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PAPER IN FOREFRONT

Evaluating the solvation properties of metal-containing ionic liquids using the solvation parameter model

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Abstract

Ionic liquids (IL) have been utilized as gas chromatography stationary phases due to their high thermal stability, negligible vapor pressure, wide liquid range, and the ability to solvate a range of analytes. In this study, the solvation properties of eight room temperature ILs containing various transition and rare earth metal centers [e.g., Mn(II), Co(II), Ni(II), Nd(III), Gd(III), and Dy(III)] are characterized using the Abraham solvation parameter model. These metal-containing ILs (MCILs) consist of the trihexyl(tetradecyl)phosphonium cation and functionalized acetylacetonate ligands chelated to various metals. They are used in this study as gas chromatographic stationary phases to investigate the effect of the metal centers on the separation selectivities for various analytes. In addition, two MCILs comprised of tetrachloromanganate and tris(trifluoromethylphenylacetylaceto)manganate anions were used to study the effect of chelating ligands on the selectivity of the stationary phases. Depending on the metal center and chelating ligand, significant differences in solvation properties were observed. MCILs containing Ni(II) and Mn(II) metal centers exhibited higher retention factors and higher peak asymmetry factors for amines (e.g., aniline and pyridine). Alcohols (e.g., phenol, *p*-cresol, 1-octanol, and 1-decanol) were strongly retained on the MCIL stationary phase containing Mn(II) and Dy(III) metal centers. This study presents a comprehensive evaluation into how the solvation properties of ILs can be varied by incorporating transition and rare earth metal centers into their structural make-up. In addition, it provides insight into how these new classes of ILs can be used for solute-specific gas chromatographic separations.

Keywords Ionic liquids · Gas chromatography · Magnetic ionic liquids · Solvation properties

Introduction

Ionic liquids (IL) are salts with melting points under 100 °C [1]. ILs have attracted attention from various areas of interdisciplinary research due to their high thermal stability, low vapor pressure, and unique separation, and reaction selectivities [2, 3]. ILs have been successfully employed as stationary phases for gas chromatography, solvents for organic synthesis, solvents for liquid–liquid extraction, sorbent coatings for solid-phase microextraction, and membrane materials for selective filtration [3–7]. Gas chromatography (GC) columns utilizing IL-based stationary phases have been commercially available for several years and often exhibit unique selectivities compared with polydimethyl(siloxane) (PDMS) and poly(ethylene glycol) (PEG)-based stationary phases [8–10]. Unique separation selectivities towards target analytes [e.g., fatty acid methyl esters (FAMEs)], polyaromatic hydrocarbons, and petrochemicals) have been demonstrated by introducing various functional groups to the IL structures or by creating dicationic/tricationic ILs [11–13].

Recently, our group has sought to incorporate transition or rare earth metals (e.g., Ni(II), Co(II), Mn (II), and Dy(III)) into hydrophobic ILs in an effort to exploit their paramagnetic properties for various analytical and bioanalytical applications

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[14–16]. Interestingly, depending on the choice of the metal center, the metal-containing ionic liquids (MCILs) exhibit vastly different extraction efficiencies toward target analytes. For example, the Ni(II)-based MCIL was shown to have superior extraction of *E. coli* cells, whereas the Mn(II)-based MCIL possessed excellent extraction efficiency toward phenolics, insecticides, and polycyclic aromatic hydrocarbons [14, 15]. A limitation of these studies is that they do not utilize a platform that permits a systematic investigation into the types and magnitude of intermolecular interactions between the analytes and MCILs. Inverse GC analysis is an ideal tool that can be exploited to examine the unique solvation properties offered by MCILs.

The first use of GC stationary phases containing metal centers dates back to the mid-1950s [17, 18]. Most of these solid stationary phases were incorporated into packed columns [19–23]. Cobalt(II) chloride and nickel(II) chloride were added to a packed column, which favored the separation of oxygen-containing compounds from other polar organic substances [19–21]. Rhodium (II), palladium(II), and silver(I) compounds were used as stationary phase additives for the separation of paraffins and olefins [24–26]. The use of metal-containing stationary phases was further extended after the invention of open-tubular capillary columns [27, 28]. To obtain liquid stationary phases, the metals were dissolved as inorganic salts in a classic liquid stationary phase, in an effort to eliminate gas-solid adsorption [29–32]. Wasiak and coworkers reported various structurally modified PDMS-based stationary phases containing metal ions (e.g., Ni(II), Co(II), and Cu(II)) [33, 34]. However, the utilization of metal-containing stationary phases for selective separation can be limited by the low solubility of the inorganic salt in the stationary phases. For example, when the concentration of Ni(II) or Co(II) in the mercaptopropylmethyl polysiloxane-based stationary phase reached the level of 0.007 or 0.04 mol mol^{-1} (molar ratio of metal and thiol group), the stationary phase changed from a viscous liquid to a gum-like material, resulting in decreased separation performance with increasing adsorptive characteristics of the stationary phase [33].

