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Liquid Phase Extraction and Separation of Noble Organometallic Catalysts by Functionalized Ionic Liquids

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Abstract: The separation of two noble organometallic catalysts from a homogeneous organic phase was investigated using liquid phase extraction with functionalized ionic liquids. Thirteen functionalized ionic liquids containing amino, hydroxy, thioether, carboxylic, or olefin functional groups were prepared by a standard neutralization method. The extractions of Jacobsen's catalyst and Wilkinson's catalyst were conducted using the functionalized ionic liquids as the extraction phase without adding any other metal complexing extractant. The distribution factors between the ionic liquid (IL) phase and toluene (organic solution phase) demonstrated that the functional groups in ILs exhibited moderate to high affinity with the metal complexes. The influence of the ionic liquid structure on the distribution factors was also investigated.

Keywords: Functionalized ionic liquids, organometallic catalyst, liquid phase extraction, distribution factor

INTRODUCTION

Room temperature ionic liquids (RTILs) have received considerable interest as alternative solvents in a wide range of applications including use as reaction solvents (1), extraction solvents (2) and for the preparation of new materials (3). Ionic liquids (ILs) have remarkable properties, which include

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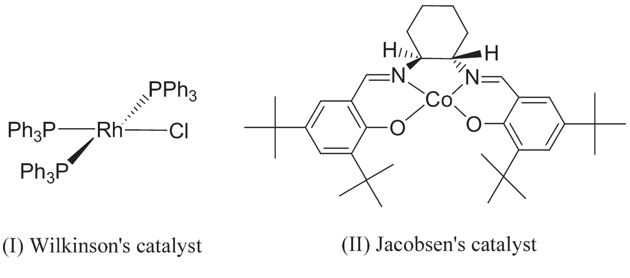
negligible vapor pressure, high thermal and chemical stability, and wide liquid phase temperature range (4). A key feature of ILs is that their properties can be tailored by judicious selection of cation, anion, and substituents (5). Extensive studies exist of ionic liquids modified with functional groups, referred to as functionalized or task specific ionic liquids (TSILs) (6). These have been utilized in metal extraction (7) and catalyst immobilization (8). So far, most functionalized ionic liquids have been designed by modifying the cation structure when combined with common anions such as BF_4^- and PF_6^- (9–12). However, a few papers have reported the modification of anions (13–15).

Since the pioneering work of Dai et al. (16) and Rogers and co-workers (17), many attempts have been made to use ILs as alternatives to traditional organic diluents for solvent extraction of metal ions (16–25). Dai and coworkers (16) examined the extraction of alkaline and alkaline earth metals into ILs using crown ether as an extractant. Their studies showed that the crown ether in ILs achieved higher extraction efficiency than that in ordinary organic diluents. Rogers and coworkers (6) developed novel ILs incorporating metal coordination groups. These "task-specific" ILs showed high extraction efficiencies when used as an extracting phase alone or when doped into nonspecific 1-alkyl-3-methylimidazolium-based ILs (7). These biphasic extractions mainly focused on the removal of metal ions from the water phase to an ionic liquid phase. Water immiscible ionic liquids were used in these studies which incorporated hydrophobic anions such as PF_6^- or Tf_2N^-.

Precious metal catalysts, e.g. Wilkinson's catalyst (I) and Jacobsen's catalyst (II) (structures are shown in Scheme 1), are widely employed in certain important homogeneous catalytic reactions. Wilkinson's catalyst, $RhCl(PPh_3)_3$ (Ph = phenyl), is widely used in homogeneous hydrogenations of alkenes (26). Other applications of Wilkinson's catalyst include: catalytic hydroboration of alkenes using catecholborane and pinacolborane (27), and selective 1,4-reductions of α,β-unsaturated carbonyl compounds in concert with triethylsilane (28). Jacobsen's remarkably efficient Co salen catalyst, [(s)-(s)-(+)-N,N'-bis(3,5-di-tert-butylsalicylidene)- 1,2-cyclohexanediamino cobalt (II)], has been used for hydrolytic kinetic resolutions (HKR) of



(I) Wilkinson's catalyst (II) Jacobsen's catalyst

Scheme 1. Structures of two homogeneous organometallic catalysts.

terminal epoxides (29), and for enantioselective catalytic ring opening of meso epoxides (30).

Homogeneous organometallic catalysts have several advantages versus heterogeneous systems. Every metal center participates and each catalytic site is identical in a given reaction. Homogeneous catalysts can be specifically tailored structurally to modify their activity and frequently operate at mild conditions. However, the separation and reuse of noble organometallic complexes can be notoriously difficult because both the products and catalysts are in the reaction solution. Wilkinson's catalyst was recovered with silica-immobilized P-donor ligands by solid-phase extraction (31). The phosphorus ligands immobilized on silica in that study could be oxidized under the rhodium extraction conditions. Simple and efficient homogeneous catalysts extraction procedures will play an important role in the development of practical homogeneous catalysis.

