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The high-efficiency and eco-friendly PEGylated ionic liquid systems for radioactive iodine capture through halogen bonding interaction

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The kinetics of iodine uptake by eco-friendly PEGylated systems was investigated and the resutls showed that most of the systems could capture iodine from the solution of iodine in cyclohexane efficiently. For example, 86% of iodine could be captured in only 3 h by PEG200/NaI system. The efficiency of iodine uptake shows high correlation with the inorganic salts used which might be due to the halogen bonding (XB) interaction between the anion of salt with I_2. Besides that, the effect of organic solvents and ionic liquids on the iodine capture were also investigated. The results indicated that PEGylated systems are flexible and reobust for iodine capture, furthermore, they might be applied to other areas as solvents.

1. Introduction

Due to the depletion of the fossil resources, the utilization of alternative energy has drawn wide and numerous attentions. Nuclear energy is one of the most important alternative energies and has occupied 16% total electric energy. One of the obstacles for the expansion of nuclear energy lies in the fear of the nuclear accident such as Chernobyl disaster in 1986 and Fukushima Daiichi nuclear accident in 2011 [1]. In these accidents, large amount of untackled nuclear wastes were released to the air, water and soil, and did serious damage to the environment and health of human being. As one of the most hazardous radionuclide nuclear waste, radioactive isotopes of iodine ($^{125/129/131}I$) are volatile, have very long half-life (the half-life of ^{129}I reaches 1.57 × 10 [7] years), and affect human metabolic processes (^{131}I) [2,3]. So it is urgent to develop reliable methods for radioactive iodine capture and storage. Many materials have been proposed for capturing I_2, such as porous zeolitic materials [4,5], especially silver-based zeolites, which have good stabilities and high I_2 removal efficiency but have adverse environment impact and low porosity [6]. Metal organic framework (MOF) materials can capture I_2 efficiency too because they have specific interior microenvironment [7–9]. The macrocyclic complexes could capture I_2 by charge-transfer interactions [10]. Porous aromatic frameworks with three sorption sites have be used for I_2 capture [11]. However, these materials have drawbacks such as lack of high adsorption capacities, expensive, and difficult to synthesis.

As an analogue of hydrogen bonding, halogen bonding (XB) [12–14] is defined as an interaction involving halogens as electron acceptors, which can be described in general as D···X-Y, where D is any electron donor, X is the electrophilic halogen atom, and Y is usually carbon, halogen, and nitrogen. Halogen atoms could be used in recognition processes in the gas, liquid, and solid phases due to directionality of electron acceptors and electron donor [15–17]. Especially, ionic liquids [18–20] and quasi-ionic liquids deep eutectic solvents (DESs) [21] have been used for efficient removing radioactive iodine due to the formation of XB between solvents (ionic liquids or DESs) and I_2 molecule. Those solvents have showed high iodine removal efficiency. However, the DESs and ionic liquids are expensive, difficult to synthesis, highly hydroscopic [22–25], and the stability [26,27] as well as environmental effects of DESs and ionic liquids are questionable [28]. Therefore, developing novel solvents, which are environmentally benign and cheap for capturing iodine with high efficiency is still desirable.

Liquid poly(ethylene glycol) (PEG) (molecular weight < 800 $gmol^{-1}$) is usually regarded as environmental benign solvent, it is economical, biocompatible and had been used in materials synthesis, chemical reactions, and colloid and surface areas as green solvent [29–32]. PEGylated quasi-ionic liquid systems which are comprised with PEG and inorganic salts have been developed and used for electrodeposition of aluminium [33]. It shows that inorganic salts have significant influences on solvent systems, which could influence the properties of the solvents [34,35], and hence

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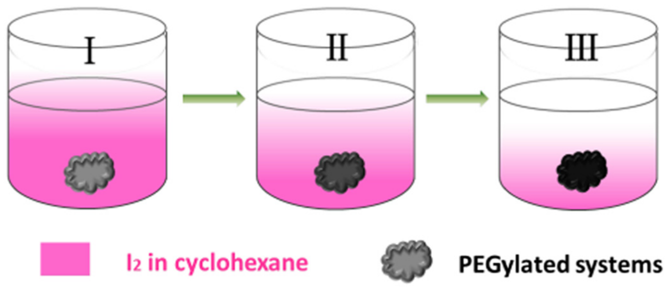

Scheme 1. The schematic diagram of procedure of I_2 capture by PEGylated systems.