By combining metal-containing anions with a bulky phosphonium cation, the resulting MCILs possess a high concentration (ranging from 1.4 to 1.8 mol L^{-1}) of transition and rare earth metal centers [e.g., Ni(II), Mn(II), Dy (III), and Nd(III)] and are liquids at room temperature, making them ideal gas-liquid chromatography (GLC) stationary phases. In this study, the solvation properties of eight room temperature MCILs were investigated using the Abraham solvation parameter model. Seven of the MCILs possess different transition and rare earth metal centers as well as different chelating ligands. In addition, one MCIL lacking any ligand within the anion component was used for comparison. Significant differences in solvation properties of MCILs were observed depending on the choice of metal center as well as the presence and type of the chelating ligands. Fifteen meter columns possessing high efficiency were prepared using Mn(II)- and Dy(III)-based MCILs. The separation selectivity of the MCIL-based GC columns toward different analyte groups were compared with commercial PDMS (Rtx-5) and IL-based (SLB IL-111) columns. Vastly different separation selectivities for a wide range of analytes, particularly amines and alcohols, were observed. The results from this study are the first to provide an understanding into how the structural basis of MCILs affect their solvation characteristics and how their unique structural properties can be exploited in selective solute-specific gas chromatographic separations.

Materials and methods

Eight MCILs were examined in this study. Their chemical structures are shown in Fig. 1. They consist of six hexafluoroacetylacetonate-based MCILs, namely IL **1**, trihexyl(tetradecyl)phosphonium tris(hexafluoroacetylaceto)nickelate(II) ($[P_{66614}^{+}]$ $[Ni(II)(hfacac)_3^{-}]$); IL **2**, $[P_{66614}^{+}]$ tris(hexafluoroacetylaceto)cobaltate(II) ($[Co(II)(hfacac)_3^{-}]$); IL **3**, $[P_{66614}^{+}]$ tris(hexafluoroacetylaceto)manganate(II) ($[Mn(II)(hfacac)_3^{-}]$); IL **4**, $[P_{66614}^{+}]$ tetrakis(hexafluoroacetylaceto)dysprosate(III) ($[Dy(III)(hfacac)_4^{-}]$); IL **5**, $[P_{66614}^{+}]$ tetrakis(hexafluoroacetylaceto)gadolinate(III) ($[Gd(III)(hfacac)_4^{-}]$); and IL **6**, $[P_{66614}^{+}]$ tetrakis(hexafluoroacetylaceto)neodymate(III) ($[Nd(III)(hfacac)_4^{-}]$). Additionally, IL **7** $[P_{66614}^{+}]$ tris(trifluoromethylphenylacetylaceto)manganate(II) ($Mn(II)(tfmphacac)_3^{-}]$) and IL **8** $[P_{66614}^{+}]_2$ tetrachloromanganate(II) ($[MnCl_4^{2-}]$) were used to examine the effect of chelating ligands. All MCILs were synthesized and characterized according to previously reported methods [14, 35].

Butyraldehyde, 1-chlorobutane, ethyl acetate, methyl caproate, and 2-nitrophenol were purchased from Acros Organics (Morris Plains, NJ, USA). Bromoethane was purchased from Alpha Aesar (Ward Hill, MA, USA). Ethyl benzene was purchased from Eastman Kodak Company (Rochester, NJ, USA). Acetic acid, *N,N*-dimethylformamide and toluene were purchased from Fisher Scientific (Pittsburgh, PA, USA). 2-Chloroaniline, *p*-cresol, naphthalene, *o*-xylene, *p*-xylene, and 1-bromohexane were purchased from Fluka (Steinheim, Germany). Benzaldehyde, 1-chlorohexane, 1-chlorooctane, cyclohexanol, cyclohexanone, 1-iodobutane, 1-nitropropane, octylaldehyde, 1-pentanol, 2-pentanone, propionitrile, 1-decanol, acetophenone, aniline, benzonitrile, benzyl alcohol, 1-bromooctane, 1-butanol, 1,2-dichlorobenzene, dichloromethane, 1,4-dioxane, 1-octanol, phenol, pyridine, pyrrole, *m*-xylene, 2-propanol, and propionic acid were purchased from Sigma Aldrich (St.

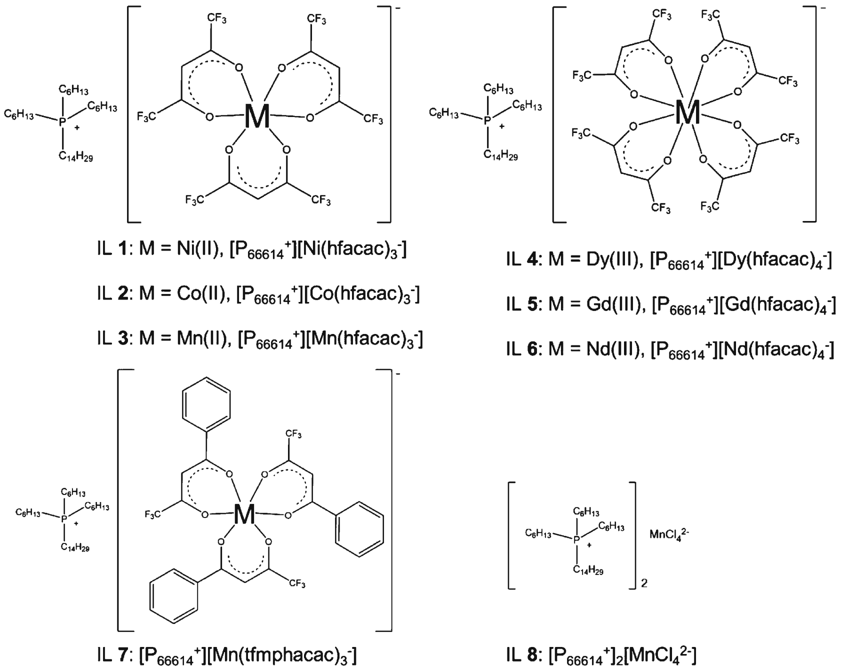

Fig. 1 Chemical structures of the eight metal-containing ILs examined in this study