We now report the facile extraction and recovery of both Wilkinson's and Jacobsen's catalysts from toluene by liquid-liquid extraction using novel functionalized ionic liquids as the sole extraction phase without adding any other extractant. Amino, hydroxy, carboxylic, thioether or olefinic functional groups have been incorporated into both the cations and anions of ILs to prepare a series of functionalized ionic liquids. These ILs were water-soluble and therefore were tested to extract precious organometallic complex catalysts from organic solutions.

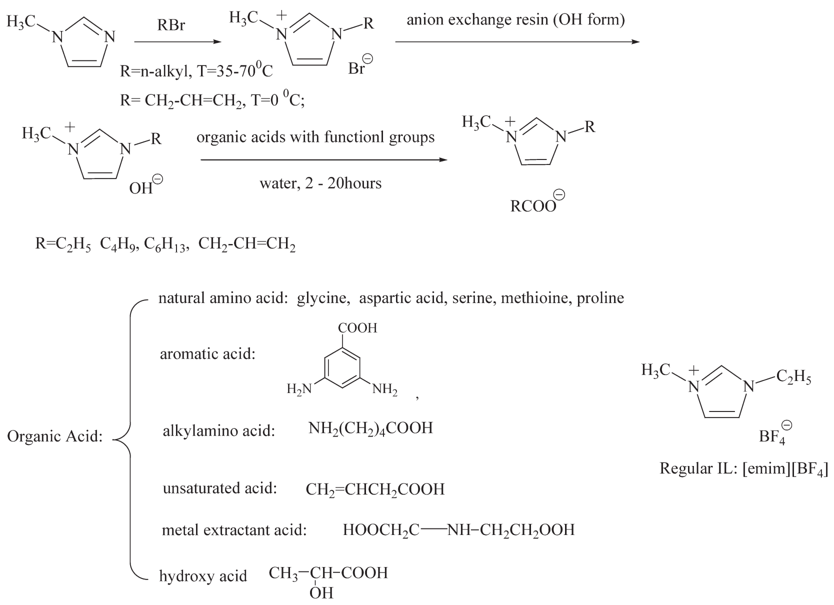
EXPERIMENTAL

General Supplies and Equipment

Amino acids, other organic acids, Wilkinson's catalyst, and Jacobsen's catalyst were purchased from Aldrich (Milwaukee, WI, USA). All other chemicals and solvents were purchased from Aldrich (Milwaukee, WI, USA), Fluka (Ronkonkoma, NY, USA), or Fisher Scientific (Pittsburgh, PA, USA). A Beckman DU-640 spectrophotometer was used in the determination of UV-Vis absorbance of organometallic complexes in toluene. ^{1}H NMR spectra were obtained on a Bruker Avance 300 MHz nuclear magnetic resonance spectrometer in DMSO-d_6.

General Procedures for Preparing Functionalized Ionic Liquids

The major synthetic procedure with some modifications followed a neutralization method reported by Ohno and coworkers (13). As shown in Scheme 2, the first synthetic step was the quaternization of the 1-methyl imidazole with alkyl bromides at 35–70°C without any solvent present. The reaction temperature was increased with an increase in the alkyl bromide's chain



Scheme 2. Preparation of functionalized ionic liquids.

length. The reaction between 1-methyl imidazole and allyl bromide is highly exothermic. Therefore the reaction should be carefully performed while cooling in an ice bath and then the solution was stirred at room temperature for 20 h. The reactions were run at a 30–35 g scale and the product yields are high (about 92–97%).

Quaternization was used to introduce a carbon-carbon double bond unto the cation's structure. Double bonds are well known to show significant coordination ability with soft acid metal ions such as silver, cuprous and some low-valence precious metal complexes of rhodium or platinum.

The second step was to exchange bromide for hydroxide anions by elution of aqueous imidazolium bromide solution through a strongly basic anion-exchange resin (Amberlite IRA-400), which had been pretreated to its hydroxide form. The immidazolium hydroxide obtained in the second step was used directly as a diluted aqueous solution without purification. Finally, the functionalized organic acids dissolved or suspended in water, were neutralized by dropwise addition of the aqueous imidazolium hydroxide solution with cooling for 2 to 20 hours. The excess organic acid was removed by filtration after vigorously stirring the reaction residue with sodium carbonate in acetonitrile or dichloromethylene. The ionic liquids were vacuum dried at 70°C overnight after evaporation of the organic solvent. Most of the new ionic liquids were free flowing and nearly colorless or pale yellow transparent liquids at room temperature. General yields in this step were 60–70%.

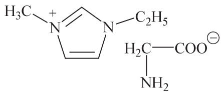
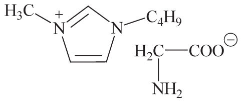
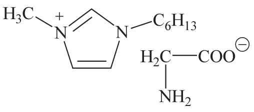
The structures and ^{1}H NMR characterizations of the thirteen functionalized ionic liquids prepared are listed in Tables 1 and 2.

Extraction of Organometallic catalysts by Ionic Liquids

Feedstock solutions of Wilkinson's catalyst and Jacobsen's catalyst were prepared by dissolving exact amounts of these catalysts (15 mg) in anhydrous toluene (30 ml) in capped vials. Desired concentrations of catalyst solution could be obtained by further diluting the feedstock solution with anhydrous toluene.

