Articles

Electrochemistry, Stability, and Alkene Complexation Chemistry of Copper(I) Triflate in Aqueous Solution. Potential for Use in Electrochemically Modulated Complexation-Based Separation Processes

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Copper(I) trifluoromethanesulfonate (CuOTf), which is insoluble in water, reacted with vinyl sulfonate anion (VS) to form a water soluble complex (concentrations > 0.1 M). Acidic CuOTf solutions prepared with relatively large VS/Cu(I) ratios were comparable in stability to solutions containing excess chloride ion. Reversible binding of alkenes (ethylene, 1,3-butadiene and 1-butene) to copper(I) in aqueous CuOTf/VS solutions was observed by ^{1}H-NMR. The copper(I) displayed a competitive reaction with VS and the alkenes. This allowed the binding affinity of the alkenes to the copper(I) to be calculated based on the proton chemical shift for VS. The strength of alkene complexation followed the order ethylene > 1-butene ≈ 1,3-butadiene. The electrochemistry for the Cu(II/I) couple showed a quasi-reversible reaction that depended on acidity and the concentration of VS in the solution. Binding to copper(I) caused substantial amounts of the alkenes to be absorbed into CuOTf/VS solutions from the gas phase, especially at low [VS]/[Cu(I)] ratios. Calculations indicated that CuOTf in aqueous solution containing VS is superior to CuCl in chloride media for electrochemically modulated complexation-based separation of alkenes from alkanes.

I. Introduction

The synthesis, molecular structure, and bonding mode of copper(I) complexes with alkenes have been of great interest in connection with the separation of alkenes from mixtures including alkanes and with the role of copper(I) at the receptor site of the plant hormone ethylene.[1−3] In a series of papers, our groups have explored the use of electrochemically modulated complexation (EMC), which is a combination of electrochemistry and selective solute extraction, as an innovative separation technology.[4−11] The electrochemistry and application of iron tetrakis(*p*-sulfonatophenyl)porphyrin as an electroactive chemical complexing agent for a carrier-mediated separation of hazardous nitrogen heterocycles was reported.[5] Modeling studies of the EMC process focused on the mass and energy balance, the concentrations of species in the different phases, the maximum fraction of solute removed from the feed phase, and the maximum fraction that could be concentrated in the receiving phase.[6,8] Recently, the separation of carbon monoxide from nitrogen[10] and ethylene from ethane[11] was demonstrated using an aqueous copper(II/I) in HCl/KCl complexing system. However, small binding affinities of ethylene and carbon monoxide to copper(I) were observed due to competitive complexation with chloride ions.

A redox electrolyte that provides an effective EMC separation of alkenes from alkanes has several requirements. A high binding affinity of alkenes to copper(I) contributes to extraction of a large amount of alkenes from the feed mixture. In the system of copper(II/I)/aqueous HCl/KCl, competition between halide ions and alkenes for ligand sites on copper(I) is an important factor for both binding affinity of alkenes to copper(I) and for stability of copper(I).[10−12] Therefore, the use of a more weakly coordinating counteranion would be expected to allow copper(I) solutions to have larger capacities for absorption of alkenes. Rapid interfacial mass transfer for extraction and concentration of alkenes requires rapid complexation kinetics for the reaction of alkenes with copper(I). High solubility of copper(I) in a nontoxic, nonvolatile solvent where it is stable with respect to oxidation or disproportionation is also necessary. Aqueous solutions containing electrolytes are ideal for the EMC separation of alkenes from alkanes because of their high conductivity and because hydrocarbons have relatively low physical solubilities in polar, protic solvents. Rapid electrode

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kinetics for the Cu(II/I) couple is important for efficient conversion of electrical energy into chemical free energy. Furthermore, the Cu(II/I) couple must be chemically reversible at potentials where no deleterious side reactions occur, such as formation of copper metal or chlorine and hydrogen gases.

In this paper, the characteristics of copper(I) trifluoromethanesulfonate (CuOTf) in aqueous solutions as a carrier for alkenes in EMC separations were investigated using ^{1}H-NMR, UV−vis, cyclic voltammetry, and solubility measurements. In contrast to copper(I) in chloride media where 1:1 binding with alkenes is observed,[12] CuOTf has the potential for binding of several alkenes. However, CuOTf has a relatively low solubility in water. This problem was addressed by adding water-soluble vinyl sulfonate (VS), which forms a complex with copper(I) but still allows for complexation to other alkenes.