IL **1**: M = Ni(II), $[P_{66614}^{+}][Ni(hfacac)_3^{-}]$

IL **2**: M = Co(II), $[P_{66614}^{+}][Co(hfacac)_3^{-}]$

IL **3**: M = Mn(II), $[P_{66614}^{+}][Mn(hfacac)_3^{-}]$

IL **4**: M = Dy(III), $[P_{66614}^{+}][Dy(hfacac)_4^{-}]$

IL **5**: M = Gd(III), $[P_{66614}^{+}][Gd(hfacac)_4^{-}]$

IL **6**: M = Nd(III), $[P_{66614}^{+}][Nd(hfacac)_4^{-}]$

IL **7**: $[P_{66614}^{+}][Mn(tfmphacac)_3^{-}]$

IL **8**: $[P_{66614}^{+}]_2[MnCl_4^{2-}]$

Louis, MO, USA). All analytes were used as received. Untreated fused silica capillary (i.d. 250 μm) and a SLB IL-111 column (30 m × 250 μm × 0.20 μm) were obtained from Supelco (Bellefonte, PA, USA). The Rtx-5 column (30 m × 250 μm × 0.25 μm) was purchased from Restek (Bellefonte, PA, USA). The two purchased commercial columns were cut to 15 m for a comparison with the MCIL-based GC columns.

Preparation of GC columns

Five or 15-m untreated fused silica capillary columns were coated with MCILs using the static coating method. The MCIL coating solution was prepared at a concentration of 0.45% (w/v) in dichloromethane in order to produce an approximate film thickness of 0.28 μm. The coated capillary columns were conditioned from 40–110 °C at 3 °C/min and held for 2 h. The column efficiency was determined using naphthalene at 100 °C. The list of prepared columns is shown in Table 1. All columns had efficiencies ranging from 1800 to 3700 plates/m. Compared with most traditional ILs containing the $[P_{66614}^{+}]$ cation, it was observed that the MCILs examined in this study possessing the hexafluoroacetylacetonate (hfacac) or trifluoromethylphenylacetylacetonate (tfmphacac) ligand exhibited more superior wetting ability on the surface of the untreated capillary. The thermal stability of ILs **1-6** were previously reported [35]. Thermal stability diagrams of ILs **7** and **8** are shown in Table S1 in the Electronic Supplementary Material (ESM). MCILs with hfacac and tfmphacac ligands are less thermally stable than MCILs without chelating ligand.

Preparation of probe solute standards and chromatographic conditions

The analyte standards were prepared in dichloromethane at a concentration of 1 mg/mL. A mixture of analytes was prepared using 15 different compounds with a concentration of 1 mg/mL. All separations were performed on an Agilent 7890B gas chromatograph with a flame ionization detector. Helium was used as the carrier gas with a flow rate of 1 mL/min. The injector and detector temperatures were held at 250 °C. The detector used hydrogen as a makeup gas at a flow rate of 30 mL/min and air flow was held at 400 mL/min.

A list of the 46 analytes and their corresponding solute descriptors is provided in Table S1 (see ESM). All probe molecules were dissolved in methylene chloride and injected individually at three different oven temperatures (50, 80, and 110 °C). Analytes possessing low boiling points exhibited low retention at higher temperatures, whereas others exhibited very strong retention on the stationary phase (in some cases, beyond 3 h). As a result, not all probe molecules could be subjected to regression analysis at the temperatures studied. Multiple linear regression analysis and statistical calculations were performed using the program Analyze-it (Leeds, UK).

Results and discussion

The MCILs examined in this study (see Fig. 1) were carefully selected to compare the effect of metal centers and chelating ligands on the solvation properties. All eight MCILs contain the same phosphonium cation. Six of the MCILs (ILs **1**–**6**)

Table 1 Characteristics of metal-containing ionic liquid-based stationary phases examined in this study

IL no.	Abbreviation	Metal center	Film thickness (μm)	Length (m)	Efficiency (plates/meter)
1	$[P_{66614}^{+}][Ni(hfacac)_3^{-}]$	Ni(II)	0.28	5	2800
2	$[P_{66614}^{+}][Co(hfacac)_3^{-}]$	Co(II)	0.28	5	2700
3	$[P_{66614}^{+}][Mn(hfacac)_3^{-}]$	Mn(II)	0.28	5	2700
			0.28	15	3700
4	$[P_{66614}^{+}][Dy(hfacac)_4^{-}]$	Dy(III)	0.28	5	2400
			0.28	15	3700
5	$[P_{66614}^{+}][Gd(hfacac)_4^{-}]$	Gd(III)	0.28	5	2200
6	$[P_{66614}^{+}][Nd(hfacac)_4^{-}]$	Nd(III)	0.28	5	2700
7	$[P_{66614}^{+}][Mn(tfmphacac)_3^{-}]$	Mn(II)	0.28	5	2400
8	$[P_{66614}^{+}]_2[MnCl_4^{2-}]$	Mn(II)	0.28	5	1800

contain the hfacac chelating ligand but with different metal centers (e.g., Ni(II), Co(II), Mn(II), Dy(III), Gd(III), and Nd(III)). IL **7** contains the tfmphacac chelating ligand, whereas IL **8** consists of the $[MnCl_4^{2-}]$ anion and lacks any chelating ligand. In this study, the solvation properties of all eight MCILs were examined using the solvation parameter model developed by Abraham in the 1990s [36–38]. This model, represented by Equation 1, has been used extensively to examine the solvation properties of a wide range of ILs.