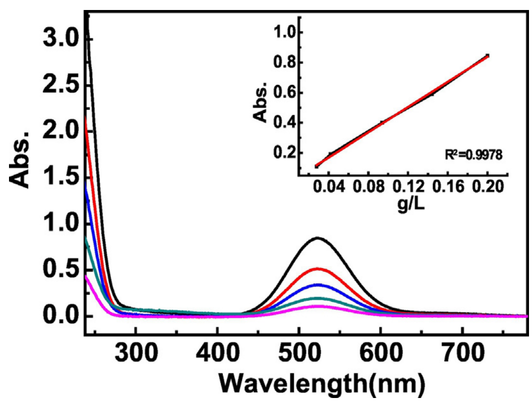

Fig. 1. The concentration/intensity of UV/Vis absorption peak of I_2 in cyclohexane.

altering the reaction mechanism and yield in solvents [36]. Since the high efficient of iodine capture by ionic liquids/DESs could be mostly ascribed to the XB interactions between iodine and anions of ionic liquids or DESs, the mixture of eco-friendly and cheap PEGylated quasi-ionic liquid systems might also have high efficiency for iodine capture because some types of salts could also have XB interactions with iodine. Therefore, the iodine capture by PEGylated quasi-ionic liquid systems was investigated. The range of the PEGylated systems can be broadened by variation of PEG and salts. Especially, PEGylated systems are cheap and easily obtained than other ionic liquids and DESs.

The procedure of the I_2 absorbed into the PEGylated systems was schematically showed in Scheme 1. The colour of the solution of the I_2 in cyclohexane changed lighter and lighter with the time (from I to III), which means that more and more I_2 molecules were absorbed into the PEGylated systems.

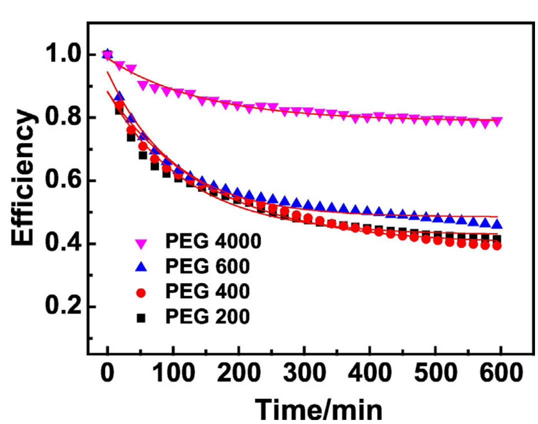

Fig. 2. The I_2 capture kinetics of pure PEG with different molecular weight at room temperature.

2. Experiment

2.1. Materials

PEG200, PEG400, PEG600 and PEG4000 were purchased from Beijing Chemical Reagent Company. The ionic liquid 1-butyl-3-methylimidazolium acetate ([Bmim]OAc) and 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) were purchased from Lanzhou Greenchem ILs, LICP, CAS, China (Lanzhou, China) with a purity over 99.9%. Ionic liquids and PEGs were dried at 60 °C under vacuum for 96 h before use. Water content of the PEGs and ionic liquids are less than 1000 ppm after the drying process. I_2 was purchased from Sinopharm Chemical Reagent Co., Ltd. The sodium and chloride salts with purities higher than 98% were purchased from J&K Scientific Ltd. These materials were used without further purification.

2.2. Calibration plot of iodine in cyclohexane by UV/Vis spectra

The concentration of I_2 in cyclohexane was measured by UV/Vis spectra experiment. At first, calibration plot of iodine in cyclohexane were obtained by measurement UV/Vis spectra of known concentration of I_2 in cyclohexane. The optical length of used sample pool is 10 mm, and the wavelength range used is 280–700 nm. The intensity of absorption peak at $\lambda = 522$ nm was used for quantitation of I_2.

2.3. Iodine capturing experiments

In situ UV-vis spectroscopy was used for determination of the capture efficiency, and the detailed procedures could be seen in our previous work [37]. Simply, at first, ca. 0.2 g PEGylated solvent and ca. 2 g I_2/cyclohexane solution (0.3 g I_2 in 500 ml cyclohexane) were placed into the UV cuvette (1 cm). Then the cuvette was sealed and UV/Vis experiments were carried out at an interval of 6 min with pure cyclohexane as a blank. Therefore, iodine capture efficiency could be obtained by the ratio of iodine absorption peak (ca. 522 nm) at a selected time with that of the beginning measurement.

2.4. Iodine recyclability

The procedure of PEGylated systems recyclability experiment is similar to the I_2 storage experiment. Since cyclohexane is insoluble in PEGylated systems (with captured I_2), it could be easily separated from the solution. Then the PEGylated systems with captured I_2 were putting in the platinum pan of TGA instrument. The TGA experiments were carried out at different temperatures for checking the recyclability of PEGylated systems.

3. Results and discussion

3.1. Calibration plot of iodine in cyclohexane

To obtain the concentration of the I_2 in cyclohexane, calibration experiments of iodine in cyclohexane were carried out and the results were given in Fig. 1. The curve of calibration was obtained by five solutions (0.028, 0.042, 0.094, 0.144 and 0.200 g/L). Fig.1 shows that the intensity of absorption peak is proportional with the quantity of I_2, which means that the concentration of the I_2 in cyclohexane could be obtained by the UV/Vis measurements.