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Partition Behavior of Chlorophenols and Nitrophenols between Hydrophobic Ionic Liquids and Water

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S *Supporting Information*

ABSTRACT: The partition of various chlorinated and nitrated phenols between hydrophobic ionic liquids and aqueous solutions of different pH values was investigated at 298.2 K. Ionic liquids used are 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([BMIm][NTf$_2$]), 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide ([BMPyr][NTf$_2$]), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm][PF$_6$]), 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl)amide ([OMIm][NTf$_2$]), and 1-methyl-3-octylimidazolium tetrafluoroborate ([OMIm][BF$_4$]). Partition coefficients ($P_{\mathrm{IL/W}}$) of the electrically neutral form (ArOH) and the dissociated anionic form (ArO$^-$) were determined. For a given phenol, the $P_{\mathrm{IL/W}}$(ArOH) value in the ionic liquid/water system is generally independent of the kind of the ionic liquid and smaller than that in the 1-octanol/water system. Exceptionally, the $P_{\mathrm{IL/W}}$(ArOH) value in the [OMIm][BF$_4$]/water system is larger than those in the other ionic liquid/water systems and comparable to or greater than that in the 1-octanol/water system. The interaction energies of the ionic liquids with the phenolic hydroxyl group were evaluated. It is shown from the dependence of the interaction energy on the acid-dissociation constant of the phenol that the ionic liquid behaves as both an electron-pair donor and an acceptor like water rather than 1-octanol. The $P_{\mathrm{IL/W}}$(ArO$^-$) value depends largely on the kind of ionic liquid, showing that an ionic liquid formed by a more hydrophobic cation and a more hydrophilic anion has a higher extractability for the phenolate anions. The substituent effects on $P_{\mathrm{IL/W}}$(ArO$^-$) are also different from those on $P_{\mathrm{IL/W}}$(ArOH).

INTRODUCTION

Liquid−liquid extraction is a simple and powerful technique for the purposes of recovery, removal, or concentration of organic compounds in aqueous solutions. However, the organic solvents used for the liquid−liquid extraction are generally volatile, flammable, and harmful for the environment. To use ionic liquids as replacements for conventional organic solvents is attracting increasing attention because the ionic liquids are almost nonvolatile and their flammability and harmfulness are low.[1−3] The authors recently reported the partition coefficients of benzene and its various derivatives between hydrophobic ionic liquids and water.[4] The partition behavior of benzene and its alkylated and chlorinated derivatives in the ionic liquid/water two-phase systems could be accounted for by the regular solution theory. This means that the ionic liquids behave like normal molecular solvents, where an ion pair corresponds to a solvent molecule. For these non- or less-polar solutes, the ionic liquids studied have similar extraction properties to 1-octanol, because the solubility parameters of the ionic liquids, particularly bis(trifluoromethanesulfonyl)amide-based ionic liquids, are close to that of 1-octanol. On the other hand, the partitioning of the benzene derivatives having polar substituents in the ionic liquid/water systems is largely influenced by the specific solute−solvent interactions in the ionic liquid phase as well as in water. The strength of the specific interaction between each substituent and solvent pair was evaluated by determining the contribution of the substituent to the standard Gibbs free energy of transfer from heptane to the solvent. It was shown that each ionic liquid has the properties as both an electron donor and an acceptor.

In this study, we have investigated the partition behavior of chlorinated and nitrated phenols between several ionic liquids and water. The phenolic hydroxyl group is one of the substituents having strong interaction with ionic liquids.[4] A purpose of this study is to evaluate the substituent effects of −Cl and −NO$_2$ on the partition coefficients of phenols and the interaction between the phenolic hydroxyl group and ionic liquids. Another purpose is to clarify the partition behavior of these environmentally important compounds. Although several studies have been performed on the extraction of phenols with ionic liquids,[5−10] the data of the partition coefficients (as equilibrium constants) reported are limited.

The ionic liquids used in this study are five kinds of hydrophobic ones: 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([BMIm][NTf$_2$]), 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide ([BMPyr][NTf$_2$]), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm][PF$_6$]), 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl)amide ([OMIm][NTf$_2$]), and 1-methyl-3-octylimidazolium tetrafluoroborate ([OMIm][BF$_4$]). The partitioning solutes are 14 kinds of phenols: phenol, 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2,3-dichlorophenol, 3,5-dichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol, 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, 2,6-dinitrophenol, and 2,4,6-trinitrophenol.