$$Log\ k = c + eE + sS + aA + bB + lL \quad (1)$$

As shown in Equation 1, *k* is the retention factor of each probe molecule on the MCIL stationary phase at a specific temperature (50 °C, 80 °C, or 110 °C). The solute descriptors (*E*, *S*, *A*, *B*, and *L*) of the 46 probe molecules have been previously reported and are listed in Table S1 (see ESM). The solute descriptors are defined as: *E*, the excess molar refraction calculated from the solute's refractive index; *S*, the solute dipolarity/polarizability; *A*, the solute hydrogen bond acidity; *B*, the solute hydrogen bond basicity; and *L*, the solute gas-hexadecane partition coefficient determined at 298 K. Multiple linear regression analysis was performed using the solute descriptors of probe molecules and their retention factors to determine the solvation interactions between the probe molecules and IL-based stationary phases. The c term is the intercept of the regression line. The system constants (*e*, *s*, *a*, *b*, and *l*) are used to characterize the strength of each solvation interaction. The system constants are defined as: *e*, the ability of the stationary phase to interact with analytes by electron lone pair interactions; *s*, a measure of the dipolarity/polarizability of the stationary phase; *a,* the hydrogen bond basicity of the IL stationary phase; *b*, the hydrogen bond acidity of the IL stationary phase; and *l* describes the dispersion forces/cavity formation of the IL. The system constants of all eight MCILs at 50 °C, 80 °C, and 110 °C are listed in Table 2. For the majority of the MCILs studied, the system constants exhibit a smooth decrease as the column temperature is increased. The multiple linear regression fits are statistically sound, as represented by the Fisher coefficients, which range from 400 to 696.

Effect of metal center on system constants

Since ILs **1–8** possess the same $[P_{66614}^{+}]$ cation, the variation in system constants can be attributed to the different counteranions. Among ILs **1–6,** the Dy(III)-based MCIL (IL **4**) possessed the highest dipolarity/polarizability (s = 1.74 at 80 °C), whereas the Nd(III)-based MCIL (IL **6**) exhibited the lowest dipolarity/polarizability value (s = 1.17 at 80 °C). The Mn(II)-based MCIL (IL **3**) exhibited by far the highest hydrogen bond basicity (a = 2.34 at 80 °C) among the six MCILs containing the hfacac chelating ligands. Conversely, the Ni(II)-based MCIL (IL **1**) possessed the lowest hydrogen bond basicity (a = 0.57) at 80 °C (see Table 2). In the case of the hydrogen bond acidity (b term) for ILs **1**–**6**, all values were positive with the Nd(III)-based MCIL (IL **6**) producing a hydrogen bond acidity (b = 0.90 at 80 °C) nearly five times higher than that of the Co(II)-based MCIL (b = 0.20 at 80 °C). ILs **1**–**6** were observed to exhibit similar dispersive type interactions and can be regarded as moderately cohesive stationary phases. The transition metal based MCILs (ILs **1**–**3**) possess different molar ratios of metal center and chelating ligand than the rare-earth metal based MCILs (ILs **4**–**6**). However, no distinct trends in system constants can be observed based on the molar ratio of metal center and chelating ligand.

Effect of chelating ligand on system constants

To examine the effect of the chelating ligand on the system constants, two MCILs (IL **7** and IL **8**) were selected to compare with ILs **1**–**6**. IL **7** contains the tfmphacac chelating ligand whereas IL **8** possesses the $[MnCl_4^{2-}]$ anion and does not

Table 2 System constants of the studied metal-containing ionic liquids obtained using the solvation parameter model