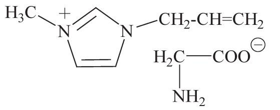
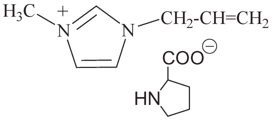
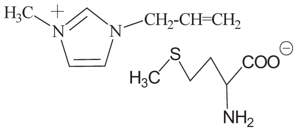
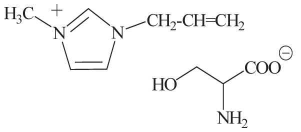
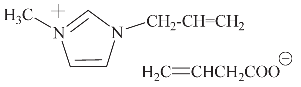
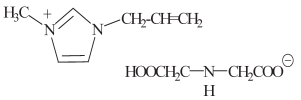
A typical extraction procedure was performed as follows: Ionic liquid (0.5 ml) was introduced into a vial (4 ml) followed by the addition of catalyst solution (1 ml). The biphasic mixture was shaken at 20°C for 30 min. After

Table 1. Structures and ^{1}H NMR characterizations of functionalized ionic liquids with structural changes in their imidazolium cations

Functionalized ionic liquids	Structure[a]	^{1}H NMR
[emim][Gly]		1.35 (3H, t, $NCH_2C\mathbf{H}_3$), 2.69 (2H, 3, $NH_2C\mathbf{H}_2COO$), 3.83 (3H, s, $NC\mathbf{H}_3$), 4.19 (2H, q, $NC\mathbf{H}_2CH_3$), 7.71 (1H, s, C(5)H), 7.81 (1H,s,C(4)H), 9.55 (1H, s, C(2)H)
[bmim][Gly]		0.89 (3H, t, $N(CH_2)_3C\mathbf{H}_3$), 1.23 (2H, m, $NCH_2CH_2C\mathbf{H}_2CH_3$), 1.76 (2H, m, $NCH_2C\mathbf{H}_2CH_2$-CH_3),2.78 (2H, d, $NH_2C\mathbf{H}_2$-COO), 3.91 (3H, s, $NC\mathbf{H}_3$), 4.23 (2H, t, $NC\mathbf{H}_2(CH_2)_2CH_3$), 7.84 (1H, s, C(5)H), 7.91 (1H,s,C(4)H), 9.78 (1H, s, C(2)H).
[hmim][Gly]		0.85(3H, t, $N(CH_2)_5C\mathbf{H}_3$), 1.25 (6H, m,$NCH_2CH_2(C\mathbf{H}_2)_3CH_3$), 1.77 (2H,m,$NCH_2C\mathbf{H}_2(CH_2)_3$-$CH_3$),2.78 (2H,d,$NH_2C\mathbf{H}_2COO$), 3.90 (3H, s, $NC\mathbf{H}_3$), 4.20 (2H, t, $NC\mathbf{H}_2(CH_2)_4CH_3$), 7.85 (2H, d, C(5)H, C(4)H), 9.89 (1H, s, C(2)H).

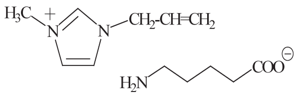
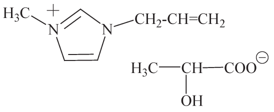
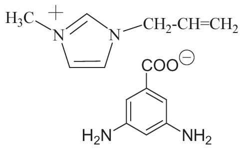
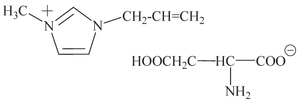
[a]For the functionalized ionic liquids in this series, the anion was held constant as glycine, and the alkyl chain length of imidazolium was increased from 2 to 6.

Table 2. Structures and ^{1}H NMR characterizations of functionalized ionic liquids with a variety of anion structures

