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Copper ingrained poly(ethylene)glycols as cost effective and reusable media for selective 1-decene/*n*-decane separation

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Liquid range polyethylene glycols containing copper ions have been used as recyclable extractive media for the selective separation of 1-decene from a mixture of 1-decene and *n*-decane. The copper(II) ions in PEG were readily converted into copper(I) and then selectively coordinated with 1-decene molecules through π -complexation. The resulting polyethylene glycol phase containing copper–olefin complex was treated with *n*-heptane at 70–80 °C to obtain pure 1-decene and the recovered poly(ethylene)glycol containing copper ions was successfully reused for several runs.

Polyethylene glycols (PEGs), available in a variety of molecular weights from 200 to tens of thousands, have found enormous applications in many fields, such as polymer electrolytes, soil improvement, pharmacy, cosmetics and bioseparations.^{1–4} Polyethylene glycols (PEGs) exhibit a number of benign characteristics such as biodegradable nature, ability to coordinate with metal ions, low flammability, being safe and non-volatile.^{5,6} In addition, PEG has the ability to serve as a phase transfer catalyst (PTC) since the polyethylene oxide chains can form complexes with metal cations; similar to crown ethers.⁷ Dramatically reduced costs of PEGs compared to crown ethers are a considerable incentive for investigating the properties of PEGs carrying a variety of metal ions. Consequently, this mutual effect of PEG chains with inorganic ions has attracted huge interest in recent years.^{8–11}

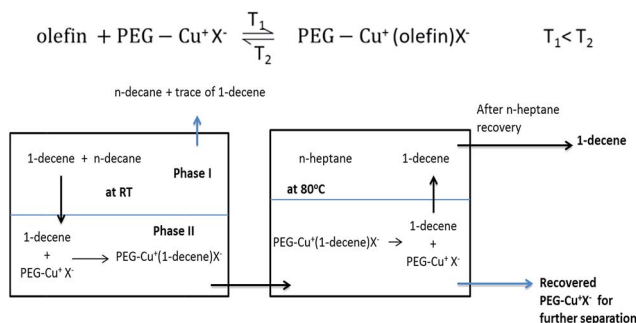
The separation of unsaturated hydrocarbons (olefins) from saturated hydrocarbons (paraffins) is an industrially important task. In general olefins are mainly produced by thermal and catalytic cracking of hydrocarbon streams. Since the product streams from these cracking processes contain alkanes and alkenes with the same carbon numbers which are of narrow boiling point differences, therefore, their separation is quite difficult and expensive by so called conventional cryogenic distillation.^{12,13} Also, comparatively less costly extractive distillation will not significantly improve this separation, because all isomers respond in a similar way to the solvent, leaving the relative volatility almost unchanged. Consequently, alternative strategies to separate olefin/paraffin mixtures that would result in cost and energy savings are of great interest. The specific and reversible interaction of metal ions particularly silver and copper with olefin molecules leads to selective recovery of the

olefins from paraffins.^{14,15} In this regard, a very few reports for the separation of olefins *via* reversible π -complexation using copper ions in aqueous¹⁶ and non-aqueous¹⁷ media are known; however separation of olefins using silver ions has been widely studied.^{18,19} Recently, silver functionalized ionic liquids owing to their negligible vapour pressure, recycling ability and non-toxic nature have been emerged to be greener and potential solvents for the separation of liquid range of olefins *via* extraction. However, expensive nature of silver salts/complexes and tedious preparation of ionic liquids make their utility limited.²⁰ Furthermore, some of the “green” aspects related to the toxicity and biodegradability of ionic liquids are still under discussion, and achieving good purity of extract remains a challenging task.

Herein we report for the first time the use of liquid range polyethylene glycols mixed with copper(II) salt for the selective separation of 1-decene from the mixture of 1-decene and *n*-decane. The coordination of copper(II) ions with polyethylene glycol resulted in the reduction of Cu²⁺ to Cu¹⁺ ions, which leads to a favorable selectivity of extraction for 1-decene *via* π -complexation from a mixture of 1-decene/*n*-decane.

For the present study, we have chosen a hydrocarbon phase containing *n*-decane and 1-decene as a representative example and PEG₂₀₀ and PEG₄₀₀ as extractive medium. We have used *n*-decane and polyethylene glycol in 1 : 1 ratio (by volume). The schematic presentation of the separation of 1-decene/*n*-decane by reversible π -complexation with copper ions in poly(ethylene) glycol extractive medium is shown in Scheme 1. The whole process for the selective separation of 1-decene comprises of three steps: firstly, transfer of 1-decene from hydrocarbon phase to PEG phase through the formation of Cu–olefin complex at room temperature; secondly, separation of the PEG phase containing Cu–olefin complex from hydrocarbon phase by physical method; thirdly, reversing the complex to recover the

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Scheme 1 Schematic presentation of *n*-decane/1-decene separation.