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EXPERIMENTAL SECTION

Chemicals. [BMIm][NTf$_2$], [BMPyr][NTf$_2$], [BMIm][PF$_6$], and heptane were the same as used previously.[4] [OMIm][NTf$_2$] (Merck, Darmstadt, Germany; high purity grade) and [OMIm][BF$_4$] (Merck; for synthesis grade) were washed three times with deionized water. 3,5-Dichlorophenol (Wako Pure Chemical Industries, Osaka, Japan; extra-pure reagent grade) was purified by vacuum sublimation at 308 K. Water was distilled and further deionized with a Milli-Q Labo system (Millipore, Billerica, MA). Other reagents were of guaranteed reagent grade and used without further purification.

For the ionic liquids saturated with water at (298.2 ± 0.2) K, the densities and water content were measured with a DMA35n oscillating U-tube density meter (Anton Paar, Graz, Austria) and a AQ-7 Karl Fischer coulometric titrator (Hiranuma Sangyo, Mito, Japan), respectively. The densities of water-saturated [OMIm][NTf$_2$] and [OMIm][BF$_4$] determined from five measurements for each were $(1.3276 \pm 0.0002)\ \mathrm{g \cdot cm^{-3}}$ and $(1.0832 \pm 0.0002)\ \mathrm{g \cdot cm^{-3}}$, respectively; the densities for the other ionic liquids were reported previously.[4] Values of the mass fraction water content from four measurements for each were 0.0135 ± 0.0005, 0.0114 ± 0.0002, 0.0230 ± 0.0003, 0.0093 ± 0.0001, and 0.11 ± 0.02 for [BMIm][NTf$_2$], [BMPyr][NTf$_2$], [BMIm][PF$_6$], [OMIm][NTf$_2$], and [OMIm][BF$_4$], respectively. These values are in good agreement with the literature ones determined at 298.15 K: 0.01463 for [BMIm][NTf$_2$],[11] 0.0113 for [BMPyr][NTf$_2$],[12] 0.0231 for [BMIm][PF$_6$],[12] 0.008628 for [OMIm][NTf$_2$],[11] and 0.0108 (at 295 K) for [OMIm][BF$_4$].[13]

Apparatus. Chlorinated or nitrated phenols in aqueous solutions were determined by micellar electrokinetic chromatography (MEKC). The apparatus used was a Photal CAPI-3200 capillary electrophoresis system (Otsuka Electronics, Osaka, Japan) equipped with a fused-silica capillary tube (50 μm inner diameter (i.d.), 375 μm outer diameter (o.d.), 62 cm total length, 50 cm effective length) and a photodiode array detector. The pH measurements were conducted with a Docu-pH+ meter (Sartorius AG, Gottingen, Germany) equipped with a glass electrode.

Partition Experiments. A water-saturated ionic liquid and an ionic liquid-saturated water were placed in a stoppered glass tube, together with a few kinds of phenols where the concentration was $(2 \cdot 10^{-4}$ to $2 \cdot 10^{-3})\ \mathrm{mol \cdot dm^{-3}}$ for each against the volume of the aqueous phase. Here, the volume of the viscous ionic liquid phase was accurately evaluated from the mass by using the density, and the volume ratio of the ionic liquid phase to the aqueous phase was adjusted to 1/10. The pH of the aqueous solution was preadjusted to 1.7 to 12.3 using aqueous solutions of HCl, NaH_2PO_4, Na_2HPO_4, and NaOH, where the ionic strength of the aqueous phase was always less than $0.02\ \mathrm{mol \cdot dm^{-3}}$. The two-phase mixture in the glass tube was equilibrated by stirring with a magnetic stirrer for 1 h at (298.2 ± 0.2) K. After the two phases were separated by centrifugation, the concentrations of the phenols in the aqueous phase were measured by MEKC as follows. The capillary tube was filled with pH 8.6 buffer containing $0.050\ \mathrm{mol \cdot dm^{-3}}$ sodium dodecyl sulfate, $0.010\ \mathrm{mol \cdot dm^{-3}}$ NaH_2PO_4, and $0.010\ \mathrm{mol \cdot dm^{-3}}$ $Na_2B_4O_7$, and it was thermocontrolled at 303 K. The sample solution containing the phenols was injected from the end of the capillary by siphoning at a height difference of 25 mm for 30 s, where benzyl alcohol $(5 \cdot 10^{-4}\ \mathrm{mol \cdot dm^{-3}})$ was added to the sample solution as an internal standard. The separation was conducted by applying a constant voltage of 20 kV as a positive potential to the injection end, and the solutes were detected by UV-light absorption at 200 nm. The concentrations of the phenols in the ionic liquid phase were calculated based on the mass balance or directly measured by MEKC after back extraction of them from the ionic liquid phase to $0.1\ \mathrm{mol \cdot dm^{-3}}$ aqueous NaOH solution. The ratio of the molar concentration in the ionic liquid phase to that in the aqueous phase was calculated as the distribution ratio (D). The pH of the aqueous phase at equilibrium was measured with a pH meter. The uncertainties for log D and pH were generally within 0.02.

