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Paramagnetic Surface Active Ionic Liquids: Interaction with DNA and MRI Application

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ABSTRACT

Paramagnetic surface active ionic liquids (PMSAILs) have been synthesized wherein long alkyl chain bearing imidazoilium, pyridinium or isoquinolinium are cationic and bromotrichloroferrate (III) is paramagnetic counterion constituents. PMSAILs have been investigated for their aggregation properties using surface tension, conductivity, and dynamic light scattering (DLS). Interaction of PMSAILs with DNA in aqueous solutions has been examined through CD, fluorescence, ITC, DLS, zeta potential, and agarose gel electrophoresis. DNA compaction has been observed upon interaction with PMSAILs in dilute solutions. PMSAIL with isoquinolinium cation was found more efficient towards the DNA compaction. Decompaction of DNA could be achieved simply with the addition of NaCl. Further, the application of PMSAILS as MRI contrast materials has been explored. All the investigated PMSAILS exhibited excellent dual mode T_1 & T_2 contrast property in low concentration regime. To improve the real-time practical importance, MRI results have been compared with clinically available Gd-BOPTA based MRI contrast agent.

1. Introduction

In the surface science, especially in the colloid branch, ionic liquids (ILs) have taken unique position due to their greener aspects and better performance compared to conventional surfactants. Inherent amphiphilic nature of desired constituent ions in ILs has rendered superior surface active properties viz. adsorption efficiency, effectiveness in surface tension reduction, low CAC, and ability to form various nanostructure etc. [1]. ILs with long alkyl chains in either cation or anion or in both have been termed as a surface active ionic liquids (SAILs) [2] and exhibit combined properties of ILs and surfactants [3]. Like, conventional surfactants, SAILs also form various self-assembled structures such as micelles, [4] elongated, spherical, cylindrical, disk-like micelles, [5] worms like micelles, [6] vesicles, [2] tubules and ribbon shaped vesicles [7] and multilamellar structures of vesicles [8] etc. These aggregates resembles to biological compartment and bilayer membranes, specially the vesicles [9]. The variations in morphologies of aggregates have found uses in industrial [10], chemical [11], and pharmaceutical [12, 13] applications.

Hayashi, and Hamaguchi introduced the ILs with magnetic properties by simply exchange of Cl^- anion with $[FeCl_4]^-$ [14]. Such paramagnetic ionic liquids (PMILs) have found their multiple uses in desulfurizations [15], organic synthesis [16], microextraction [17–19], electro-catalysis [20], probe for vesicles [21], self-assemble media for surfactants [22], acidic catalysis [23], density measurement [24], paramagnetic polymer synthesis [25, 26], microemulsion formulation [27], synthesis of chitosan supported magnetic IL based catalysis [28], CO_2 separation [29], application in analytical [30, 31] and other various applications [32], Similar to SAILs, a new type of paramagnetic ionic liquid has been introduced by Paul Brown and Julian Eastoe group which are magnetoresponsive and have been called as Paramagnetic Surface Active Ionic Liquids (PSAILs), also termed as a “Magnetic Surfactant”. This PSAILs may have symmetric $[FeCl_4]^-$ or asymmetric anion $[FeCl_3Br]^-$ [33].

ILs [34], conventional surfactants [35] and SAILs [36] have been studied with genomic DNA at deep understanding level in pharmacokinetic and biotechnology field. Similarly PMILs have also been studied with DNA and explored for their utility in DNA preservation and stability [37], extraction of DNA [38] etc. The PMSAILs with azo group along with magnetic responsive moiety have been used in controlled DNA release process [39]. These PMSAILs have shown the ability to form aggregates or nanosphere upon interaction with DNA, and these

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self-assembled structures have been further used in drug delivery [40]. Paul Brown et al. demonstrated the migration of DNA and proteins molecule under low magnetic field strength with keeping their native nature constant by using PMSAILs [41]. It is clear that PMSAILs have significant importance as biotechnological tool. Carla I. Danielhas et al. shows the enhancement in r_1 relaxation rate of magnetic IL $[P_{66614}][FeCl_4]$ in mixture of ionic liquids ($[P_{66614}][Cl]$ + $[P_{66614}][FeCl_4]$) with DMSO solvent [42]. They also explored the future advantages of PMILs in contrast application. We have taken the indication from their work and studied the self-assembly of newly synthesized PMSAILs and their MRI properties for potential use as contrast reagent.

In this report we have showed dual response (T_1 and T_2 relaxation) in MRI from PMSAILs which is rare and found in hybrid nanomaterials only [43, 44]. These PMSAILs may eliminate the adverse effect of Gd metal ion on cell functionality [45] or harmful effect from metallic nanoparticles on cell and its physiology [46–48]. Studies on the physical interaction of PMSAILs with DNA also showed that after certain concentration of PMSAILs DNA precipitates due to compactness. This ability is more pronounced with isoquinolinium head group then imidazolium and pyridinium.

2. Materials and Methods

2.1. Material

Isoquinoline (> 98% purity), pyridine (> 98% purity), 1-bromododecane (> 98% purity) were purchased from TCI Chemical (India) Pvt. Ltd. 1-Methyl imidazole was purchased from Spectrochem, India. ACS reagents such as ferric chloride hexahydrate (97% purity), ethidium bromide, trizma base (99.9% purity), and sodium salt of deoxyribonucleic acid (DNA) from salmon testes were purchased from Sigma-Aldrich. Methanol, acetonitrile, ethyl acetate, and n-hexane solvents of AR grade were procured from SD-fine chem. Ltd., India. All the chemicals were of AR grade and were used as received. Millipore grade water with specific conductivity 3 $\mu S \cdot cm^{-1}$ and surface tension 71 $mN \cdot m^{-1}$ was used for the solutions preparation.