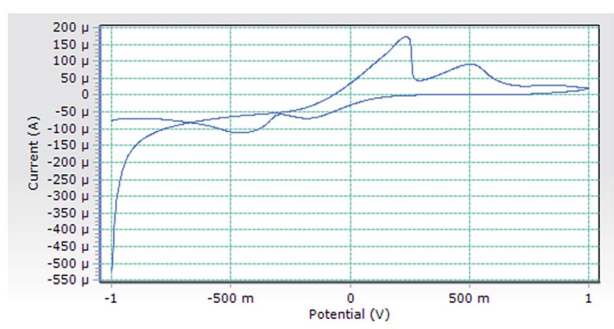


Fig. 1 Cyclic voltammograms (1 mM copper(II)) in PEG with scan rate of 100 mV s⁻¹ at GCE.

olefin by treating the PEG phase with *n*-heptane at higher temperature.

At first, the separation of 1-decene from *n*-decane using PEG solution containing copper ions (0.02 mol L⁻¹) have been studied. For each experiment, 5 ml of PEG containing copper ion (0.02 mol L⁻¹) as an extractive phase and 5 ml of *n*-decane containing 0.02 mol L⁻¹ 1-decene as hydrocarbon phase were used. Copper(II) ions in the extractive medium in the presence of PEG readily reduced to copper(I) ions. These copper(I) ions were selectively coordinated to 1-decene molecules through π -complexation to form 1 : 1 copper-olefin complex species. The *in situ* reduction of copper(II) ions in PEG to copper(I) ions was confirmed by cyclic voltametric studies as shown in Fig. 1. The

cyclic voltammogram for copper(II) tetrafluoroborate in PEG₂₀₀ was found to be in good agreement with the existing literature report.²¹ As suggested in the literature PEG not only reduces the copper(II) ions to copper(I) ions but also provide the stability to these ions through complexation.²¹

To see the effect of various copper precursors, copper(II) chloride and copper(II)tetrafluoroborate were used as the source of copper ions for the selective separation of olefins. Liquid poly(ethylene)glycols *e.g.* PEG₂₀₀ and PEG₄₀₀ were used to dissolve the copper salts for the concentration of copper ions 0.04 mol L⁻¹. Among the various extractants studied, copper(II) tetrafluoroborate dissolved in PEG₂₀₀ was found to be optimum for the maximum separation of 1-decene from the mixture of *n*-decane and 1-decene (Table 1, entry 5). To determine the effect of copper ions on the selectivity of the paraffin/olefin separation process, pure PEG solvents without copper were also studied. The pure poly(ethylene)glycols did not show any selectivity for the separation of 1-decene, confirming that the copper ions are essentially required for the separation of olefins from a mixture containing paraffin/olefin (Table 1, entry 1 and 2). Similarly the use of other solvents such as methanol, acetonitrile and water gave a very poor separation of 1-decene (Table 1, entry 7–9), which is most likely due to the inability of these solvents to reduce copper(II) ions to copper(I) ions.

The selectivity for the separation of 1-decene from *n*-decane were also studied under varying concentration of copper ions in PEG₂₀₀ from 0.01 to 0.06 mol L⁻¹ (Fig. 2). It was found that with the increase in copper ion concentration in PEG, transfer of 1-decene from hydrocarbon phase gradually increased till olefin to Cu ratio 1 : 2. Thus the optimum concentration of copper ions for 0.02 mol L⁻¹ 1-decene was found to be 0.04 mol L⁻¹ as shown in Fig. 2. Further increase in concentration of copper ions affected the extraction of olefin adversely, which is probably due to the hindrance caused by excess metal ions.

It is well documented in the literature that copper(I) ions readily coordinate with olefins to give reversible π -complexes at lower temperatures.^{22–25} To evaluate the effect of temperature on the extraction of olefin, experiments were conducted at varying range of temperature 283 K to 323 K (Fig. 3). It was observed that the separation of 1-decene by Cu-PEG solution was increased with decrease in temperature which is quite relevant with the exothermic nature of the formation of π -complexes.

Table 1 Effect of various extractants on the selectivity for the separation of 1-decene^a

Entry	Extractant	Conc. of Cu ion (mol L ⁻¹)	1-Decene extraction (%)	Std. deviation
1	PEG ₂₀₀	—	—	—
2	PEG ₄₀₀	—	—	—
3	CuCl ₂ in PEG ₂₀₀	0.04	90.9–92.0	0.778
4	CuCl ₂ in PEG ₄₀₀	0.04	88.7–90.0	0.919
5	Cu(BF ₄) ₂ in PEG ₂₀₀	0.04	98.3–99.2	0.636
6	Cu(BF ₄) ₂ in PEG ₄₀₀	0.04	96.7–98.1	0.990
7	Cu(BF ₄) ₂ in ethanol	0.04	71.6–72.4	0.566
8	Cu(BF ₄) ₂ in acetonitrile	0.04	68.9–70.2	0.919
9	Cu(BF ₄) ₂ in water	0.04	74.7–76.2	1.061

^a Condition: PEG : *n*-decane (1 : 1; by volume), hydrocarbon phase (*n*-decane) consisting of 1-decene (0.02 mol L⁻¹) at 293 K, time 4 h.