II. Experimental Section

Materials. Copper(I) trifluoromethanesulfonate−*x*-1,3-butadiene (CuOTf) was synthesized as follows. In 80 mL of benzene and 2 g of cuprous oxide, trifluoromethanesulfonic acid anhydride 5.5 g was added under a nitrogen atmosphere and the mixture was refluxed at 90 °C overnight. Addition of 1,3-butadiene resulted in the formation of a white powder (79% yield) that was filtered and dried. Elemental analysis of the product indicated a 1/1 mol ratio for Cu/S and binding of a nonstoichiometric amount of 1,3-butadiene. In the solid state, 1,3-butadiene can be removed from the product by applying vacuum.

Benzene was distilled with reflux including dispersed sodium in light oil, after pretreatment with molecular sieve overnight. Sodium vinyl sulfonate (VS) was obtained by addition of the purchased aqueous solution (Aldrich, 25 wt %) into methanol, centrifugation of the obtained white precipitate, and drying overnight under vacuum. Cuprous oxide, cuprous chloride, trifluoromethanesulfonic acid anhydride, trifluorosulfonic acid, trifluorosulfonic acid-*d*, sodium trifluorosulfonate, deuterium oxide, ethylene, 1,3-butadiene, 1-butene, ethane, and *n*-butane were all at least 99% pure and were used as purchased from Aldrich. Potassium chloride and hydrochloric acid were used as reagent grade from Mallinckrodt AR.

Solubility Tests of Alkenes in Aqueous Solution. An apparatus for measuring solubilities of hydrocarbons and a detailed procedure are contained in the Supporting Information.

^{1}H-NMR Measurements of Aqueous Solution. Nuclear magnetic resonance spectroscopy was conducted on a Varian VXR-300S spectrometer run with VNMR operating software on a Sun Microsystems Model 4/60 color workstation. Various volumes (0.28, 0.37, 0.56, 1.1 mL at atmospheric pressure) of each alkene (ethylene, 1,3-butadiene, 1-butene) were injected into 1.0 mL D_2O solutions containing CuOTf (0.01 M), VS (0.06 M), and trifluorosulfonic acid-*d* (0.01 M). The volume of the headspace in the NMR tubes was 0.8 mL; therefore, the concentration for each alkene in the D_2O solution could be calculated from Henry's law using coefficients obtained with the solubility apparatus described above. Equilibrium of each specimen was confirmed by the consistency of repeated measurements.

Stability Measurements of Copper(I) by Visible Spectra. Copper(I) in aqueous solutions is potentially unstable with respect to disproportionation and to oxidation by air. Since copper(II) is a product of both of these reactions, the stability of copper(I) was measured by monitoring the absorbance at 800 nm using a Hewlett-Packard HP8452A diode-array UV−visible spectrophotometer.

Electrochemistry. Cyclic voltammetry was conducted using a PAR 363 potentiostat and a PAR 175 universal programmer. The working electrode was a glassy carbon(GC) polished with 0.5-μm alumina, rinsed thoroughly with distilled water, and then placed in a sonicator for 1 min to remove residual alumina. All potentials were measured vs the saturated calomel electrode (SCE).

III. Results and Discussion

Solubility and Stability of Copper(I) in Aqueous Solution. An important factor for successful EMC separation of alkenes from alkanes is high solubility of the carrier in the electrolyte solution. Many copper(I) salts are relatively insoluble in water. For the electrolyte system used in our prior work, KCl/HCl, the maximum solubility of copper(I) chloride was 50 mM at room temperature.[10−12] Cu(I) is even less soluble in aqueous NaOTf/HOTf than in KCl/HCl. However, CuOTf can be solubilized in aqueous media by the addition of vinyl sulfonate (VS). For example, CuOTf concentrations of >0.1 M are readily achieved with excess VS in 0.001 M HOTf solutions.

The stability of Cu(I) in water is highly dependent on the solution conditions.[13] While Cu(I) is thermodynamically unstable with respect to disproportionation in aqueous solution, high concentrations of coordinating anions such as chloride stabilize the Cu(I) state. Even for aqueous solutions containing noncoordinating anions such as perchlorate, Cu(I) can exhibit kinetic stability if oxygen and metal surfaces are excluded. In solutions where Cu(I) is thermodynamically stable, Cu(I) can be oxidized to Cu(II) by oxygen. These factors make it difficult to compare the stability of Cu(I) in chloride solutions and in triflate/VS solution quantitatively. Under comparable conditions ($pH = 1$), 0.05 M Cu(I) solutions containing either Cl^- or VS decompose slowly over a period of many hours even in the absence of air. Solutions of Cu(I) containing VS and HOTf become less stable as the concentration of VS is lowered. However, even for solutions where the concentration of VS is as low as 0.05 M, the solutions are sufficiently stable to allow the absorption of alkenes to be measured and to obtain chemically reversible electrochemical behavior.