Functionalized ionic liquids	Structure^a	^{1}H NMR
[amim] [Gly]		2.72 (2H, d, $NH_2C\mathbf{H}_2COO$), 4.15 3H, s, ($NC\mathbf{H}_3$), 5.06 (2H, d, $CH_2\text{-}CH{=}C\mathbf{H}_2$), 5.48 (2H, t, $C\mathbf{H}_2\text{-}CH{=}CH_2$), 6.07 (1H, m, $CH_2\text{-}C\mathbf{H}{=}CH_2$), 7.76 (2H,d,C(5)H, C(4)H), 9.50 (1H, s, C(2)H)
[amim] [Pro]		1.57 (2H, m, $NHCH_2C\mathbf{H}_2$), 2.66 (2H, m, $COOCHC\mathbf{H}_2$), 2.96 (2H, t, $NHC\mathbf{H}_2$), 3.25 (1H, t, $NHC\mathbf{H}COO$), 3.85 (3H, s, $NC\mathbf{H}_3$), 4.83 (2H, d, $CH_2\text{-}CH{=}C\mathbf{H}_2$), 5.32 (2H, t, $C\mathbf{H}_2\text{-}CH{=}CH_2$), 6.03 (1H, m, $CH_2\text{-}C\mathbf{H}{=}CH_2$), 7.76 (2H,d,C(5)H, C(4)H), 9.41 (1H, s, C(2)H)
[amim] [Met]		1.43 (2H, m, $CH_3SCH_2C\mathbf{H}_2$), 1.76 (2H, t, $CH_3SC\mathbf{H}_2$), 1.99 (3H, s, $C\mathbf{H}_3S$), 2.80 (1H, t, $NH_2C\mathbf{H}COO$), 3.86 (3H, s, $NC\mathbf{H}_3$), 4.88 (2H, d, $CH_2\text{-}CH{=}C\mathbf{H}_2$), 5.36 (2H, t, $C\mathbf{H}_2\text{-}CH{=}CH_2$), 6.07 (1H, m, $CH_2\text{-}C\mathbf{H}{=}CH_2$) 7.76 (2H, d, C(5)H, C(4)H), 9.50 (1H, s, C(2)H)
[amim] [Ser]		2.82 (1H, t, $NH_2C\mathbf{H}COO$), 3.24 (2H, m, $OHC\mathbf{H}_2CH$), 3.87 (3H, s, $NC\mathbf{H}_3$), 4.87 (2H, d, $CH_2\text{-}CH{=}C\mathbf{H}_2$), 5.34 (2H, t, $C\mathbf{H}_2\text{-}CH{=}CH_2$), 6.04 (1H, m, $CH_2\text{-}C\mathbf{H}{=}CH_2$), 7.75 (2H, d, C(5)H, C(4)H), 9.38 (1H, s, C(2)H)
[amim] [Vba]		2.72 (2H, d, $CH_2{=}CHC\mathbf{H}_2COO$), 3.87 (3H, s, $NC\mathbf{H}_3$),4.88 (4H, d, $CH_2\text{-}CH{=}C\mathbf{H}_2$ and $C\mathbf{H}_2{=}CHCH_2COO$), 5.32 (2H, t, $C\mathbf{H}_2\text{-}CH{=}CH_2$), 5.93 (1H, m, $CH_2{=}C\mathbf{H}CH_2COO$], 6.09 (1H, m, $CH_2\text{-}C\mathbf{H}{=}CH_2$), 7.76 (2H, d, C(5)H, C(4)H), 9.56 (1H, s, C(2)H)
[amim] [Imi]		3.10 (2H, s, $NHC\mathbf{H}_2COOH$), 3.54 (2H, s, $NHC\mathbf{H}_2COO$), 3.87 (3H, s, $NC\mathbf{H}_3$), 4.87 (2H, d, $CH_2\text{-}CH{=}C\mathbf{H}_2$), 5.35 (2H, t, $C\mathbf{H}_2\text{-}CH{=}CH_2$), 6.05 (1H, m, $CH_2\text{-}C\mathbf{H}{=}CH_2$), 7.75 (2H, d, C(5)H, C(4)H), 9.30 (1H, s, C(2)H)

(*continued*)

Table 2. Continued

Functionalized ionic liquids	Structure[a]	^{1}H NMR
[amim] [Apa]		1.31 (2H, m, $C\mathbf{H}_2CH_2COO$), 1.60 (2H, m, $NH_2CH_2C\mathbf{H}_2$), 1.81 (2H, t, $C\mathbf{H}_2COO$), 2.10 (2H, t, $NH_2C\mathbf{H}_2$), 3.89 (3H, s, $NC\mathbf{H}_3$), 4.87 (2H, d, CH_2-$CH{=}C\mathbf{H}_2$), 5.32 (2H, t, $C\mathbf{H}_2$-$CH{=}CH_2$), 6.05 (1H, m, CH_2-$C\mathbf{H}{=}CH_2$)
[amim] [Lac]		1.16 (3H, d, $C\mathbf{H}_3CHOH$), 3.74 (1H, m, $OHC\mathbf{H}COO$), 3.83 (3H, s, $NC\mathbf{H}_3$), 4.82 (2H, d, CH_2-$CH{=}C\mathbf{H}_2$), 5.29 (2H, t, $C\mathbf{H}_2$-$CH{=}CH_2$), 6.01 (1H, m, CH_2-$C\mathbf{H}{=}CH_2$), 7.70 (2H, d, C(5)H, C(4)H), 9.23 (1H, s, C(2)H)
[amim] [Daa]		3.86 (3H, s, $NC\mathbf{H}_3$), 4.87 (2H, d, CH_2-$CH{=}C\mathbf{H}_2$), 5.31 (2H, t, $C\mathbf{H}_2$-$CH{=}CH_2$), 5.80 (1H, s, C(4)H in phenyl], 6.04 (1H, m, CH_2-$C\mathbf{H}{=}CH_2$), 6.39 (2H, s, C(2), C(6)H in phenyl], 7.74 (2H, d, C(5)H, C(4)H), 9.56 (1H, s, C(2)H)
[amim] [Asp]		2.15 (2H, d, $C\mathbf{H}_2COOH$), 3.31 (1H, t, $NH_2C\mathbf{H}COO$), 3.87 (3H, s, $NC\mathbf{H}_3$), 4.84 (2H, d, CH_2-$CH{=}C\mathbf{H}_2$), 5.32 (2H, t, $C\mathbf{H}_2$-$CH{=}CH_2$), 6.03 (1H, m, CH_2-$C\mathbf{H}{=}CH_2$), 7.73 (2H, d, C(5)H, C(4)H), 9.20 (1H, s, C(2)H