Stationary phase/temperature (°C)	System constants								
	c	e	s	a	b	l	n [a]	R^2 [a]	F [a]
IL **1** Trihexyl(tetradecyl)phosphonium tris(hexafluoroacetylaceto)nickelate(II)									
50	-3.09	-0.59	1.79	0.91	0.49	0.79	36	0.99	440
	(0.09)[b]	(0.08)	(0.10)	(0.10)	(0.13)	(0.02)			
80	-2.96	-0.56	1.63	0.57	0.28	0.60	37	0.99	451
	(0.08)	(0.07)	(0.09)	(0.09)	(0.11)	(0.02)			
110	-3.09	-0.43	1.48	0.29	0.26	0.57	33	0.99	486
	(0.07)	(0.05)	(0.07)	(0.06)	(0.09)	(0.02)			
IL **2** Trihexyl(tetradecyl)phosphonium tris(hexafluoroacetylaceto)cobaltate(II)									
50	-2.81	-0.56	1.61	1.62	0.28	0.77	30	0.99	427
	(0.09)	(0.08)	(0.11)	(0.14)	(0.14)	(0.02)			
80	-2.86	-0.47	1.49	1.17	0.20	0.66	34	0.99	617
	(0.07)	(0.06)	(0.08)	(0.10)	(0.11)	(0.01)			
110	-2.68	-0.34	1.26	0.81	0.14	0.54	31	0.98	411
	(0.07)	(0.05)	(0.07)	(0.09)	(0.10)	(0.01)			
IL **3** Trihexyl(tetradecyl)phosphonium tris(hexafluoroacetylaceto)manganate(II)									
50	-3.18	-0.46	1.51	2.66	0.89	0.82	31	0.99	467
	(0.10)	(0.09)	(0.11)	(0.15)	(0.15)	(0.03)			
80	-2.97	-0.40	1.33	2.34	0.51	0.69	31	0.99	633
	(0.07)	(0.06)	(0.08)	(0.10)	(0.11)	(0.02)			
110	-3.03	-0.38	1.33	1.75	0.25	0.60	26	0.99	463
	(0.09)	(0.07)	(0.10)	(0.09)	(0.14)	(0.02)			
IL **4** Trihexyl(tetradecyl)phosphonium tetrakis(hexafluoroacetylaceto)dysprosate(III)									
50	-2.95	-0.68	1.86	1.82	0.68	0.77	30	0.99	406
	(0.09)	(0.09)	(0.13)	(0.20)	(0.18)	(0.02)			
80	-2.85	-0.57	1.74	1.41	0.50	0.65	30	0.99	558
	(0.07)	(0.07)	(0.11)	(0.16)	(0.14)	(0.02)			
110	-2.88	-0.43	1.67	1.38	0.38	0.52	25	0.99	452
	(0.08)	(0.07)	(0.08)	(0.09)	(0.12)	(0.02)			
IL **5** Trihexyl(tetradecyl)phosphonium tetrakis(hexafluoroacetylaceto)gadolinate(III)									
50	-2.98	-0.64	1.86	1.78	0.70	0.76	34	0.99	493
	(0.09)	(0.08)	(0.11)	(0.14)	(0.14)	(0.02)			
80	-3.01	-0.53	1.67	1.16	0.61	0.65	36	0.99	583
	(0.07)	(0.06)	(0.09)	(0.11)	(0.12)	(0.02)			
110	-3.04	-0.45	1.51	0.86	0.48	0.56	34	0.99	493
	(0.07)	(0.06)	(0.08)	(0.09)	(0.10)	(0.01)			
IL **6** Trihexyl(tetradecyl)phosphonium tetrakis(hexafluoroacetylaceto)neodymate(III)									
50	-2.73	-0.40	1.27	1.50	1.15	0.75	31	0.99	444
	(0.07)	(0.06)	(0.08)	(0.10)	(0.11)	(0.02)			
80	-2.69	-0.40	1.17	1.12	0.90	0.62	29	0.99	474
	(0.08)	(0.07)	(0.08)	(0.08)	(0.11)	(0.02)			
110	-2.73	-0.35	1.04	0.81	0.80	0.55	26	0.99	403
	(0.07)	(0.06)	(0.08)	(0.10)	(0.11)	(0.02)			
IL **7** Trihexyl(tetradecyl)phosphonium tris(trifluoromethylphenylacetylaceto)manganate(II)									
50	-3.09	-0.43	1.66	2.91	-0.25	0.82	36	0.99	463
	(0.09)	(0.08)	(0.10)	(0.14)	(0.13)	(0.02)			
80	-3.04	-0.35	1.51	2.19	-0.28	0.70	34	0.99	400
	(0.09)	(0.07)	(0.08)	(0.11)	(0.11)	(0.02)			
110	-3.05	-0.23	1.27	1.38	-0.08	0.60	31	0.99	507
	(0.07)	(0.05)	(0.07)	(0.10)	(0.10)	(0.02)			
IL **8** Trihexyl(tetradecyl)phosphonium tetrachloromanganate(II)									
50	-3.00	-0.29	1.94	3.88	-0.73	0.76	31	0.99	565
	(0.09)	(0.08)	(0.11)	(0.14)	(0.14)	(0.02)			
80	-2.96	-0.18	1.75	3.30	-0.71	0.63	33	0.99	614
	(0.07)	(0.06)	(0.09)	(0.11)	(0.12)	(0.02)			
110	-3.11	-0.14	1.63	2.76	-0.66	0.56	32	0.99	696
	(0.07)	(0.06)	(0.08)	(0.09)	(0.10)	(0.01)			

[a] Note: *n*, number of probe analytes subjected to multiple linear regression analysis; R^2 , correlation coefficient; *F*, Fisher coefficients

[b] The values in parentheses represent the standard deviation of each system constant

contain any chelating ligand (see Fig. 1). ILs **3**, **7**, and **8** are all Mn(II)-based MCILs (see Fig. 1 and Table 2). MCILs with hfacac ligands (ILs **1**–**6**) possess positive values for the hydrogen bond acidity (see Table 2). However, IL **8** exhibits a large negative value (b = –0.71 at 80 °C). This result seems to indicate that the hydrogen bond acidity of MCILs can be strongly influenced by the chelating ligand or the absence of a ligand. The system constants for [$P_{66614}{}^{+}$]-based ILs with various anions (e.g., chloride, bis[(trifluoromethyl)sulfonyl]imide, triflate, and tetrafluoroborate) were previously reported [39] and are listed in Table S2 of ESM. The hydrogen bond acidity (b term) of all reported phosphonium ILs were negative, since there are no acidic hydrogens that can act as hydrogen-bond donors. In addition, the value of hydrogen bond acidity was also negative or close to zero for the [$P_{66614}{}^{+}$] tetrachloroferrate IL, which possesses structural similarity to IL **8** [40]. Interestingly, IL **7** containing the tfmphacac ligands also possesses a negative hydrogen bond acidity value (see Table 2), which is opposite to IL **3** with the hfacac ligand, despite the structural similarities. This result indicates that