Evidence for Competitive Complexation of Alkenes with Copper(I) in Aqueous Solution. As discussed above, CuOTf can be made soluble in aqueous solutions *via* complexation with VS. Evidence for binding of VS and other alkenes to copper(I) was obtained using ^{1}H-NMR (Figure 1). Figure 1a depicts the spectrum of free VS in aqueous solution. When CuOTf was dissolved in the solution, the proton peaks for VS shifted upfield (Figure 1b) which is consistent with electron donation from Cu(I) through the formation of a π-complex. Since distinct resonances for free and complexed VS were not observed, it can be assumed that the complexation kinetics were rapid relative to the ^{1}H-NMR time scale.

Binding of ethylene with copper(I) in solutions containing VS was also observed. The chemical shift for protons on unbound ethylene in D_2O was 5.2 ppm, however, this resonance is found near 4.2 ppm for solutions containing Cu(I) as shown in Figure 1c,d. The position of the bound ethylene resonances depended on the total concentration of ethylene as expected. The peaks attributed to ethylene in Figure 1 readily disappeared when the solution was purged with nitrogen. Rapidly reversible binding of gaseous alkenes with copper(I) was also observed for 1,3-butadiene and 1-butene.

Careful inspection of Figure 1c,d indicated that the peaks for VS moved downfield as the concentration of ethylene increased. Similar downfield shifts in the VS resonances were observed upon addition of 1,3-butadiene and 1-butene. These observations indicate that VS and alkenes are competing for the available binding sites on copper(I). Chemical shifts for the (H_a) protons on VS as a function of alkene pressure are depicted in Figure 2. Qualitative extrapolation of the curves in Figure 2 to infinite alkene pressure is reasonably consistent with the chemical shift observed for H_a in free VS ($=6.5$, see Figure 1a). A more positive proton chemical shift for VS represents a larger binding affinity for the alkenes in solution. Therefore, the order of binding affinity of the alkenes is ethylene > 1-butene $\approx$ 1,3-butadiene.

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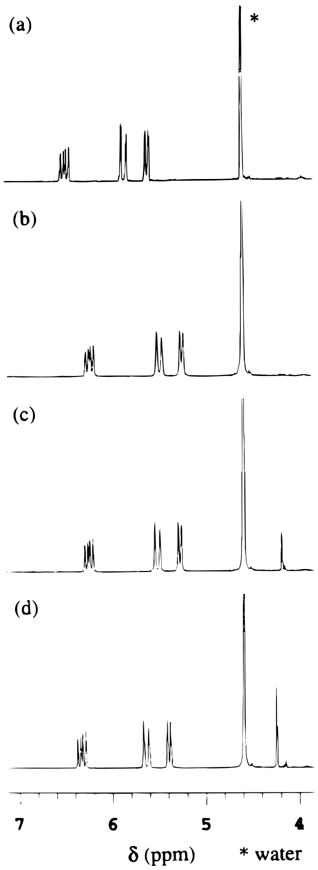


Figure 1. Proton chemical shifts for VS and ethylene binding to copper(I) in aqueous solution (D_2O): (a) VS (1.00 M) and CF_3SO_3D (0.10 M); (b) solution a and CuOTf (0.10 M); (c) solution b and ethylene (0.03 M); (d) solution b (0.15 M).

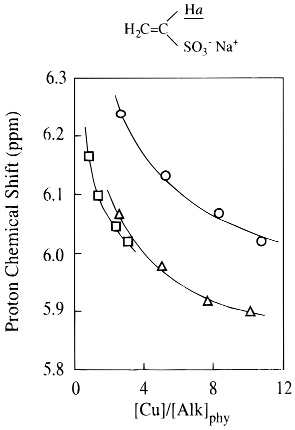


Figure 2. Chemical shift of the H_a proton in VS binding to copper(I) in aqueous solution containing CF_3SO_3D (0.10 M), CuOTf (0.01 M), and VS (0.06 M) at [VS]/[Cu] = 6. Supplied gases: ethylene (○), 1,3-butadiene (□), 1-butene (△).