2.2. Synthesis of Paramagnetic Surface Active Ionic Liquids

Bromide precursors (a2, b2, and c2, Fig. S1) and ferric chloride hexahydrate (1:1 mol eq.) were taken in methanol solvent and reaction mixtures were kept for reflux over the day. After completion of the reaction, the solvent was removed by rota-evaporator and product was dried under vacuum. The product was washed with a little volume of water to remove unreacted ferric chloride. Products were completely dried and stored in a vacuum desiccator to make it free from any moisture issue. Characterization was done with UV–visible and Raman spectra, CHNS, ICP-OES (Inductive coupled plasma optical emission spectroscopy for % Fe) and is given in supporting information. Scheme 1. shows the molecular structure of synthesized PMSAILs.

DNA stock solution was prepared by dissolving an appropriate amount of DNA in 50 mL 80 $mmol.L^{-1}$ trizma base hydrochloride (TE.HCl) buffer solution and kept it overnight for complete solubilisation. The actual concentration of DNA was determined using NanoDrop® Spectrophotometer ND-1000. 90–92 $ng.\mu L^{-1}$ DNA concentration was used in whole study.

2.3. Methods

2.3.1. UV–Visible and Raman Spectroscopy

The synthesized asymmetric anion $[FeCl_3Br]^-$ was verified by using Shimadzu UV-2700 UV–VIS spectrophotometer, Japan and LabRAM HR Evolution Horiba Jobin Yvon Raman spectrometer, Japan at 298.15 K. For UV measurement, samples were prepared in acetonitrile solvent.

2.3.2. Conductivity Measurements

Conductivity was measured on digital Eutech auto temperature conductivity meter model PC 2700, Thermo Scientific, US, assemble with a conductivity cell and temperature probe. Cell constant for the cell used was 1.0. The solution temperature was maintained by using Julabo thermostat at 25 °C (with accuracy ± 0.1 °C). The degree of counterion binding (β) has been calculated from equation provided in Annexure 2 of supporting information.

2.3.3. Tensiometry

Tensiometry was employed to measure the critical micellar concentration (*CMC*) and surface parameters. The surface tension measurements were done using automated Attension force Tensiometer Sigma 700, Biolin Scientific, Sweden with Du Noüy ring method. The surface tension values have collected in triplicate and the average value of them has been considering for further calculation. Uncertainty which was calculated by means of standard deviation in measurements of each reading and was found to be ± 0.1 $mN \cdot m^{-1}$.

2.3.4. Dynamic Light Scattering (DLS)

DLS was used to measure the size of aggregates formed by PMSAILs in aqueous solution by using NaBiTec Spectro-Size300 light scattering apparatus (NaBiTec, Germany) with a He-Ne laser (660–670 nm, 4 mW) at angle of 90. Zetasizer Nano ZS light scattering apparatus (Malvern Instruments, U.K.) with a He-Ne laser (633 nm, 4 mW) at angle of 90 was used for measure the hydrodynamic diameter of DNA in absence and presence of PMSAILs at various concentration.

2.3.5. Far-UV Circular Dichroism Spectroscopy

Far-UV circular dichroism (CD) spectra of DNA in Tris.HCl buffer at pH 7.4 was recorded in triple measurement at the wavelength range 200–400 nm in a Jasco J-815 CD spectrometer, US under N_2 environment with temperature 298.15 K. Experiments were carried out in a quartz cuvette having a path length of 1 mm. The spectra were collected at a scan rate 100 nm/min. The response time and the bandwidths were 2 s and 0.2 nm, respectively.

2.3.6. Ethidium bromide exclusion assay

According to previous report [49], 50 μL solution of 0.1 mM EB was mixed with 2 mL of buffer, and the fluorescence spectra of water-EB were recorded in the absence of DNA and the presence of DNA from 500 to 700 nm at an excitation wavelength (λ_{ex}) of 530 nm using a Fluorolog horiba Jobin Yvon fluorescence spectrophotometer. The PMSAILs solution was added successively up to 10 mM Fe concentration in 2 mL cuvette containing EB-DNA complex and recorded the spectra at 298.15 K. The percentage of EB binding was observed due to the replacement of EB by PMSAILs from DNA was calculated using Eq. (9) given in Annexure 2 of supporting information.

2.3.7. Determination of Zeta Potential (ζ)

The surface charge of negative DNA in the presence of PMSAILs were measured from Zeta potential (ζ) experiment using a Zetasizer Nano ZS light scattering apparatus (Malvern Instruments, U.K.) with a He-Ne laser (633 nm, 4 mW) at 298.15 K. For measurements, solution was transferred through 0.25 μm membrane filter into 'DTS 1060' cell possessing gold-coated electrode. The Smoluchowski approximation was selected during measurements.

2.3.8. Isothermal Titration Calorimetry (ITC)

Enthalpy changes (dH) due to micellization and the interaction of DNA in successive injections with PMSAILs in buffer solution were measured using MicroCal ITC200 microcalorimeter, U.K. with an instrument controlled Hamiltonian syringe having volume capacity of

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