[a] For the functionalized ionic liquids in this series, the cation, 1-allyl-3-methylimidazolium, was held constant and the anions were varied.

shaking, the upper toluene phase (0.5 ml) was pipetted out by a syringe and transferred to a disposable UV-grade polymethacrylate cuvette. The UV-Vis spectrum was obtained using a Beckman DU-640 spectrophotometer.

Determination of the Distribution Factors of the Two Organometallic Complexes

The concentrations of the Wilkinson's and Jacobsen's catalysts in the toluene phase were determined by UV-VIS spectroscopy using calibration curves.

Standard calibration curves were obtained by plotting absorbance at a specific wavelength against a series of standard metal complex concentrations in toluene. The concentration of the metal complex in each ionic liquid was calculated by mass balance. Finally, the distribution factors were calculated by $C_{ILs}/C_{toluene}$, the concentration of metal complex in the ionic liquid phase divided by concentration of metal complex in the toluene phase.

RESULTS AND DISCUSSION

With pure toluene as a blank, the full UV-Vis spectra in toluene of the each of the two organometallic catalysts are shown in Figs. 1 and 2. The absorbance of the rhodium catalyst falls between 270–500 nm showing a single and wide peak. The cobalt catalyst's absorbance consists of three peaks when the concentration is 0.1 mg/ml. However, the latter two peaks merges to a single and wide peak when the concentration increases to 0.4 mg/ml. Calibration curves were obtained by a linear regression fitting of the observed absorbance data (Figs. 3 and 4). Theoretically, the calibration curves should pass the origins according to the Beer-Lambert law. However, in our results, neither calibration curve intercepted the origin. The reason for this deviation is not clear. Possible explanations are: (1) toluene shows moderate absorption at around 300 nm ($A = 0.1$). The Y-axis interception in the rhodium catalyst calibration curve (obtained at 309 nm) is greater than that in cobalt's curve (obtained at 450 nm) because toluene shows negligible absorbance at 450 nm; (2) the low rhodium catalyst solubility in toluene may lead to light scattering due to particulates in the solution; (3) the association-dissociation equilibrium of the organometallic complex in toluene shifts as a function of concentration.

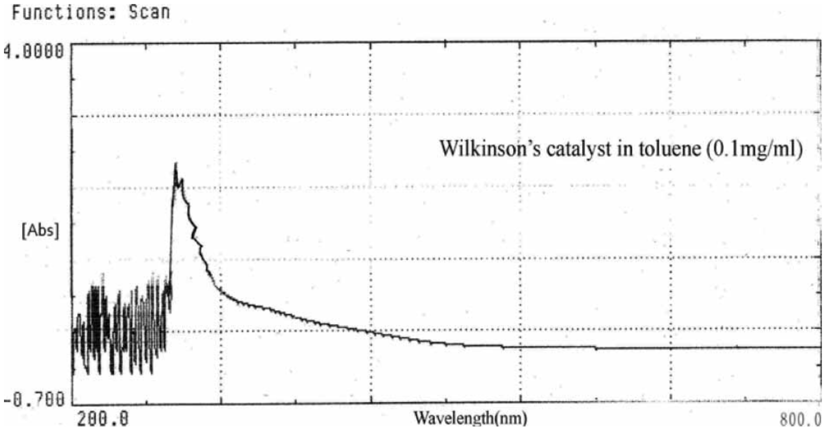


Figure 1. UV-Vis absorbance spectra of Wilkinson's catalyst in toluene.

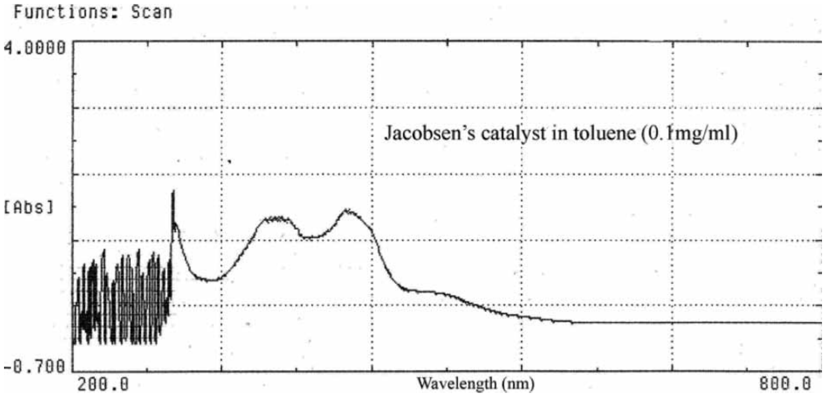


Figure 2. UV-Vis absorbance spectra of Jaobsen's catalyst in toluene.