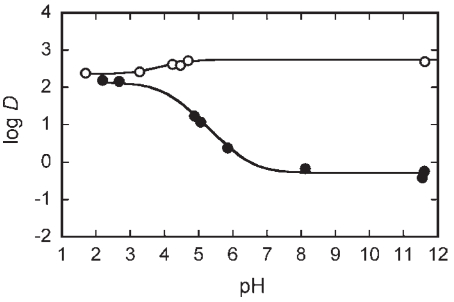

Figure 1. Distribution ratio of 2,4-dinitrophenol in the [BMIm][NTf$_2$]/water (filled circles) and [OMIm][BF$_4$]/water (open circles) systems as a function of pH of the aqueous phase. The regression curves are based on eq 2.

Partition coefficients of 2,4-dinitrophenol and 2,6-dinitrophenol in the heptane/water system were also determined in a similar manner to the distribution ratios in the ionic liquid/water systems; a $0.10\ \mathrm{mol \cdot dm^{-3}}$ aqueous HCl solution was used as the aqueous phase to suppress the dissociation of the phenols.

RESULTS

The distribution ratios of the phenols measured at different pH values of the aqueous phase are listed in the Supporting Information. In Figure 1, the dependence of log D on the aqueous pH is shown for the partition of 2,4-dinitrophenol in the [BMIm][NTf$_2$]/water and [OMIm][BF$_4$]/water systems. Under the conditions where the pH is lower than the acid-dissociation index in water ($\mathrm{p}K_a = 4.07$[14]), the distribution ratio is nearly independent of the pH value. The log D value decreases or increases with an increase in the aqueous pH when the pH is near to the pK_a value. The pH dependence of log D, however, becomes small again in the higher pH region. These results indicate that the phenol can be partitioned not only in the neutral form but also in the anionic form.

The distribution ratio of a phenol (ArOH) can be expressed as follows:

$$D = ([\mathrm{ArOH}]_{\mathrm{IL}} + [\mathrm{ArO^-}]_{\mathrm{IL}})/([\mathrm{ArOH}]_{\mathrm{W}} + [\mathrm{ArO^-}]_{\mathrm{W}}) \tag{1}$$

Here, subscripts IL and W denote the ionic liquid phase and the aqueous phase, respectively. This equation is transformed into eq 2 by introducing the partition coefficient of the neutral form ($P_{\mathrm{IL/W}}(\mathrm{ArOH})$), that of the anionic form ($P_{\mathrm{IL/W}}(\mathrm{ArO^-})$), and the acid-dissociation constant (K_a):

$$D = P_{\mathrm{IL/W}}(\mathrm{ArOH})/(1 + K_a/[\mathrm{H^+}]_{\mathrm{W}}) + P_{\mathrm{IL/W}}(\mathrm{ArO^-})/([\mathrm{H^+}]_{\mathrm{W}}/K_a + 1) \tag{2}$$

Literature values[14−20] of pK_a for all of the phenols are listed in Table 1. The $P_{\mathrm{IL/W}}(\mathrm{ArOH})$ and $P_{\mathrm{IL/W}}(\mathrm{ArO^-})$ values were determined by least-squares fitting of eq 2 to the experimental

Table 1. Partition Coefficients[a] of Electrically Neutral Phenols in Various Solvent (S)/Water (W) Systems at 298.2 K