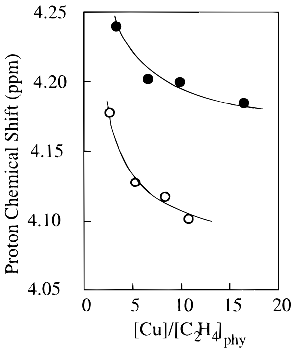
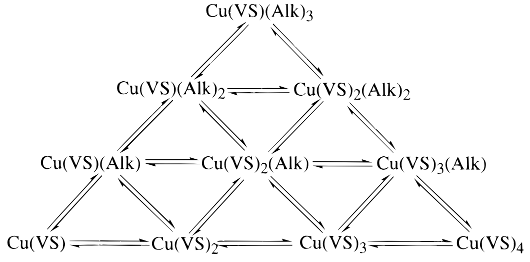


Figure 3. Chemical shift of methylene protons for ethylene binding to copper(I) in aqueous solution containing CF_3SO_3D (0.10 M), CuOTf (0.01 M), and VS (0.06 or 0.10 M) with different [VS]/[Cu] = 6 (○) and 10 (●).

Scheme 1. Proposed Competitive Exchange Reactions of Unsaturated Hydrocarbons (Alk) and Vinyl Sulfonate (VS) to Copper(I) in Aqueous Solution Where the Remaining Coordination sites on Cu(I) Would be Occupied by Water



(*) VS: sodium vinylsulfonate
Alk: ethylene, *1,3*-butadiene, or *1*-butene

Proton chemical shifts for ethylene were also measured as a function of ethylene concentration for ratios of VS to CuOTf equal to 6 and 10 (Figure 3). Salomon and Kochi demonstrated that a linear dependence of chemical shifts for the vinyl protons for alkenes on [Cu]/[alkene] was presumptive evidence for the presence of only a single Cu(I) species in rapid equilibrium with free alkene.[14] The fact that the plots in Figure 3 are clearly non-linear supports the hypothesis that several Cu(I) complexes are in rapid equilibria with free ethylene. These Cu(I) species could involve multiple binding of alkenes or VS as indicated in Scheme 1. The plots in Figure 3 are qualitatively consistent with a competitive complexation scheme like the one in Scheme 1. The ethylene resonances shift downfield at higher $[C_2H_4]_{phy}$ and are observed further downfield at higher [VS]/[Cu] ratios. Furthermore, the plot for [VS]/[Cu] = 6 is more steeply sloped than the plot for [VS]/[Cu] = 10 because $[C_2H_4]_{phy}$ has a greater effect of the fraction of ethylene molecules bound to Cu(I) when there is less competition from VS. Similar trends in the chemical shifts for the vinyl protons were observed for solutions of 1,3-butadiene and 1-butene. Scheme 1 presumes that copper(I) in aqueous solutions will assume four-coordinate, tetrahedral geometry. Although Cu(I) complexes that are trigonal-pyramidal,[15,16] trigonal,[17] and square-pyramidal[18] are known, these complexes contain chelate ligands such as bi-2,2′-pyridylamine.

Salomon and Kochi reported a dichotomy in the direction of vinyl proton shifts in π-complexes of mono- and bidentate alkene ligands bound to Cu(I). Resonances for monodentate alkenes were shifted upfield (greater shielding) upon complexation whereas resonances for bidentate alkenes were shifted downfield (deshielding).[14] Although no 1,3-dienes were investigated in their study, the result indicates that 1,3-butadiene is probably bound to Cu(I) in a monodentate fashion since complexation resulted in an upfield shift for the vinyl protons.

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Table 1. Solubility of Alkenes in Aqueous Solutions Containing CuOTf (0.09 M), CF_3SO_3H (0.01 M), and Various Concentrations of VS

	[VS] = 1.0 M			[VS] = 0.50 M			[VS] = 0.20 M		
	ethylene	butadiene	butene	ethylene	butadiene	butene	ethylene	butadiene	butene
initial pressure of alkene (Torr)	730	646	677	638	693	687	648	646	672
pressure of alkene at equilibrium (Torr)	693	610	667	581	642	668	539	560	627
solubility of alkene in solution containing Cu^IOTf ($\times 10^2$, M)	1.4	1.4	0.4	2.2	2.0	0.7	4.2	3.4	1.7
solubility of alkene in solution containing $Cu^{II}(OTf)_2$ ($\times 10^3$, M)	2.2	6.7	2.3	1.8	7.1	2.3	1.7	6.2	2.1