Modification of the hydrophobicity of ILs is an important feature of the controllable design of ionic liquids. The anions of ionic liquids generally play a major role in determining their water solubilitiy (32). For example, ILs with NO_3^- or CF_3COO^- as anions are water soluble; ILs with PF_6^-, $N(CF_3SO_2)_2^-$ as anions are water immiscible. Finally, the solubility of ILs with BF_4^- anion is cation-dependent. The new functionalized ionic liquids are water soluble due to the hydrophilic properties of the carboxylic acid anions. When the alkyl chain length in the methyl imidazolium cation increases to six carbons, the functionalized ionic liquids are still water miscibile. The strong hydrophilic property of these ionic liquids makes them immiscible with some weakly polar organic solvents. Preliminary screening of the miscibility of the ILs with organic solvents demonstrated that these novel ILs are not miscible with toluene. This immiscibility was exploited to extract and recover noble organometallic catalysts from toluene solutions by liquid-liquid biphasic extraction.

The data in Table 3 confirms the capability of the functionalized ionic liquids to extract the two catalysts. Coordination of the metal complexes by functional groups on the ILs confers this ability. In control tests, the conventional non-functionalized ionic liquid, [emim][BF_4], exhibited no ability to extract either Wilkinson's rhodium catalyst or Jacobsen's cobalt catalyst. In contrast, the functionalized ionic liquids displayed moderate to very strong extraction capability for both catalysts (measured by the distribution factors). Two similar trends in the extraction capability were found for both catalysts. When glycine was the anion, the distribution factors went up substantially with an increase in the alkyl chain length in the imidazolium cations. The distribution factor D_J was only 4.6 when [emim][Gly] was used as the extracting ionic liquid (Table 3). D_J rose to 71 using [bmim][Gly] and finally jumped to 869 when [hmim][Gly] was used. This increase in extraction capability going from ethyl to butyl and to hexyl

Table 3. Distribution factors of the Wilkinson's and Jacobsen's catalysts between ILs and toluene

ILs	[emim][Gly]	[bmim][Gly]
D_W	0.03	1.7
D_J	4.6	71
ILs	[emim][BF_4]	[hmim][Gly]
D_W	0	8.8
D_J	0	869
ILs	[amim][Pro]	[amim][Daa]
Dw	3.1	23.8
D_J	0.47	19.8
ILs	[amim][Ser]	[amim][Gly]
Dw	2.7	2.3
D_J	0.12	1.3
ILs	[amim][Apa]	[amim][Lac]
Dw	8.1	0.68
D_J	5.3	1.7
ILs	[amim][Met]	[amim][Vba]
Dw	76	6.4
D_J	66.4	5.8
ILs	[amim][Asp]	[amim][[Imi]
Dw	0.57	2.9
D_J	0.93	3.5

Distribution factor $= C_{ILs}/C_{toluene}$, concentration of metal complex in the ionic liquid phase divided by concentration of metal complex in the toluene phase. Dw: distribution factor of Wilkinson's catalyst; D_J: distribution factor of Jacobsen's catalyst. The concentration of organometallic complex in toluene phase was determined by UV-VIS spectrophotometer using a calibration curve and the concentration of metal in ionic liquids phase was calculated by mass balance. The structures of the ionic liquids are shown in Tables 1 and 2.

groups on the imidazolium cation is remarkable. This augmentation of distribution factors is ascribed to the enhanced hydrophobic properties of the ionic liquids with longer alkyl chain length in immidazolium cations. Jacobsen's and Wilkinson's catalysts are more soluble in a hydrophobic solvent than in hydrophilic solvent.

The ionic liquids with amino and thioether groups exhibited higher extraction capabilities for the rhodium or cobalt complexes than ionic liquids with hydroxy or carboxylic groups. Also as shown in Table 3, the distribution factor D_J was 66.4 when ionic liquid [amim][Met] with the methionate anion was used. D_J was far lower at 1.7 when [amim][Lac] with the lactate as anion was used. In a similar vein, D_W was 23.8 when [amim][Daa] containing

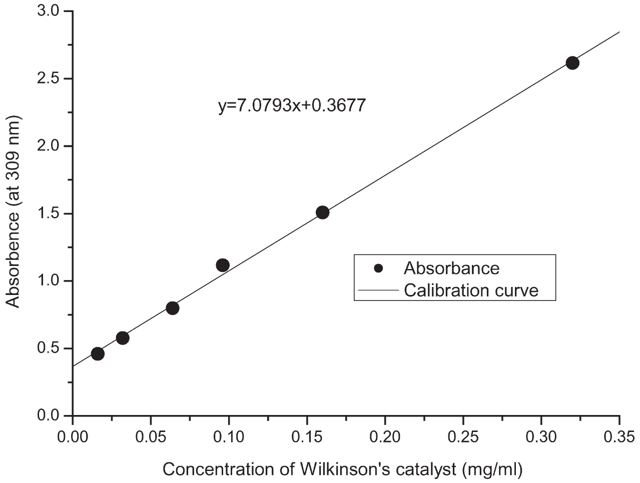


Figure 3. Absorption-concentration calibration curve for Wilkinson's catalyst in toluene, at a wavelength $\lambda = 309$ nm.

two amino groups in its 3,5-diaminobenzoate anion was used. D_W was only 2.9 when [amim][[Imi] was used. These results clearly confirmed that amino and thioether groups possess a stronger coordination ability than either hydroxy or carboxylic acid groups in the extraction of the rhodium and cobalt complexes.