			log $P_{S/W}$(ArOH)						
	solute	pK_a	S = [BMIm][NTf$_2$]	[BMPyr][NTf$_2$]	[BMIm][PF$_6$]	[OMIm][NTf$_2$]	[OMIm][BF$_4$]	1-octanol	heptane
1	phenol	9.994^{b}	$1.333^{i,j}$	$1.369^{i,j}$	$1.218^{i,j}$	$1.24^{j} \pm 0.01$	1.68 ± 0.01	1.46^{k}	-1.90^{n}
2	2-chlorophenol	8.25^{c}	1.90 ± 0.01	1.96 ± 0.01	1.80 ± 0.01		2.17 ± 0.02	2.15^{k}	0.79^{o}
3	3-chlorophenol	8.80^{c}	1.923 ± 0.006	1.94 ± 0.02	1.80 ± 0.03			2.50^{k}	-0.07^{p}
4	4-chlorophenol	9.16^{c}	1.90 ± 0.02	1.92 ± 0.02	1.78 ± 0.03		2.32 ± 0.03	2.39^{k}	-0.11^{p}
5	2,3-dichlorophenol	7.44^{d}	2.41 ± 0.02	2.40 ± 0.04	2.30 ± 0.02		2.96 ± 0.04	3.15^{l}	1.33^{o}
6	3,5-dichlorophenol	7.92^{d}	2.39 ± 0.01	2.38 ± 0.03	2.23 ± 0.02		2.91 ± 0.03	3.56^{l}	0.42^{o}
7	2,4,6-trichlorophenol	6.21^{e}	2.63 ± 0.07		2.30 ± 0.06			3.75^{l}	0.90^{m} (hexane)
8	pentachlorophenol	4.90^{e}	3.63 ± 0.04		3.13 ± 0.04			5.04^{l}	2.99^{o}
9	2-nitrophenol	7.22^{f}	2.06 ± 0.03	$1.95^{i} \pm 0.03$	1.96 ± 0.05	1.98 ± 0.07	2.16 ± 0.02	1.79^{k}	1.40^{q}
10	3-nitrophenol	8.35^{f}	$1.60^{i} \pm 0.01$	$1.56^{i} \pm 0.01$	1.56 ± 0.02	$1.55^{i} \pm 0.05$	2.18 ± 0.02	2.00^{k}	-1.40^{q}
11	4-nitrophenol	7.14^{f}	$1.60^{i} \pm 0.02$	$1.55^{i} \pm 0.02$	1.59 ± 0.04			1.96^{k}	-2.00^{q}
12	2,4-dinitrophenol	4.07^{g}	2.13 ± 0.04	2.09 ± 0.04	2.14 ± 0.03	2.13 ± 0.10	2.36 ± 0.05	1.51^{m}	0.422 ± 0.001
13	2,6-dinitrophenol	3.73^{g}	2.13 ± 0.03	2.11 ± 0.04	2.27 ± 0.03			1.18^{m}	0.125 ± 0.002
14	2,4,6-trinitrophenol	0.33^{h}	2.38 ± 0.05	2.41 ± 0.04	2.45 ± 0.33			2.03^{m}	

[a] Uncertainties are the standard errors from least-squares fits. [b] Reference 15. [c] Reference 16. [d] Reference 17. [e] Reference 18. [f] Reference 19. [g] Reference 14. [h] Reference 20. [i] Reference 4. [j] Calculated neglecting the extraction of ArO^-. [k] Reference 21. [l] Reference 22 (at 293.2 K). [m] Reference 23. [n] Reference 24. [o] Reference 25. [p] Reference 26. [q] Reference 27.

Table 2. Partition Coefficients[a] of Anionic Phenolates in Ionic Liquid (IL)/Water (W) Systems at 298.2 K

		log $P_{IL/W}$(ArO^-)				
	solute	IL = [BMIm][NTf$_2$]	[BMPyr][NTf$_2$]	[BMIm][PF$_6$]	[OMIm][NTf$_2$]	[OMIm][BF$_4$]
1	phenol					0.27 ± 0.05
2	2-chlorophenol	−1.91 ± 0.20	−1.50 ± 0.10	−1.35 ± 0.03		1.17 ± 0.04
3	3-chlorophenol	−1.29 ± 0.06	−1.51 ± 0.24	−0.33 ± 0.09		
4	4-chlorophenol	−0.81 ± 0.26	−0.67 ± 0.13	−0.54 ± 0.07		1.33 ± 0.10
5	2,3-dichlorophenol	−1.41 ± 0.07	−1.48 ± 0.17	−0.74 ± 0.03		2.06 ± 0.04
6	3,5-dichlorophenol	−1.27 ± 0.09	−1.22 ± 0.21	−0.48 ± 0.05		2.27 ± 0.03
7	2,4,6-trichlorophenol	−0.31 ± 0.14		0.09 ± 0.09		
8	pentachlorophenol	0.91 ± 0.03		1.44 ± 0.03		
9	2-nitrophenol	−0.79 ± 0.28		−0.48 ± 0.11	−0.38 ± 0.08	1.69 ± 0.04
10	3-nitrophenol			−0.90 ± 0.13		1.37 ± 0.03
11	4-nitrophenol			−0.36 ± 0.10		
12	2,4-dinitrophenol	−0.28 ± 0.05	−0.40 ± 0.05	0.32 ± 0.03	0.42 ± 0.04	2.75 ± 0.03
13	2,6-dinitrophenol	−0.28 ± 0.04	−0.48 ± 0.04	0.40 ± 0.02		
14	2,4,6-trinitrophenol	0.911 ± 0.007	0.54 ± 0.01	1.57 ± 0.01	$1.82^{b} \pm 0.02$	$3.76^{b} \pm 0.06$

[a] Uncertainties are the standard errors from least-squares fits. [b] Calculated neglecting the extraction of ArOH.

