker Jr, J. R., DNA complexing with polyamidoamine dendrimers: implications for transfection. *Bioconjugate Chem.*, 1999, **10**, 843–850.
73. Storrie, H. and Mooney, D. J., Sustained delivery of plasmid DNA from polymeric scaffolds for tissue engineering. *Adv. Drug Deliv. Rev.*, 2006, **58**, 500–514.
74. Jewell, C. M., David, M. and Lynn, D. M., Multilayered polyelectrolyte assemblies as platforms for the delivery of DNA and other nucleic acid-based therapeutics. *Adv. Drug Deliv. Rev.*, 2008, **60**, 979–999.
75. Nabel, G. J. *et al.*, Direct gene transfer with DNA–liposome complexes in melanoma: expression, biologic activity and lack of toxicity in humans. *Proc. Natl. Acad. Sci. USA*, 1993, **90**, 11307–11311.
76. Ulmer, J. B. *et al.*, Heterologous protection against influenza by injection of DNA encoding a viral protein. *Science*, 1993, **259**, 1745–1749.
77. Mannelli, P., Minimni, A., Tombelli, S., Wang, R. H., Spirits, M. M. and Mascini, M., Direct immobilisation of DNA probes for the development of affinity biosensors. *Bioelectrochemistry*, 2005, **66**, 129–138.
78. Pedano, M. L. and Rivas, G. A., Immobilization of DNA at glassy carbon electrodes: a critical study of adsorbed layer. *Sensors*, 2005, **5**, 424–447.
79. Sehena, M., Sahlen, D., Heller, R., Chai, A., Brown, P. O. and Davies, R. W., Parallel human genome analysis: microarray-based expression monitoring of 1000 genes. *Proc. Natl. Acad. Sci. USA*, 1996, **93**, 10614–10619.
80. Hook, F., Ray, A., Mordey, R., Kasemo, B. and Kolter, R., Characterization of RNA and DNA immobilization and subsequent hybridization with DNA using acoustic-shear-wave attenuation measurements. *Langmuir*, 2001, **17**, 8305.
81. Chatterji, D. and Rajdev, P., Macromolecular recognition at the air–water interface: application of Langmuir–Blodgett technique. *Curr. Sci.*, 2008, **95**, 1226–1236.

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