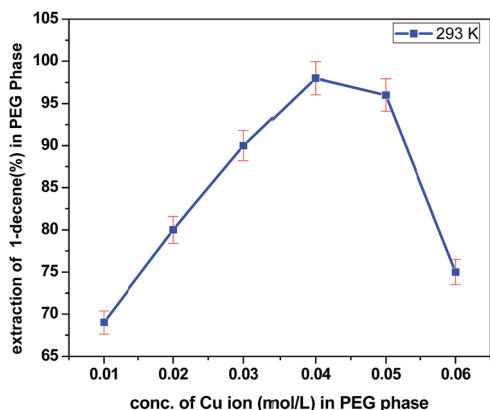


Fig. 2 Effect of copper ion concentration in PEG on extraction of 1-decene (*n*-decane : PEG₂₀₀ = 1 : 1 by volume (5 ml each); [Cu²⁺] = 0.01–0.06 mol L⁻¹; time 4 h).

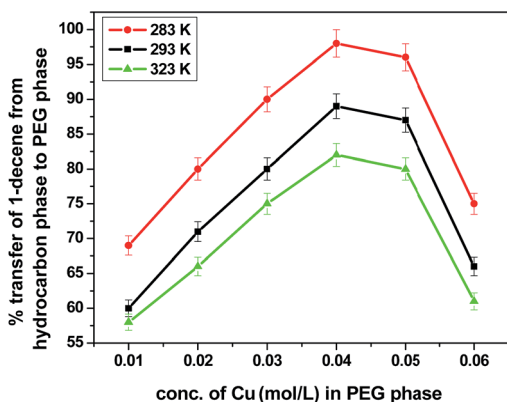


Fig. 3 Effect of temperature on extraction of 1-decene from *n*-decane/1-decene mixture (*n*-decane : PEG₂₀₀ = 1 : 1) (by volume, 5 ml each); conc. of 1-decene in hydrocarbon phase = 0.02 mol L⁻¹; [Cu²⁺] = 0.04 mol L⁻¹; time 4 h.

It was also found that with increase in the initial concentration of olefin (0.01–0.04 mol L⁻¹) in hydrocarbon/organic phase, the percentage of extraction decreased. The results shown in Fig. 4 indicated that increasing the initial concentration of 1-decene from 0.01 to 0.02 mol L⁻¹ in feed, the percentage of extraction increased at all three temperatures, whereas further increase from 0.02 to 0.04 mol L⁻¹ resulted to the significant decrease in extraction of 1-decene. This is most likely due to the limited availability of the copper ions for the complexation with the excess olefin molecules.

Furthermore, in the present study we developed a simple and efficient approach for the recovery of the pure olefin from the PEG phase containing copper–olefin complex. Few of the literature reports suggested the use of polar solvents for the recovery of olefins from metal–olefin complex *via* extractive distillation approach.^{26,27} However, this process associated with the drawbacks of poor recovery of the olefin. To overcome such limitations, we have chosen *n*-heptane, which is completely miscible with olefin but remains insoluble in PEG, for the recovery of pure 1-decene from the PEG–copper phase. PEG phase

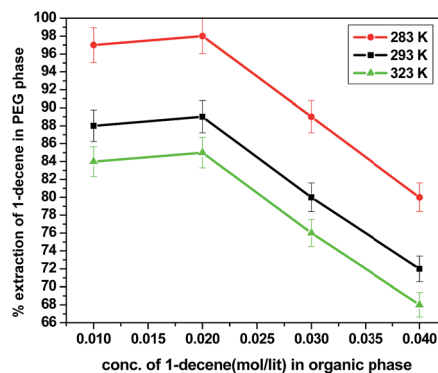


Fig. 4 Effect of initial concentration of 1-decene in feed on the percentage of extraction of 1-decene at different temperature (*n*-decane : PEG₂₀₀ = 1 : 1) (by volume, 5 ml each); conc. of 1-decene in organic phase 0.01–0.04 mol L⁻¹; [Cu²⁺] = 0.04 mol L⁻¹; time 4 h.