D and [H^+] data using a KaleidaGraph statistical software package (Synergy Software, Reading, PA), and are summarized in Tables 1 and 2, respectively.

■ DISCUSSION

Partition Coefficients of Electrically Neutral Phenols. The $P_{IL/W}$(ArOH) values in Table 1 clearly show that the partition coefficient in a given ionic liquid/water system increases with an increase in the number of chlorine atoms or nitro groups in the phenol molecule. The substituent effect is greater for the chlorine atom than for the nitro group. In addition, the substituent effect is generally not sensitive to the position of the substituent, except for the result that the 2-nitrophenol has a greater partition coefficient than 3-nitrophenol and 4-nitrophenol.

It is also clear that there are no remarkable differences between the partition coefficients for a given phenol in the [BMIm][NTf$_2$]/water, [BMPyr][NTf$_2$]/water, and [OMIm][NTf$_2$]/water systems. In other words, the differences in the cation structure between these ionic liquids have little influence on the partition coefficients of the phenols. Similarly, the difference in the anion between [BMIm][NTf$_2$] and [BMIm][PF$_6$] has only a small effect on the partition coefficients of the phenols. Exceptionally, the partition coefficient in the [OMIm][BF$_4$]/water system is significantly larger than that in the other ionic liquid/water systems, suggesting that $[BF_4]^-$ has a higher affinity with the phenol than $[NTf_2]^-$ and $[PF_6]^-$.

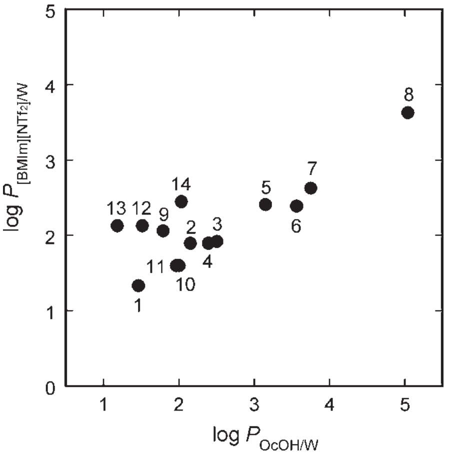

Figure 2. Relationship between the partition coefficients in the [BMIm][NTf_2]/water system and those in the 1-octanol/water system. The numbers of solutes correspond to those in Table 1.

Literature values[21−27] of the partition coefficients in heptane/water and 1-octanol/water systems are also listed in Table 1 for comparison. The partition coefficients in the ionic liquid/water systems are all larger than those in the heptane/water systems. This is mostly attributed to the specific ionic liquid−phenol interactions other than dispersion forces.[4] In Figure 2, the relationship between the partition coefficients in the [BMIm][NTf_2]/water system ($P_{[\mathrm{BMIm}][\mathrm{NTf_2}]/\mathrm{W}}$) and those in the 1-octanol/water system ($P_{\mathrm{OcOH/W}}$) is shown, because the similarity of ionic liquids as extraction solvents to 1-octanol has often been discussed.[1,6,7,28] Actually, a good linear correlation is found for many phenols, except for the phenols possessing at least one nitrogen group at the ortho-position [2-nitrophenol (no. 9), 2,4-dinitrophenol (no. 12), 2,6-dinitrophenol (no. 13), and 2,4,6-trinitrophenol (no. 14)]. The partition coefficients in the [BMIm][NTf_2]/water system are generally smaller than those in the 1-octanol/water system, whereas the partition coefficients of the ortho-nitrated phenols are greater in the [BMIm][NTf_2]/water system than in the 1-octanol/water one. The same is true for the [BMPyr][NTf_2]/water, [BMIm][PF_6]/water, and [OMIm][NTf_2]/water systems. The partition coefficients in the [OMIm][BF_4]/water system are comparable to or greater than those in the 1-octanol/water system.

