Green chemistry advancement in methane storage: A biodegradable surfactant for improved gas hydrate formation and sustainability

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Materials

Methyl oleate, sodium methoxide, maleic anhydride, sodium chloride (NaCl), isopropanol, and sodium bisulfite were procured from Sigma Aldrich. Arkan Gas supplied methane gas with a purity of 99.99%. Deionized water and 3.5 wt % NaCl solution were used for the preparation of promoter solutions. Dulbecco's Modified Eagle Medium (DMEM), Fetal Bovine Serum (FBS), 3-[4,5-dimethylthiazole-2-yl]-2,5-diphenyltetrazolium bromide (MTT), and penicillin-streptomycin were purchased from Gibco BRL (Gaithersburg, MD). Moreover, the MRC-5 and NIH/3T3 cells was obtained from Pasteur Institute, Tehran, Iran.

Characterization methods

The CHNS/O analysis was carried out on an Eager 300 Flash EA1112 elemental analyzer (Waltham, MA, USA). Attenuated total internal reflection Fourier-transform infrared (ATIR-FTIR) of the DSOS sample was carried out using a Thermo Scientific Nicolet 5700 FTIR spectrometer (Waltham, MA, USA). DSOS spectrum weas recorded in the region of 600-4000 cm^{-1} with a resolution of 4 cm^{-1}. The ^{1}H NMR spectrum was recorded using a Bruker DRX-300 Avance spectrometer (Karlsruhe, Germany) using D_2O as a solvent and tetramethylsilane (TMS) as the internal standard.

Simulation details

The initial configuration resulted in a simulation box with dimensions of 6.015, 6.015, and 18.970 nm in the *X*-, *Y*-, and *Z*-directions, respectively. Equilibrium molecular dynamics simulations were

carried out using the GROMACS package [1], version 2021. Initially, an NVT simulation for 0.1 ns was performed to relax the initial configuration, keeping the hydrate layer fixed. Subsequently, NPT simulations were conducted at 2 ºC and 90 bar, using the Nose-Hoover thermostat and the Berendsen/Parrinello-Rahman barostat [1]. Pressure coupling was applied only along the *Z*-direction to maintain the *X* and *Y* dimensions of the simulation box. The equations of motion were solved using the leapfrog algorithm with a time step of 1.0 fs [1]. A harmonic restraint force (k = 2000 kJ/mol.nm) was applied to the water and methane molecules in the hydrate layer to keep them in their initial positions, while other molecules in the system were free to move during the simulations [1]. To obtain statistically reliable numerical results, each simulation was run for 1000 ns, which took approximately 480 computing hours. Three independent hydrate growth simulation runs with different velocity distributions were performed for each system to compute error bars. To assess methane solubility, surface tension of a methane-water interface, and interfacial surface area, approximately 100 ns NPT simulations were performed for each system featuring methane-water interfaces at 2 ºC and 90 bar. The methane-water interface model was developed by combining aqueous and gas phases into 6.015 × 6.015 × ~ 18.733 nm^3 simulation boxes. To ensure the simulations reached equilibrium, the convergence of system energy and the density profiles of methane and water along the direction perpendicular to the methane-water interfaces were examined. Similar methods were employed to quantify the fluid-fluid interfacial tensions for various other systems [2–4]. To investigate the impact of DSOS on hydrate growth, a layer of their molecules was positioned at the methane-water interfaces at different surface densities ranging from 0 to 7.34×10^{-7} mol/m^2. It is noteworthy that surfactants accumulate at interfaces even at very low bulk concentrations [5]. Since the objective of this study is to quantify the effect of the promoter on hydrate growth and other interfacial properties, no DSOS were present in the bulk solutions of

the systems studied. Error bars were derived from three independent simulation runs for each system. DSOS molecules were modeled using the General Amber Force Field (GAFF) [6,7]. Na^+ ions were modeled as charged Lennard-Jones (LJ) spheres with parameters suggested by Dang [8]. Methane was represented by the united-atom version of the TraPPE-UA force field [9]. Water was modeled using the TIP4P/Ice model [10]. All non-bonded interactions were described using 12−6 Lennard-Jones (LJ) potentials with a cutoff distance of 1.4 nm. Electrostatic interactions were modeled using the Coulombic potential, with long-range corrections handled using the particle–particle particle–mesh (PPPM) approach [11]. The Lorentz−Berthelot combining rules were used to calculate unlike LJ interactions [12].

MTT assay

MRC-5 and NIH/3T3 cells were grown in Dulbecco's Modified Eagle medium (DMEM; GIBCO, Grand Island, NY) supplemented with 10% fetal bovine serum and 1% Penicillin/Streptomycin and incubated at 37 ºC. To assess cell viability, 5×10^4 cells were seeded in each well of a 96-well plate and overnight incubation. Different concentrations of DSOS solution in PBS were then added to each well. DMEM medium alone served as a negative control. After 24 h, 20 μL of MTT solution (5 mg/mL in DMEM) was added to each well and incubated for 3.5 h at 37 ºC. Subsequently, 60 μL of DMSO was added per well, followed by a 30-min incubation at room temperature. The resulting formazan crystals were dissolved, and their absorbance was measured at 570 nm with a reference wavelength of 630 nm. Each sample was assayed in quadruplicate (n=4) [13].

Cells viability (%) = [Sample absorbance - Blank absorbance]/[Control absorbance - Blank absorbance] (1)

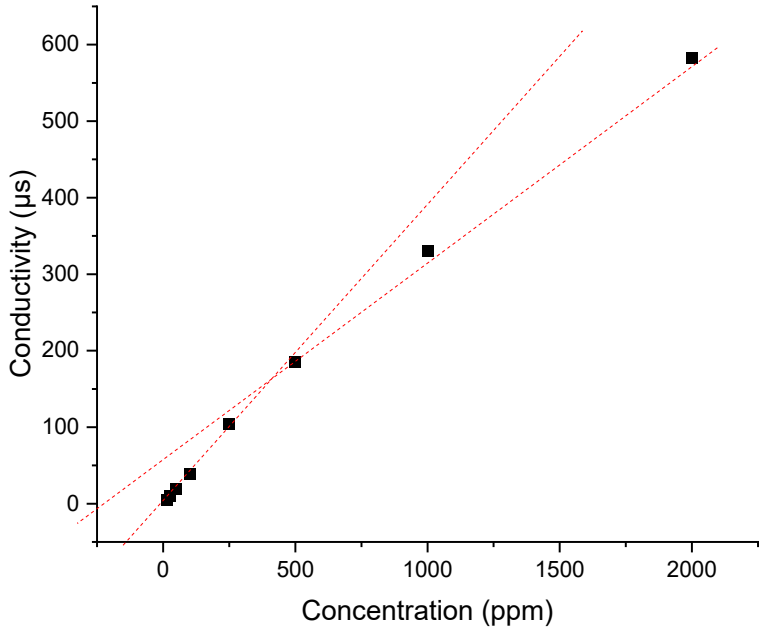

Fig. S1. The CMC value of DSOS.

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