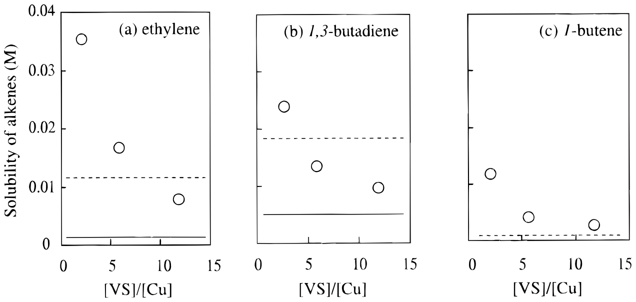

Figure 4. Solubility of alkenes in aqueous solution containing CuOTf (0.09 M), CF_3SO_3H (0.01 M) and various concentrations of VS: (a) ethylene equilibrated at 394 Torr; (b) 1,3-butadiene equilibrated at 465 Torr; (c) 1-butene equilibrated at 394 Torr; (—) physical solubility in the solution; (--) solubility in aqueous solution containing CuCl (0.05 M), KCl (1.00 M), and HCl (0.10 M).

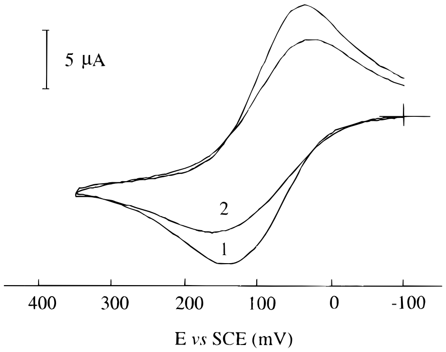

Figure 5. Cyclic voltammograms of Cu(II/I) in aqueous solution under ethylene atmosphere at 20 mV/s: (1) CuOTf (5 mM), VS (330 mM), and CF_3SO_3H (0.010 M); (2) CuOTf (4 mM), VS (14 mM), CF_3SO_3H (0.010 M), and CF_3SO_3Na (0.100 M).

Solubility of Alkenes in Aqueous Solution Containing CuOTf. The Henry's law solubility coefficients for ethane and *n*-butane were found to be 1.3×10^{-6} (M/Torr) and 1.8×10^{-6} at 25 °C, respectively, in aqueous solutions containing CuOTf (0.10 M), CF_3SO_3H (0.01 M), and VS (0.20 M). As expected, these values were independent of supplied pressure and were almost the same as those in a control solution containing $Cu^{II}(OTf)_2$ instead of Cu^IOTf. In contrast, the solubility of alkenes in aqueous solutions containing CuOTf were considerably larger than their physical solubilities measured in the control solution and were dependent on the ratio of [VS]/[Cu(I)], as shown in Figure 4 and Table 1. The fact that the alkene solubilities were higher for lower [VS]/[Cu(I)] ratios is consistent with the competitive binding scheme proposed from the ^{1}H-NMR experiments. The dashed lines in Figure 4 represents the alkene solubilities for the copper(I) chloride system used in prior EMC separation experiments. Using [VS]/[Cu(I)] ratios less than five provided greater solubility with the CuOTf system for ethylene and 1-butene and similar solubility for 1,3-butadiene.

Electrochemistry of Cu(II/I) in Aqueous Solution. In EMC processes, it is essential that the complexing agent can be electrolyzed between its two redox states within the potential window afforded by the electrolyte. As discussed in ref 10, electrolysis of Cu(II,I) in chloride media at carbon electrodes was difficult due to the slow heterogeneous kinetics observed for reduction of Cu(II). Application of negative overpotentials to increase the rate of this process resulted in deposition of copper metal on the cathode and the evolution of hydrogen gas. Hydrogen evolution is especially problematic due to the requirement of using 0.1 M HCl for solubility reasons. This is less of a problem with CuOTf because concentrations >10 mM can be achieved at pH 2−3 using VS. In addition, the heterogeneous kinetics for Cu(II,I) in triflate media are substantially more facile that in chloride media at a glassy carbon electrode.