For quantitative evaluation of the specific interactions between the ionic liquids and the phenols, we considered the partition between ionic liquids and heptane (Hep), because heptane has no specific interaction with the solutes. The $P_{\mathrm{IL/Hep}}$ values can be calculated from the following relation:

$$\log P_{\mathrm{IL/Hep}} = \log P_{\mathrm{IL/W}} - \log P_{\mathrm{Hep/W}} \tag{3}$$

The standard Gibbs free energy of transfer of a phenol (ArOH) from heptane to a solvent S, $\Delta G°_{\mathrm{Hep}\to\mathrm{S}}(\mathrm{ArOH})$, is equal to $-2.303RT \log P_{\mathrm{S/Hep}}(\mathrm{ArOH})$. Therefore, the contribution of a phenolic hydroxyl group to $\Delta G°_{\mathrm{Hep}\to\mathrm{S}}(\mathrm{ArOH})$ is given by

$$\Delta G°_{\mathrm{Hep}\to\mathrm{S}}(-\mathrm{OH}) = -2.303RT\{\log P_{\mathrm{S/Hep}}(\mathrm{ArOH}) - \log P_{\mathrm{S/Hep}}(\mathrm{ArH})\} \tag{4}$$

Here, ArH denotes the parent compound for ArOH: benzene for phenol; chlorobenzene for 2-, 3-, and 4-chlorophenols; 1,2-dichlorobenzene for 2,3-dichlorophenol; 1,3-dichlorobenzene for 3,5-dichlorophenol; and nitrobenzene for 2-, 3-, and 4-nitrophenols. The partition coefficients of the parent compounds were previously reported.[4] The $-\Delta G°_{\mathrm{Hep}\to\mathrm{S}}(-\mathrm{OH})$ values calculated for S = [BuMeIm][NTf_2], [BuMePyrr][NTf_2], [BuMeIm][PF_6], 1-octanol, and water are summarized in Table 3. The $-\Delta G°_{\mathrm{Hep}\to\mathrm{S}}$ value of a polar functional group can be regarded as a measure of the strength of the specific interaction between the functional group and S.[4]

Most of the $-\Delta G°_{\mathrm{Hep}\to\mathrm{S}}(-\mathrm{OH})$ values are positive, indicating that the hydroxyl group interacts with the solvents S. The $-\Delta G°_{\mathrm{Hep}\to\mathrm{S}}(-\mathrm{OH})$ values with the three ionic liquids are close to each other, indicating that these ionic liquids are similar in the interaction with the phenolic hydroxyl group. Except for 3,5-dichlorophenol, 3-nitrophenol, and 4-nitrophenol, the interaction of the hydroxyl group with the solvent generally decreases in the following solvent order: water > 1-octanol > ionic liquids. The donor numbers of the solvents are reported to be 18.0, 20.3, and ca. 10 for water,[29] 1-octanol,[30] and NTf_2-based ionic liquids,[31] respectively. When supposing that the dominant interaction is hydrogen bonding of the phenol as an electron-pair acceptor to the solvent as an electron-pair donor, the weakest interaction of the ionic liquids is reasonable; however, the stronger interaction of water than 1-octanol is an unexpected result. Probably, the electron-pair acceptor ability (in other words, hydrogen-bond donor ability) of water makes an additional contribution to the interaction between the water and the phenols, because the acceptor number of water (54.8)[29] is much larger than that of 1-octanol (30.4).[32] For the phenols having relatively strong electron-pair acceptor ability (3,5-dichlorophenol, 3-nitrophenol, and 4-nitrophenol), the interaction of 1-octanol is stronger or comparable to that of water. This indicates that the contribution of the electron-pair donor ability of the solvent becomes more important in the interaction with these stronger electron-pair acceptors.