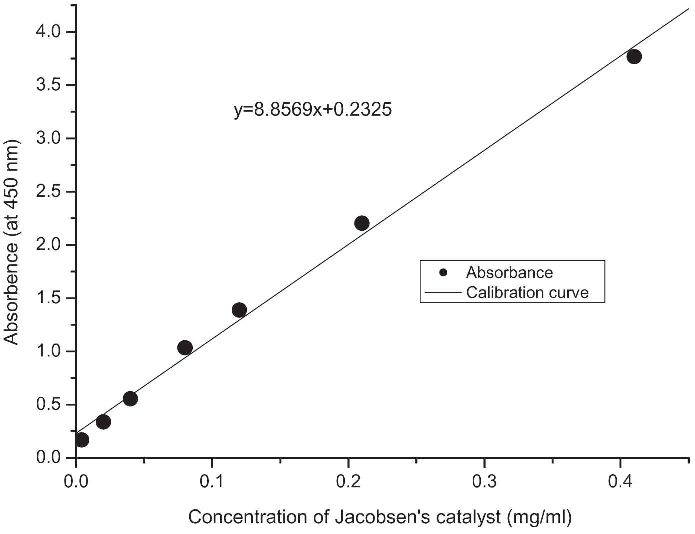


Figure 4. Absorption-concentration calibration curve for Jacobsen's catalyst in toluene, at a wavelength $\lambda = 450$ nm.

CONCLUSION

A new series of functionalized ionic liquids containing amino, hydroxy, thioether, carboxylic or olefinic groups in their anions or cations. These new functionalized ionic liquids were successfully applied to extract and recover precious organometallic complexes from the homogeneous toluene phase. Studies on the back-extraction or recovery of metal complexes from the functionalized ionic liquid phase are now in progress.

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REFERENCES

1. Olivier, H. (1999) Recent developments in the use of non-aqueous ionic liquids for two-phase catalysis. *J. Mol. Catal. A: Chem.*, 146: 285.
2. Lei, Z., Wolfgang, A., and Wasserscheid, P. (2006) Separation of 1-hexene and n-hexane with ionic liquids. *Fluid Phase Equilibria.*, 241: 290.
3. Lin, I. and Vasam, C.S. (2005) Metal-containing ionic liquids and ionic liquid crystals based on the imidazolium moiety. *J. Organomet. Chem.*, 690: 3498.
4. Dupont, J., Souza, R.F., and Suarez, P. (2002) Ionic liquid (molten salt) phase organometallic catalysis. *Chem. Rev.*, 102: 3667.
5. Welton, T. (1999) Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chem. Rev.*, 99: 2071.
6. Visser, A.E., Swatloski, R.P., Davis, J.H. Jr., and Rogers, R.D. (2001) Task-specific ionic liquids for the extraction of metal ions from aqueous solutions. *Chem. Commun.*, 135.
7. Visser, A.E., Swatloski, R.P., Reichert, W.M., Mayton, R., Sheff, S., Wierzbicki, A., Davis, J.H., Jr., and Rogers, R.D. (2002) Task-specific ionic liquids incorporating novel cations for the coordination and extraction of Hg^{2+} and Cd^{2+} synthesis, characterization, and extraction studies. *Environ. Sci. Technol.*, 36: 2523.
8. Zhu, A.L., Jiang, T., Han, B.X., Huang, J., Zhang, J.C., and Ma, X.M. (2006) Study on guanidine-based task-specific ionic liquids as catalysts for direct aldol reactions without solvent. *New J. Chem.*, 30: 736.
9. Mu, Z., Zhou, F., Zhang, S., Liang, Y., and Liu, W. (2005) Effect of the functional groups in ionic liquid molecules on the friction and wear behavior of aluminum alloy in lubricated aluminum-on-steel contact. *Tribology International*, 38: 725.
10. Holbrey, J.D., Visser, A.E., Spear, S.K., Reichert, W.M. R., Swatloski, P., Grant Broker, A., and Rogers, R.D. (2003) Mercury(II) partitioning from aqueous solutions with a new, hydrophobic ethylene-glycol functionalized bis-imidazolium ionic liquid. *Green Chem.*, 5: 129.

