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Full Length Article

Surface charge effect of nanogel on emulsification of oil in water for fossil energy recovery

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ABSTRACT

Crosslinked polymeric hydrogels in nano-size, termed as nanogels, have significant technological applications by stabilizing Pickering emulsion. Herein, we present our experimental observations and the results of the emulsion stability analysis on the effects of nanogel concentration, oil-to-water ratio, nanogel charge, and ambient temperature. The nanogel with neutral-charge showed extraordinarily high emulsifying ability, interfacial tension between decane and water was reduced from 51.98 $mN{\cdot}m^{-1}$ to less than 6.04 $mN{\cdot}m^{-1}$, compared to 47.5 $mN{\cdot}m^{-1}$ by nanosilica. When treated with neutral-charged nanogel, the oil-in-water emulsion exhibited long-term stabilization, 90% emulsion remained after one month at room temperature, showing the highest stability among the reported literature of Pickering emulsions. However, inorganic silica nanoparticles displayed emulsion stability in minutes. Of particular interest was that the emulsion volume remained 82% after thermal treatment at 65 °C for 48 h. The resulting high emulsion stability was attributed to a combination of high hydrophilicity, sufficient steric repulsion, and high surface coverage of nanogel. These observations indicated that the resulting nanogel can be a promising candidate toward enhanced oil recovery.

1. Introduction

In recent years, there have been increased research interests in using oil-in-water emulsion stabilized with inorganic nanoparticles, known as Pickering emulsion [1], for enhanced oil recovery (EOR), especially in harsh condition reservoirs. The reasons are that inorganic nanoparticles not only stabilize micron-sized oil drops by forming absorbed nanoparticle layers but also perform better resistance at harsh condition than surfactants do [2–4]. Nanosilica is the most used nano-material to form Pickering emulsions because it is commercially available and having hydrophilic property [5]. Pickering emulsion can be injected into high-permeability-zone for conformance control as it is much more viscous than displacing water and stable at high salt concentration condition [6,7]. Nanosilica facilitates residual oil recovery by reducing interfacial tension between oil and water [8–10] and forming stable Pickering emulsion *in situ* [11–13]. Despite these advantages, nanosilica is not applied in petroleum industry [14,15]. The main reason is that nanosilica cannot form stable Pickering emulsions in the absence of surface modification with grafted functional polymer chains. However, the modification is significantly time-consuming and dramatically increase production cost. Therefore, more efforts have been devoted to improving the properties of inorganic nanomaterials.

Nanogel has been used for medical diagnostic test [16,17], antibody purifications [18,19], drug delivery systems [20,21], etc. The application of crosslinked polymeric hydrogels to stabilize oil-in-water emulsion named Mickering emulsion was reported by Binks' and Ngai's group [22–24]. Binks et al. used poly(4-vinylpyridine)/silica nanocomposite microgel particles to stabilize methyl myristate in Milli-Q water and found that microgels were no longer absorbed at oil-water interfaces in their swollen form [24]. Emulsions stabilized by temperature and pH-responsive poly(*N*-isopropylacrylamide) microgels showed surprising robustness at high pH and phase separated at low pH or high temperature due to the low interface coverage of microgels [22]. The stabilization of emulsion was associated with physical properties of hydrogel particles, while surface charges are independent of emulsion stability. Recently, Pickering emulsions were reported, which stabilized solely by soft nanogels, like cyclodextrin [25], gelatin [26], chitosan [27] or ethyl cellulose [28]. However, to the best of our knowledge, there is no reported work regarding the effect of the surface charge of nanogel on the stability of Pickering emulsion in the application in EOR.

In this study, three nanogels with positive, neutral, and negative charge were synthesized using free-radical suspension polymerization as characterized by corresponding techniques. We demonstrated how the interfacial tensions between decane and nanogel water were reduced by absorbing nanogels at the interfaces. The presence of