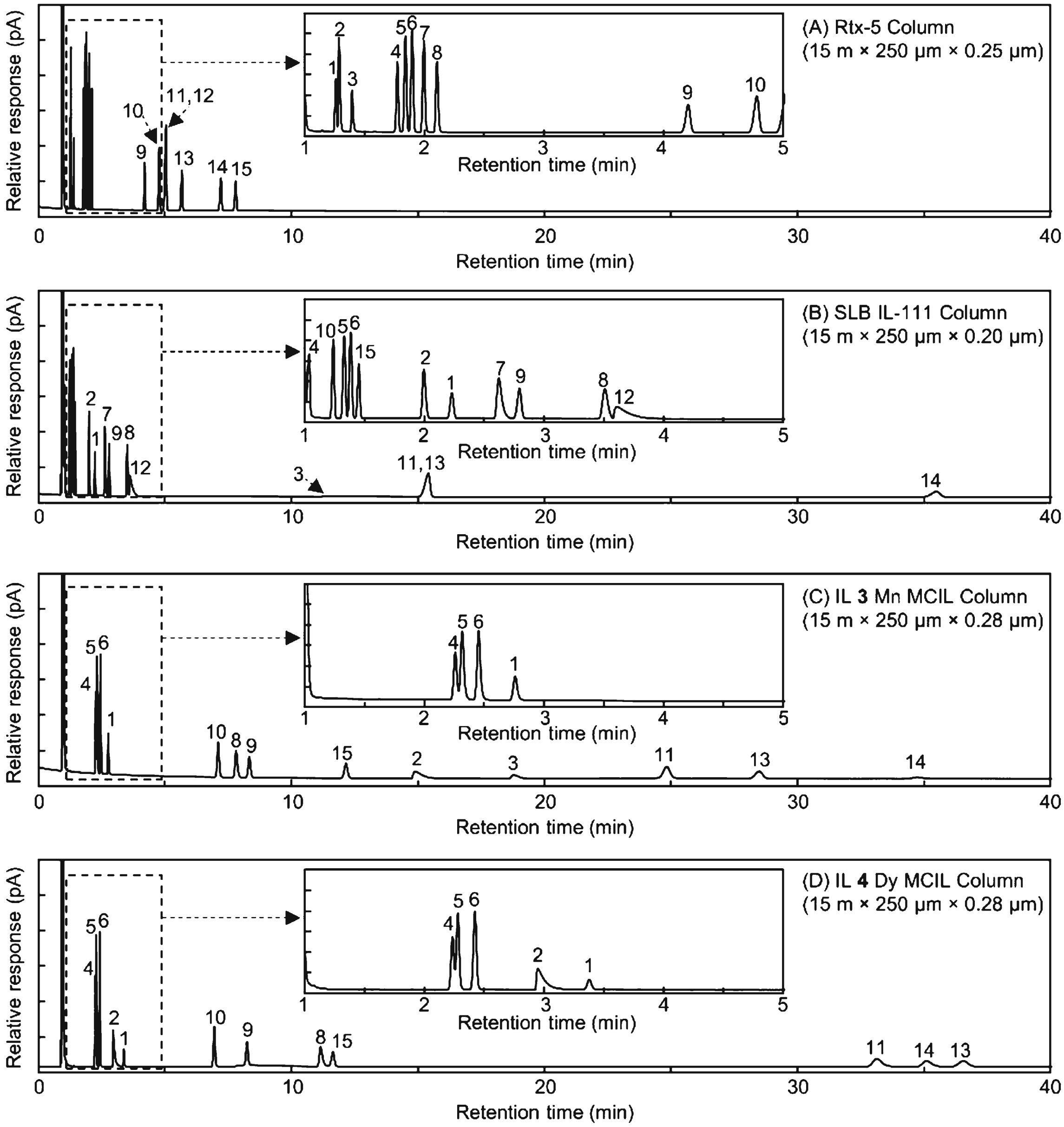

Fig. 2 Chromatographic separation of a mixture containing 15 analytes on different columns: **(A)** Restek Rtx-5 column, **(B)** Supelco SLB IL-111 column, **(C)** IL **3** Mn(II)-based MCIL column, and **(D)** IL **4** Dy(III)-based MCIL column. Analytes: 1, nitropropane, 2, pyridine, 3, *N,N*-dimethylformamide, 4, 1-chlorohexane, 5, ethylbenzene, 6, *p*-xylene, 7, cyclohexanol, 8, cyclohexanone, 9, 1,2-dichlorobenzene, 10, 1-chlorooctane, 11, acetophenone, 12, 1-octanol, 13, nitrobenzene, 14, 2-chloroaniline, 15, 1-bromooctane. Separation conditions: flow rate, 1 mL/min, isothermal separation at 80 °C. The analytes cyclohexanol and 1-octanol eluted from the Mn(II) and Dy(III)-based MCIL columns as a broad and tailing peak. *N,N*-dimethylformamide eluted from the Dy(III)-based MCIL column after 40 min

the phenyl groups may influence the proton donating capability of the tfmphacac ligand.