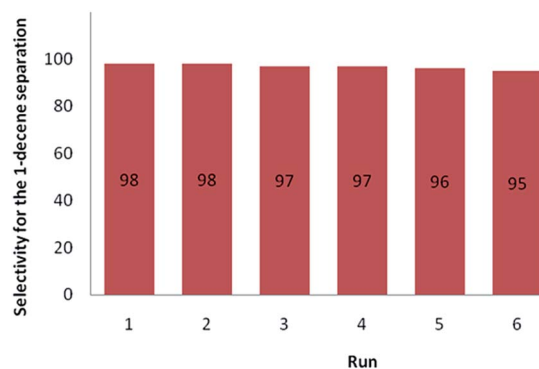


Fig. 5 Results of recycling experiments.

containing Cu–olefin complex was separated from the hydrocarbon phase simply by gravity settling and then treated with *n*-heptane at 80 °C. Removal of the solvent under reduced pressure yielded pure 1-decene. The olefin sample was further analyzed by ICP-AES and results indicated that there was no metal obtained during the recovery process. These studies suggested that copper ions remained in PEG phase, whereas olefin was selectively recovered in *n*-heptane solvent.

Last but not least, we checked the recyclability of recovered copper containing PEG₂₀₀ for six runs under the described conditions. The results of these experiments are summarized in Fig. 5. As shown, the recovered PEG–copper phase showed almost similar efficiency for the separation of 1-decene from the mixture of *n*-decane/1-decene.

Conclusions

We have demonstrated a simple and efficient system for the selective separation of 1-decene from a mixture of 1-decene/*n*-decane *via* π -complexation approach using copper(II) salt embedded polyethylene glycol. The results have shown that the copper(II)tetrafluoroborate–PEG solution has the best selectivity for the separation of 1-decene. Mixing of copper(II) salt in PEG provided *in situ* reduction of copper(II) ions to Cu(I) ions which

are favourable to coordinate with olefin molecules and therefore provided highly selective separation of 1-decene from the mixture. The copper-olefin complex containing PEG phase is extracted with hot *n*-heptane to recover the pure 1-decene. The recovered PEG phase containing copper(I) was successfully reused for several runs with negligible change in the efficiency.

Experimental section

Sample analysis

The raffinate phase and the extracted hydrocarbon were analysed by injecting a specific amount of sample (0.2 μL) by a syringe graduated in to minimum volume of 0.1 μL to a Gas Chromatography (GC) equipped with a PTV injector and a Flame Ionization Detector. The specification of GC with the column details and oven programme are mentioned below:

GC Model: VARIAN CP-3800; Column: CP-Sil 24 CB-MS-CP5817;

Dimension: 30 m \times 0.25 mm \times 0.25 μm ; injector temperature: 270 $^{\circ}\text{C}$.

Injector type: Programmed Temperature Vaporizing injector (PTV) FID detector temperature: 300 $^{\circ}\text{C}$.

Column oven temperature programme:

Rate ($^{\circ}\text{C min}^{-1}$)	Temperature ($^{\circ}\text{C}$)	Hold time (min)	Total time (min)
Initial	40	2.0	2.0
5.0	120	2.0	20
5.0	250	10	56
	Total time		56.00

The RT of components in GC:

Component	RT
<i>n</i> -Decane	13.61–13.72
1-Decene	13.85–13.88

The percentage of component extracted or separated is calculated by:

$$E_x = \frac{C_{x_0} - C_{x_t}}{C_{x_0}} \times 100$$

where, E_x = % transfer or % extraction of *x* component from feed. C_{x_0} = initial concentration (%wt) of *x* component in feed. C_{x_t} = concentration (%wt) of *x* component in feed at time *t* (min).

The concentration of hydrocarbon components from GC was calculated by taking the area percentage directly from the chromatogram at the respective RT of components. The response factor of FID was found to be almost closer to 1.00, which was calculated by comparing the % area from chromatogram at all the RTs with the percentage composition of the respective components in the standard mixture of hydrocarbons (C_8 – C_{10}).

General experimental procedure

To carry out the separation studies, initially, PEG of required specification and quantity was taken into a 50 ml round bottom flask and subsequently the copper precursor was added to get the required concentration of copper ions in the mixture under magnetic stirring at 25 $^{\circ}\text{C}$ till a homogeneous mixture is obtained. To the resulting sky blue coloured copper solution in PEG, the mixture of hydrocarbon consisting of olefin and paraffin was added and stirred at the specific condition of temperature under atmospheric condition of pressure for 4 h (240 min). After every interval of 15 minutes, the mixture was allowed to settle down and a sample of raffinate phase was taken for GC analysis for the amount of olefin transferred from the hydrocarbon phase to the glycol phase. After 4 h of stirring the transfer of olefin found to be negligible and the copper-olefin complex containing PEG phase was then separated from the hydrocarbon phase by physical method. Further the PEG phase was treated with *n*-heptane at temperature of 75–80 $^{\circ}\text{C}$ to extract the olefin separated by complexation. Finally the olefin with 99% purity was recovered by the removal of *n*-heptane by evaporation under vacuum.

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