Cyclic voltammograms for the Cu(II,I) couple were quasi-reversible under an inert atmosphere and high VS/Cu(I) ratios at pH 3. Peak currents, $I_{p,a}$ and $I_{p,c}$, were equal in magnitude and both were proportional to (scan rate)$^{1/2}$ indicating that mass transport limited electrolyses could be readily achieved without deposition of copper metal or hydrogen evolution. The peak potentials for the quasi-reversible Cu(II,I) wave at pH 3 were insensitive to the scan rate below 200 mV/s (see Supporting Information). At either higher or lower pH values, the peak potential separation increases and becomes more sensitive to scan rate, indicating that the electrode kinetics become less facile. This effect at higher pH values can probably be attributed to lower stability or solubility of Cu(I). At very low pH values, protonation of VS may occur affecting the complexation equilibria with Cu(I).

The Cu(II,I) couple in aqueous CuOTf/VS solutions remained quasi-reversible in the presence of dissolved alkenes as shown in Figure 5. In general, alkene-saturated solutions prepared with larger VS/Cu(I) ratios exhibited smaller peak potential separations. This observation is also qualitatively consistent with the presence of several Cu(I) species as indicated in Scheme 1.

An estimate for the formal potential, $E°'$, of the Cu(II,I) couple can be obtained from the average of the peak potentials in the cyclic voltammograms. For the CV's recorded under a nitrogen atmosphere, $E°' = +0.063$ V vs SCE. Similar voltammograms recorded under ethylene, 1,3-butadiene, and 1-butene yielded values of $E°' = +0.101$, $+0.094$, and $+0.083$ V, respectively. These positive shifts in $E°'$ are consistent with the ^{1}H-NMR results in that they indicate weak, reversible complexation of the alkenes with Cu(I).[19]

Potential Use of Copper(I) Triflate in EMC Processes. A first-order estimate of the potential for purifying and concentrating alkenes using aqueous copper(II,I) triflate solutions can be made using the reported EMC modeling studies.[6,8−10] The maximum or equilibrium-limited ability for a given redox electrolyte to pump a solute uphill against its concentration gradient occurs when the solute solubility is the same throughout the EMC cycle. Under this condition, one can equate the total solubility of solute in the solution containing the carrier in the

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high binding affinity state (Cu^I in this case) to the solubility in the solution containing the carrier in the low binding affinity state (Cu^{II} in this case). Since Cu(II) has virtually no binding affinity with alkenes, the low binding affinity solubility is essentially the physical solubility at a given ionic strength and is expected to obey Henry's law. By assuming that the solubility in both solutions are linearly related to solubility, one obtains

$$P_{rec}/P_{feed} = [\text{alkene}]_{Cu(I)}/[\text{alkene}]_{Cu(II)}$$

where P_{rec} and P_{feed} are the alkene pressures on the receiving/downstream and feed/upstream sides of the EMC process, respectively, and the alkene concentrations are the solubilities discussed above. The assumption that the [alkene] in the Cu(I) solution is linear with feed pressure will be true when the equilibrium constant for complexation is significantly larger than unity and the carrier is not saturated. By measuring the concentrations of alkenes at given contacting pressures for Cu(I) and Cu(II) solutions, one can use the equation above to calculate the equilibrium-limited pressure ratio P_{rec}/P_{feed} that an EMC process could achieve.

Examination of the solubility data in Table 1 indicates that the most effective EMC processes using this system would be achieved for a [VS] = 0.20 M. For conditions near atmospheric pressure, one could achieve P_{rec}/P_{feed} ratios of 25, 5.4, and 8.1 for ethene, 1-butene and 1,3-butadiene. As expected, the best calculated ratios occur when the [VS] is lowest because there is less competition for binding to Cu(I). Higher ratios would be achieved for higher concentrations of Cu(I).

The equilibrium-limited pressure ratios reported here for the copper(I) triflate system are significantly higher than those reported earlier for copper(I) chloride electrolytes.[12,13] For that system, the equilibrium pressure ratio for ethylene was 8. No absorption of butenes above the physical solubility could be detected. Since the copper(I) triflate system also exhibited more facile electrode kinetics and better chemical stability, it is a better candidate for EMC-based alkene purification processes.

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Supporting Information Available: Figure showing text giving the apparatus and procedures for measuring solubilities of hydrocarbons in aqueous solutions and a figure containing cyclic voltammograms of the Cu(II/I) couple (pH = 3) with a high VS/Cu(I) ratio at various sweep rates (3 pages). Ordering information is given on any current masthead page.

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