Separation of analyte mixtures using MCIL-based GC columns

A mixture of 15 analytes was subjected to isothermal separation (80 °C) on four different columns containing the same column length (15 m), including the commercial Rtx-5 and SLB IL-111 columns and two MCIL-based columns. The Mn(II)- and Dy(III)-based MCILs were selected as representative stationary phases because of the highest hydrogen bond basicity and dipolarity/polarizability, respectively, among the six MCILs with hfacac ligands. As shown in the Fig. 2A, the separation was performed on the Rtx-5 column, which is among the most widely used PDMS-based GC columns. All analytes were separated except for acetophenone and 1-octanol, which possess similar boiling points (202 °C and 195 °C). Since the commercial SLB IL-111 column is much more polar than the Rtx-5 column, the observed retention behavior of these analytes on this column is different (see Fig. 2B). Analytes containing nitro, amine, or hydroxy groups were strongly retained by the SLB IL-111 column compared with the Rtx-5 column. Acetophenone and nitrobenzene were observed to co-elute on the SLB IL-111 column, whereas *N,N*-dimethylformamide (DMF) exhibited a strong tailing peak starting at 11.1 min (see Fig. 2B).

As shown in Fig. 2C and D, the MCIL-based columns exhibited very different retention characteristics compared with the Rtx-5 or SLB IL-111 columns. A consistent retention order among analytes, including 1-chlorohexane, ethylbenzene, *p*-xylene, and 2-chloroaniline can be observed on all four columns. However, most of the remaining analytes such as cyclohexanone, 1,2-dichlorobenzene, 1-chlorooctane, and nitrobenzene were more strongly retained on the MCIL-based columns. Furthermore, the retention order of certain analyte pairs was reversed depending on the incorporated metal center. It has been previously reported that the retention of analytes can be modified by incorporating metal-containing salts [19, 29]. When MCILs with different metal centers were employed as the GC stationary phase, interesting chromatographic retention characteristics could be observed. As shown in Fig. 2C, pyridine eluted after nitropropane, 1-chlorooctane, and 1-bromooctane on the Mn(II)-based MCIL column (IL **3**). However, pyridine eluted before these three analytes on the Dy(III)-based MCIL column (IL **4**). The retention order of cyclohexanone and 1,2-dichlorobenzene was reversed on the two MCIL-based columns. Therefore, the separation selectivities offered by the MCIL-based columns are strongly affected by the metal center incorporated in the MCIL.

Effect of metal centers and chelating ligands on the separation selectivity for selected analytes

Retention factors of 15 selected analytes on the eight 5-m columns containing different MCIL-based stationary phases are listed in Table 3. The retention factors of 1-chlorohexane, ethylbenzene, *p*-xylene, 1,2-dichlorobenzene, 1-chlorooctane, and 1-bromooctane were similar among all eight MCIL-based columns. The retention factor of pyridine on the Ni(II)-based MCIL column (IL **1**) was

Table 3 Comparison of retention factors of selected analytes on eight different MCIL-based stationary phases with varying metal centers and chelating ligands at 80 °C (ILs **1**–**7**). IL **8** does not contain a metal chelating ligand. See structures of MCILs in Fig. 1

	Probe molecule	IL **1** Ni	IL **2** Co	IL **3** Mn	IL **4** Dy	IL **5** Gd	IL **6** Nd	IL **7** Mn	IL **8** Mn
1	1-Nitropropane	2.2	2.1	2.0	3.2	2.3	2.2	1.4	1.5
2	Pyridine	119.8	16.9	25.9	3.7	2.2	4.7	1.3	9.7
3	*N,N*-Dimethylformamide	17.3	12.0	31.0	64.6	43.2	94.2	5.3	5.4
4	1-Chlorohexane	1.2	1.4	1.4	1.7	1.2	1.4	1.2	1.0
5	Ethyl benzene	1.2	1.4	1.3	1.7	1.2	1.4	1.3	1.3
6	*p*-Xylene	1.3	1.5	1.5	1.9	1.3	1.5	1.4	1.3
7	Cyclohexanol	2.5	4.0	15.2	7.9	5.0	8.3	5.3	7.0
8	Cyclohexanone	8.5	7.5	7.7	13.5	9.7	9.8	4.2	3.0
9	1,2-Dichlorobenzene	6.6	7.2	7.1	8.5	6.4	6.7	8.4	10.2
10	1-Chlorooctane	5.7	6.3	6.0	7.2	5.2	5.7	5.7	4.2
11	Acetophenone	28.7	25.8	26.2	41.7	30.3	31.1	19.9	15.7
12	1-Octanol	11.1	18.7	123.9	44.7	22.6	47.6	24.6	30.3
13	Nitrobenzene	31.1	29.4	28.6	43.8	32.5	29.9	27.6	27.7
14	2-Chloroaniline	24.3	29.8	30.5	32.2	27.7	27.3	46.9	144.7
15	1-Bromooctane	10.0	11.4	10.8	12.7	9.0	10.0	10.9	8.2

Table 4 Effect of metal center and chelating ligand of MCILs on the selectivity of chosen solute pairs at 80 °C