11. Fei, Z., Geldbach, T.J., Zhao, D., and Dyson, P.J. (2006) From dysfunction to bis-function: on the design and applications of functionalised ionic liquids. *Chem. Eur. J.*, 12: 2122.
12. Zhao, D., Fei, Z., Ang, W.H., Scopelliti, R., and Dyson, P.J. (2007) Thiocyanate functionalised ionic liquids: synthesis, characterisation and reactivity. *Eur. J. Inorg. Chem.*, 279.
13. Fukumoto, K., Yoshizawa, M., and Ohno, H. (2005) Room temperature ionic liquids from 20 natural amino acids. *J. Am. Chem. Soc.*, 127: 2398.
14. Ohno, H. (2006) Functional design of ionic liquids. *Bull. Chem. Soc. Jpn.*, 79: 1665.
15. Kagimoto, J., Fukumoto, K., and Ohno, H. (2006) Effect of tetrabutylphosphonium cation on the physico-chemical properties of amino-acid ionic liquids. *Chem. Commun.*, 2254.
16. Dai, S., Ju, Y.H., and Barnes, C.E. (1999) Solvent extraction of strontium nitrate by a crown ether using room-temperature ionic liquids. *J. Chem. Soc., Dalton Trans.*, 1201.
17. Rogers, R.D., Visser, A.E., Swatloski, R.P., and Hartman, D.H. (1999) Metal ion separations in room temperature ionic liquids: potential replacements for volatile organic diluents. In *Metal Separation Technologies Beyond 2000: Integrating Novel Chemistry with Processing*; Liddell, K.C. and Chaiko, D.J. (eds.); The Minerals, Metals & Materials Society: Warrendale, PA., 139–147.
18. Chun, S., Dzyuba, S.V., and Bartsch, R.A. (2001) Influence of structural variation in room-temperature ionic liquids on the selectivity and efficiency of competitive alkali metal salt extraction by a crown ether. *Anal. Chem.*, 73: 3737.
19. Dietz, M.L. and Dzielawa, J.A. (2001) Ion-exchange as a mode of cation transfer into room-temperature ionic liquids containing crown ethers: implications for the "greenness" of ionic liquids as diluents in liquid–liquid extraction. *Chem. Commun.*, 2124.
20. Nakashima, K., Kubota, F., Maruyama, T., and Goto, M. (2003) Ionic liquids as a novel solvent for lanthanide extraction. *Anal. Sci.*, 19: 1097.
21. Visser, A.E. and Rogers, R.D. (2003) Room-temperature ionic liquids: new solvents for f-element separations and associated solution chemistry. *J. Solid State Chem.*, 171: 109.
22. Wei, G.-T., Yang, Z., and Chen, C.J. (2003) Room temperature ionic liquids as a novel medium for liquid/liquid extraction of metal ions. *Anal. Chim. Acta*, 488: 183.
23. Shimojo, K. and Goto, M. (2004) First application of calixarenes as extractants in room-temperature ionic liquids. *Chem. Lett.*, 33: 320.
24. Luo, H., Dai, S., and Bonnesen, P.V. (2004) Solvent extraction of Sr^{2+} and Cs^{+} based on room-temperature ionic liquids containing monoaza-substituted crown ethers. *Anal. Chem.*, 76: 2773.
25. Hirayama, N., Deguchi, M., Kawasumi, H., and Honjo, T. (2005) Use of 1-alkyl-3-methylimidazolium hexafluorophosphate room temperature ionic liquids as chelate extraction solvent with 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione. *Talanta*, 65: 255.
26. Osborn, J.A., Jardine, F.H., Young, J.F., and Wilkinson, G. (1966) The preparation and properties of tris(triphenylphosphine)halogenorhodium(I) and some reactions thereof including catalytic homogeneous hydrogenation of olefins and acetylenes and their derivatives. *J. Chem. Soc. A.*, 1711.

27. Evans, D.A., Fu, G.C., and Hoveyda, A.H. (1988) Rhodium(I)-catalyzed hydroboration of olefins. The documentation of regio- and stereochemical control in cyclic and acyclic systems. *J. Am. Chem. Soc.*, 110: 6917.
28. Ojima, I. and Kogure, T. (1972) Selective reduction of α,β-unsaturated terpene carbonyl compounds using hydrosilane-rhodium(I) complex combinations. *Tetrahedron Lett.*, 5035.
29. Tokunaga, M., Larrow, J.F., Kakiuchi, F., and Jacobsen, E.N. (1997) Asymmetric catalysis with water: efficient kinetic resolution of terminal epoxides by means of catalytic hydrolysis. *Science*, 277: 936.
30. Jacobsen, E.N., Kakiuchi, F., Konsler, R.G., Larrow, J.F., and Tokunaga, M. (1997) Enantioselective catalytic ring opening of epoxides with carboxylic acids. *Tetrahedron Lett.*, 38: 773.
31. Kramer, J., Nollen, E., Buijs, W., Driessen, W.L., and Reedijk, J. (2003) Investigations into the recovery of Wilkinson's catalyst with silica-immobilised P-donor ligands. *Reac. Funct. Polym.*, 57: 1.
32. Seddon, K.R., Stark, A., and Torres, M.J. (2000) Influence of chloride,water,and organic solvents on the physical properties of ionic solids. *Pure Appl. Chem.*, 72: 2275.