For a given S, the $-\Delta G°_{\mathrm{Hep}\to\mathrm{S}}(-\mathrm{OH})$ value is much smaller for the ortho-substituted phenols than for the meta- or para-substituted ones. Particularly, the $-\Delta G°_{\mathrm{Hep}\to\mathrm{S}}(-\mathrm{OH})$ values of 2-nitrophenol are nearly zero for all of the solvents. This result can be explained in terms of the intramolecular hydrogen bonding between the ortho-substituent (−Cl or $-NO_2$) and the hydrogen atom of the phenolic hydroxyl group. For a more detailed discussion, the $-\Delta G°_{\mathrm{Hep}\to\mathrm{S}}(-\mathrm{OH})$ values for S = [BuMeIm][NTf_2], [BuMeIm][PF_6], 1-octanol, and water are plotted as a function of pK_a (at 298.2 K in water) of the phenol in Figure 3. When S = 1-octanol (Figure 3c), a negative correlation is observed for the phenols having no substituents in the ortho-position (solute nos. 1, 3, 4, 6, 10, and 11). This suggests that the hydrogen atom of the phenolic hydroxyl group forms a hydrogen bond with the oxygen atom of the 1-octanol because the interaction becomes stronger with increasing acidity of the phenol. A similar relation is observed for the interaction of 1-octanol with the phenols having one chlorine atom in the ortho-position (solute nos. 2 and 5). On the other hand, as seen from Figure 3d, the interaction of water with the phenols having no ortho substituents decreases with increasing pK_a in the pK_a range of 7.15 (no. 11) to 8.35 (no. 10) but increases in the higher pK_a region. It appears that these different correlations in the lower and higher pK_a regions may reflect the contributions from hydrogen bonding of the hydrogen atom of the phenol to the oxygen atom of water and from that of the hydrogen atom of water to the oxygen atom of the phenol, respectively. Figure 3a and b for *S* = ionic liquids are similar to Figure 3d (S = water)

Table 3. Contributions of a Hydroxyl Group to Standard Gibbs Energies of Transfer of Electrically Neutral Phenols from Heptane to Solvents (S) at 298.2 K

		$-\Delta G^\circ_{\mathrm{Hep}\rightarrow\mathrm{S}}(-\mathrm{OH})/\mathrm{kJ\cdot mol^{-1}}$				
	solute	IL = [BMIm][NTf$_2$]	[BMPyr][NTf$_2$]	[BMIm][PF$_6$]	[OMIm][NTf$_2$]	[OMIm][BF$_4$]
1	phenol	12.4	12.7	12.5	14.4	18.2
2	2-chlorophenol	6.9	7.5	7.7	8.2	12.2
3	3-chlorophenol	11.9	12.3	12.6	15.1	17.1
4	4-chlorophenol	12.0	12.4	12.7	14.7	17.3
5	2,3-dichlorophenol	7.1	7.5	7.9	10.2	11.6
6	3,5-dichlorophenol	13.1	13.9	14.0	17.9	17.8
9	2-nitrophenol	−0.7	−1.0	−1.2	0.1	0.4
10	3-nitrophenol	12.7	12.7	12.5	17.3	16.4
11	4-nitrophenol	16.1	16.1	16.1	20.5	19.8

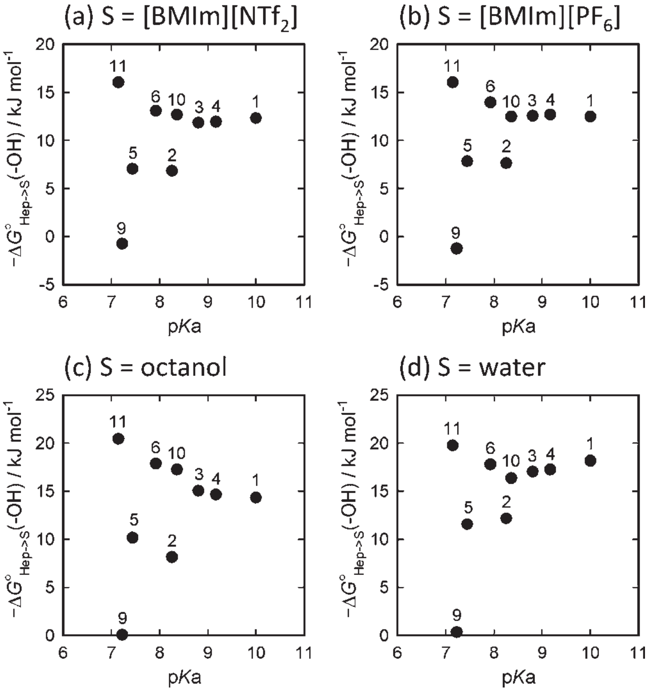

Figure 3. $-\Delta G^\circ_{\mathrm{Hep}\rightarrow\mathrm{S}}(-\mathrm{OH})$ values for S = [BuMeIm][NTf$_2$] (a), [BuMeIm][PF$_6$] (b), 1-octanol (c), and water (d) as a function of pK_a of the phenol. The numbers of solutes correspond to those in Table 1.

rather than Figure 3c (S = 1-octanol). This result is consistent with the previous conclusion that the ionic liquids have both electron-donor and -acceptor abilities; the component cation and anion of the ionic liquids are expected to act as an acceptor and a donor, respectively.[4] The contribution of water dissolved in the ionic liquid phase seems to be small from the fact that the partition coefficient of phenol between water-saturated [BMIm][NTf$_2$] and heptane is nearly equal to that between dry [BMIm][NTf$_2$] and heptane.[4]