Solute pair[b]	IL **1** Ni	IL **2** Co	IL **3** Mn	IL **4** Dy	IL **5** Gd	IL **6** Nd	IL **7** Mn	IL **8** Mn
Naphthalene/*p*-xylene	18.9	16.8	17.9	18.3	18.9	16.7	18.8	22.4
1-Octanol/1-butanol	23.9	23.2	40.0	26.8	21.7	26.0	24.1	18.3
1-Butanol/*p*-xylene	0.4[a]	0.5[a]	2.1	0.9[a]	0.8[a]	1.2	0.7[a]	1.3
Naphthalene/benzonitrile	1.5	1.7	1.7	1.4	1.4	1.6	2.0	2.4
1-Bromooctane/benzene	39.1	34.9	38.8	31.6	31.7	25.1	40.2	50.2
1-Nitropropane/1-pentanol	2.0	1.1	0.2[a]	0.9[a]	1.0	0.5[a]	0.6[a]	0.5[a]
Butyraldehyde/benzene	1.9	1.4	1.5	1.9	1.9	1.6	1.7	0.5[a]
Cyclohexanone/cyclohexanol	3.4	1.9	0.5[a]	1.7	1.9	1.2	0.8[a]	0.4[a]
Methyl caproate/1-butanol	9.4	5.0	1.3	3.8	4.4	2.8	2.4	1.0
Octylaldehyde/1-pentanol	9.7	5.3	1.2	4.1	4.6	2.6	2.6	1.3
Pentanone/1-pentanol	1.4	0.7[a]	0.2[a]	0.7[a]	0.7[a]	0.4[a]	0.3[a]	0.2[a]
Benzyl alcohol/naphthalene	0.5[a]	0.4[a]	0.4[a]	0.4[a]	1.3	1.8	2.1	2.4
2-Chloroaniline/naphthalene	1.0	1.2	1.2	0.9[a]	1.1	1.1	1.8	5.0
Pyridine/naphthalene	4.8	0.7[a]	1.0	0.1[a]	0.1[a]	0.2[a]	0.1[a]	0.3[a]

[a] By the definition of selectivity, the value should not be smaller than unity. However, in some cases, the solute pairs exhibited reversed elution order, which makes it impossible to report selectivities greater than one for all MCIL-based columns

[b] Additional solutes from those listed in Table 3 were used to make the selectivity comparisons

119.8, which is an order of magnitude higher than all other MCIL-based columns. Cyclohexanol and 1-octanol exhibited the highest retention on IL **3** (Mn(II)-based MCIL) and lowest retention on the Ni(II)-based MCIL column (IL **1**). The Dy(III)-based MCIL exhibited unique selectivity toward analytes with carbonyl and nitro groups (e.g., 1-nitropropane, nitrobenzene, cyclohexanone, and acetophenone), as the retention factor of these analytes are among the highest on this column. *N,N*-dimethylformamide was strongly retained on the IL **6** (Nd(III)) and IL **4** (Dy(III)) MCIL-based columns. These results further demonstrate the unique separation selectivities offered by the different metal centers. A comparison of IL **3** and IL **8** shows that the [$MnCl_4^{2-}$] anion provides lower retention factors of alcohols, while exhibiting significantly higher retention of 2-chloroaniline, but lower retention of pyridine and *N,N*-dimethylformamide.

Interesting separation behavior can be further illustrated by examining the selectivity of solute pairs. As shown in Table 4, the selectivities of selected analyte pairs were notably affected by the choice of MCILs with different metal centers and chelating ligands. The retention order of butanol/*p*-xylene, 1-nitropropane/1-pentanol, and pyridine/naphthalene were reversed on different MCIL-based columns. The Ni(II)-based MCIL (IL **1**) showed strong selectivity toward pentanone, 1-nitropropane, and pyridine compared with all the other MCILs. Alcohols (e.g., 1-butanol, 1-pentanol, and cyclohexanol) were more strongly retained on the Mn(II)-based MCIL column (IL **3**). Interestingly, the retention order of cyclohexanone and cyclohexanol was the same on all three Mn(II)-based MCILs (ILs **3**, **7**, and **8**), but were reversed on all other MCIL stationary phases. The selectivity between 2-chloroaniline and naphthalene was the highest on the IL **8** column (possessing the [$MnCl_4^{2-}$] anion). The IL **8** stationary phase also showed reversed retention order for butyraldehyde and benzene compared with all the other MCIL-based columns.

Conclusions

In this study, the solvation properties for a total of eight MCILs were investigated for the first time using the Abraham solvation parameter model. Different solvation properties of MCILs were observed depending on the metal centers and chelating ligands. The Mn(II)-based MCIL (IL **3**) possessed the highest hydrogen bond basicity, whereas the Dy(III)-based MCIL (IL **4**) exhibited the highest dipolarity/polarizability. A separation of a test mixture of analytes with various functional groups was compared using two MCIL-based columns, a commercial PDMS column, and a commercial IL-based column. The retention factors of analytes such as 1-chlorohexane, ethylbenzene, and *p*-xylene remained consistent on four columns. However, the retention factors of other analytes were vastly different on the MCIL-based columns compared with the commercial PDMS and IL-based columns. The system constants obtained for MCILs in this study provide insight for the future design of solute-specific GC stationary phases using room temperature ILs with various metal centers. Furthermore, this study describes the type and magnitude of intermolecular interactions between different analyte groups and MCILs possessing transition and rare earth metals. This enhanced understanding of solvation characteristics can be exploited in future analytical and bioanalytical applications involving these very unique and interesting materials.

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Compliance with ethical standards

Conflicts of interest The authors declare no conflicts of interest.

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