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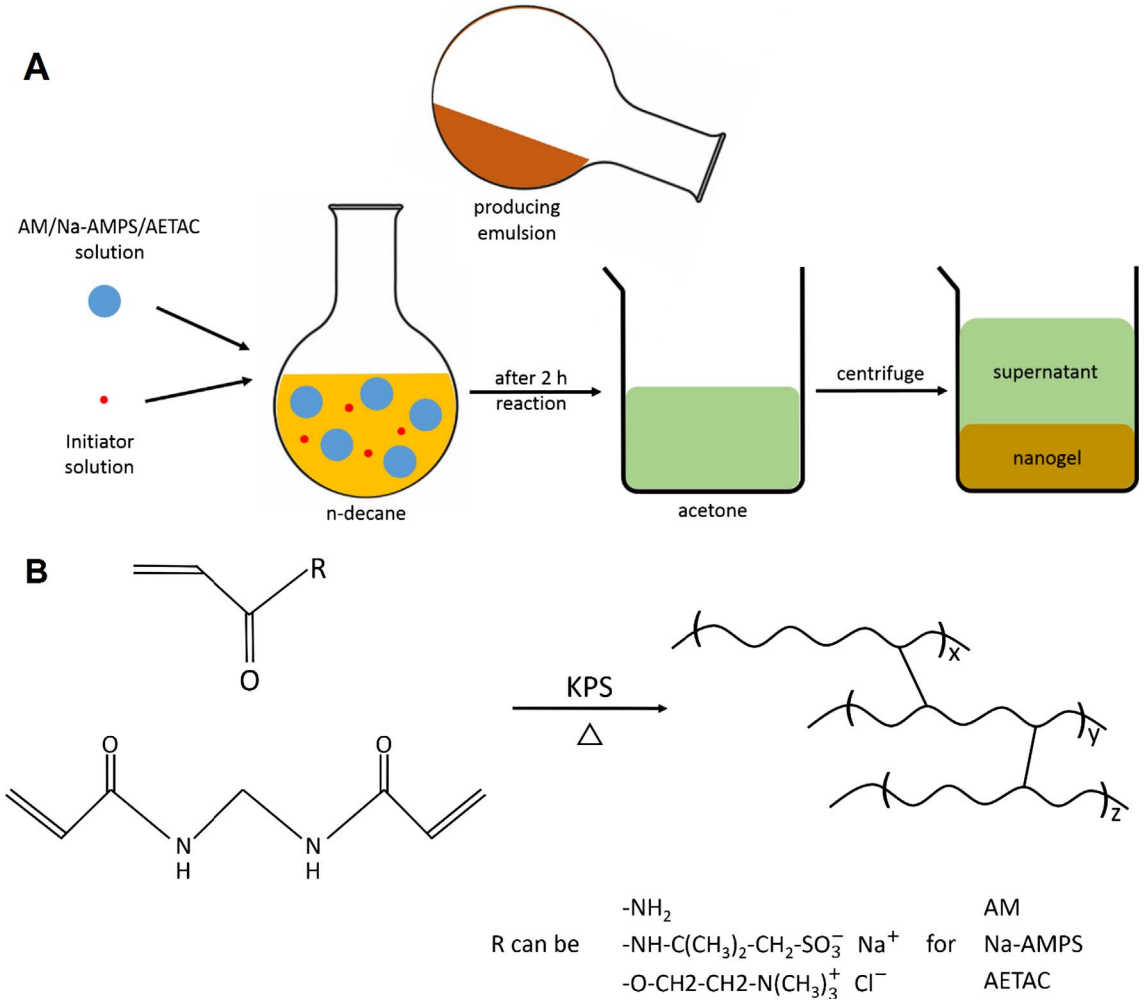

Scheme 1. Schematic representation of (A) suspension polymerization and purification of nanogel and (B) the synthetic procedures for the preparation of crosslinked polymer nanogels, obtained via suspension polymerization.

hydrophilic and pendant polymer chains enabled us to prepare stable oil-in-water emulsion at high temperatures. The emulsion stabilized by neutral-charged nanogels, which had minimum electrostatic repulsion among nanogels at absorbed layer, was compared with emulsions stabilized by positive and negative charged nanogels. This demonstration showed the advantages of reducing interfacial tension and forming stable oil-in-water emulsions by adsorbing nanogels at the interfaces for enhanced oil recovery.

2. Experimental

2.1. Materials

All chemicals and reagents were purchased from Sigma-Aldrich (St. Louis, MO) and used as received except further noted. Acryloyloxyethyltrimethyl ammonium chloride (AETAC) was purchased from Sigma-Aldrich and used as received. Acrylamide (AM) was purified by recrystallization from acetone and dried under vacuum at 25 °C for one day. To prepare Na-AMPS in the lab scale, solid NaOH was added to a stirring solution of 2-Acrylamido-2-methylpropane sulfonic acid (AMPS) in ethanol at room temperature. The reaction mixture was vigorously stirred for 1 h and the precipitate was filtered, washed with ethanol and dried under vacuum at 25 °C for one day [29]. Nanosilica (20–30 nm) was purchased from US Research Nanomaterials, Inc without further purification. 1 wt% sodium chloride (NaCl) solution was used throughout experiments.

2.2. Nanogel synthesis

All nanogels were prepared by suspension polymerization. A typical nanogel polymerization is as follows: a stirring solution of acryloyloxyethyltrimethyl ammonium chloride (AETAC) (9.684 g, 0.05 mol) and *N*,*N*′-methylene bis(acrylamide) (MBAA) (0.077 g, 0.05 mmol) in water (10.24 mL) was added to n-decane (40 mL) containing Span® 80 (21 g) and Tween® 60 (9 g) in a 250 mL three-neck flask and bubbled with nitrogen while kept in a preheated water bath at 40 °C for 15 min. Then, ammonium persulfate (0.02 g, 0.088 mmol) in water (0.2 mL) was added to the flask under stirring. The emulsion mixture was stirred at 40 °C for 2 h, the resulted emulsion was precipitated into acetone and the precipitate was isolated by centrifugation. The precipitate was rinsed with acetone several times to remove surfactants and unreacted monomers. The final product was isolated as a white powder and dried under vacuum at 45 °C overnight for further characterization and evaluations.

2.3. Morphology and size distribution studies

Scanning electron microscopy (SEM) images were collected on a Hitachi S-4700 FESEM microscope (Tokyo, Japan) operated at 15.0 kV to elucidate the microstructures of the nanogels. All images were captured of nanogels coated with Au/Pd prior to imaging. The size distribution of nanogels was examined by Dynamic light scattering (DLS) (Malvern NanoSizer ZS90). The measurements were carried out at a