Partition Coefficients of Anionic Phenolates. It is an important feature of the ionic liquids that they can extract ionic phenolate species without the addition of an ion-pairing agent. A possible mechanism for the extraction of ionic species is ion exchange with the constituent ions of ionic liquid.[33] For example, the extraction of a phenolate anion through ion exchange mechanism can be described as follows:

$$\mathrm{ArO_W^-} + \mathrm{A_{IL}^-} \rightleftarrows \mathrm{ArO_{IL}^-} + \mathrm{A_W^-};$$
$$K_{\mathrm{ie}} = [\mathrm{ArO^-}]_{\mathrm{IL}}[\mathrm{A^-}]_{\mathrm{W}}/[\mathrm{ArO^-}]_{\mathrm{W}}[\mathrm{A^-}]_{\mathrm{IL}} \qquad (5)$$

Here, A^- and K_{ie} denote the constituent anion of the ionic liquid and the equilibrium constant for the ion exchange, respectively. In this case, the following equation is derived.

$$P_{\mathrm{IL/W}}(\mathrm{ArO^-}) = [\mathrm{ArO^-}]_{\mathrm{IL}}/[\mathrm{ArO^-}]_{\mathrm{W}} = K_{\mathrm{ie}}[\mathrm{A^-}]_{\mathrm{IL}}/[\mathrm{A^-}]_{\mathrm{W}} \qquad (6)$$

Therefore, the partition coefficient of the phenolate anion determined in this work is not the equilibrium constant but corresponds to the distribution ratio of the anion.

The $P_{\mathrm{IL/W}}(\mathrm{ArO^-})$ values in Table 2 show that the phenolate anion with more chlorine atoms or more nitro groups is generally more likely to be partitioned into the ionic liquid phases. The effect enhancing the partition coefficient is greater for a nitro group than for a chlorine atom. The chlorine atom in the ortho-position has a smaller effect, enhancing the partition coefficient than that in the meta- or para-positions. These substituent effects for the partition of the phenolate anions are different from those observed for the partition of the neutral phenols. It appears that charge delocalization in the phenolate anion induced by the electron-withdrawing substituents (−Cl and $-\mathrm{NO_2}$) makes an important contribution to the increase of $P_{\mathrm{IL/W}}(\mathrm{ArO^-})$.

The partition coefficient of the phenolate anion depends largely on the kind of ionic liquid. The extractability of a given phenolate ion generally varies with the constituent ion of the ionic liquid as follows: [OMIm][NTf$_2$] > [BMIm][NTf$_2$] ≈ [BMPyr][NTf$_2$]; [OMIm][BF$_4$] > [OMIm][NTf$_2$]; [BMIm][PF$_6$] > [BMIm][NTf$_2$]. That is to say, an ionic liquid formed by a more hydrophobic cation and a more hydrophilic anion has a higher extractability for the phenolate anions. This result can be explained on the basis of eq 6. For a given A^-, the concentration of A^- in the aqueous phase should decrease with increasing hydrophobicity of the ionic liquid cation. For a given $\mathrm{ArO^-}$ and a given ionic liquid cation, the K_{ie} value is expected to increase with increasing hydrophilicity of A^-. Further studies on the extraction mechanisms are in progress and will be reported elsewhere.

■ CONCLUSION

In the partitioning of electrically neutral phenols between an ionic liquid and water, the interaction of the phenolic hydroxyl group with the ionic liquid plays an important role. For the ionic liquids studied, the strength of the interaction with a given phenol is generally insensitive to the kind of the ionic liquid. The chlorine atom and the nitro group in the ortho-position of the hydroxyl group greatly reduce the interaction of the hydroxyl group with the ionic liquid. The interaction receives contributions from hydrogen bonding of the ionic liquid to the oxygen atom of the phenol and from that of the hydroxyl hydrogen atom of the phenol to the ionic liquid. Differently from the case of the neutral phenols, the partition coefficients of the phenolate anions are very dependent on the kind of the ionic liquid. An ionic liquid formed by a more hydrophobic cation and a more hydrophilic anion has a higher extractability for the phenolate anions, and this fact is concerned with the extraction mechanism by anion exchange. In addition, the effects of the substituents on $P_{IL/W}(ArO^-)$ are different from those on $P_{IL/W}(ArOH)$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Distribution ratios of various phenols measured at different pH values of the aqueous phase at 298.2 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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