Measurement and Correlation of Partition Coefficients for Phenolic Compounds in the 1-Butyl-3-methylimidazolium Hexafluorophosphate/Water Two-Phase System

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Partition coefficients for phenol; *o*-, *m*-, and *p*-cresols; 3,5-xylenol; and α-naphthol in an ionic liquid/water two-phase system were measured at 298.2 K. 1-Butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) was used as the ionic liquid. Further, the infinite dilution partition coefficients were also determined by extrapolation. The infinite dilution partition coefficients were correlated by regular solution theory. Interaction parameters between phenolic compounds and [bmim][PF_6] pairs were determined by plotting the infinite dilution partition coefficients against the solubility parameters of the phenolic compounds. The correlated results are in good agreement with the experimental data.

Introduction

Phenolic compounds are of great importance in many industrial processes. Trace amounts of these compounds in wastewater from manufacturing plants can have significant detrimental effects on water quality because they are toxic to aquatic life. These compounds need to removed from wastewater discharges for the purpose of environmental conservation. Liquid−liquid extractions by organic solvent/water two-phase systems have been reported as a method for trapping phenolic compounds from wastewater.[1,2] Recently, however, the use of organic solvents has been shown to have problems associated with toxicity, volatility, and flammability. Room temperature ionic liquids have been considered as a replacement for organic solvents in liquid−liquid extraction because they have fundamentally unique properties, very low vapor pressure, the ability to dissolve both ionic and nonionic species, and non-flammability. The partition coefficients of phenolic compounds in ionic liquid/water two-phase systems are one of the fundamental physicochemical properties in liquid−liquid extraction.

Carda-Broch et al.[3] have reported the partition coefficients of a large number of organic compounds between 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6])/water and [bmim][PF_6]/heptane two-phase systems. The partition coefficients of benzene derivatives in the [bmim][PF_6]/water system have been also studied and compared with those in the 1-octanol/water system by Rogers and co-wokers.[4] Abraham et al.[5] correlated the partition coefficients of some solutes (such as iodomethane, benzamide, and fluoranthene, etc.) in [bmim][PF_6]/water, 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim][PF_6])/water, and ammonium sulfate/water two-phase systems by a linear free-energy relationship. The partition coefficients have been compared with those in some organic solvent/water systems. Extractions of phenolic compounds from the aqueous phase to the [bmim][PF_6] phase have been performed over a range of pH by Khachatryan et al.[6] However, the partition coefficients of phenolic compounds in ionic liquid/water systems are scarce.

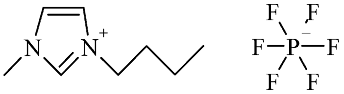

Figure 1. Molecular structure of 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]).

Herein, the partition coefficients of the phenolic compounds (phenol; *o*-, *m*-, and *p*-cresols; 3,5-xylenol; and α-naphthol) in the [bmim][PF_6]/water two-phase system were measured at 298.2 K in order to evaluate the ability of [bmim][PF_6] for the liquid−liquid extraction of phenolic compounds from wastewater. Furthermore, the infinite dilution partition coefficients were determined by the extrapolation of the partition coefficients to zero concentration. The regular solution theory[7] was adopted to correlate the infinite dilution partition coefficients. The solubility parameter of [bmim][PF_6] and interaction parameters for [bmim][PF_6]/solute pairs were determined by plotting the infinite dilution partition coefficients versus the solubility parameters of the solutes. The correlated results were compared with the experimental data.

Experimental Section

Materials. The ionic liquid/1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) which has a density of 1.37 $g\cdot cm^{-3}$ at 298 K was supplied by the Kanto Kagaku Co. Ltd. The ionic liquid was an organic synthesis reagent. The structural formula is shown in Figure 1. The phenolic compounds (phenol; *o*-, *m*-, and *p*-cresols; 3,5-xylenol; and α-naphthol) were purchased from the Wako Pure Chemical Co. Ltd. Table 1 shows the molecular formulas, melting points, solubilities in water at 298 K, and molar masses of the phenolic compounds. They were special grade reagents, and the purities were checked by gas chromatographic analysis. The peak area percentage of the main compounds were more than (99.9, 99.9, 99.8, 99.9, 99.8, and 99.9) % for phenol; *o*-, *m*-, and *p*-cresols; 3,5-xylenol; and α-naphthol, respectively. In the pH range used in the present

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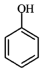
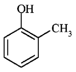
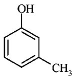
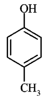
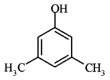
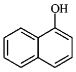
Table 1. Properties of Phenolic Compounds

solute	structural formula	melting point/K	solubility in water at 298 K/mol·L^{-1}	molar mass/g·mol^{-1}
phenol		314.05 [8]	1.007 [10]	94.11
o-cresol		302.95 [8]	0.247 [10]	108.14
m-cresol		284.95 [8]	0.214 [10]	108.14
p-cresol		307.89 [8]	0.201 [10]	108.14
3,5-xylenol		336.75 [8]	0.036 [10]	144.17
α-naphthol		368.5 [9]	0.0111 [11]	122.17

study, the partition coefficients of phenolic compounds in the [bmim][PF$_6$]/water two-phase system show a slight variation with pH.[3] They were used without further purification. Water was deionized using Milli-Q Labo (Millipore Corporation). The resistivity was 18.0 to 18.2 MΩ·cm. The values of pH in the aqueous phase were 4.85, 5.41, 4.96, 4.87, 4.55, and 4.15 for phenol; *o*-, *m*-, and *p*-cresols; 3,5-xylenol; and α-naphthol, respectively.

Apparatus and Procedure. The measurements of the partition coefficients of phenolic compounds in [bmim][PF$_6$]/water two-phase system were performed in a glass cell that was 10 mL in volume. The cell was placed in a constant temperature water bath regulated at (298.2 ± 0.1 K). A magnetic stirrer was used to agitate the content in the cell. A Karl Fischer moisture titrator (Kyoto Electric Manufacturing Co. Ltd.) was used to analyze the water amount in the [bmim][PF$_6$] phase. UV spectrophotometer (V-550, JASCO Co.) measurements were adopted to analyze the composition of the phenolic compounds in the ionic liquid and water phases.

The mutual solubilities of [bmim][PF$_6$] and water were measured before measurements of the partition coefficients. Water (2 mL) was contacted with 1 mL of [bmim][PF$_6$] in the glass cell at 298.2 K. The sample in the cell was agitated by the magnetic stirrer for 10 min and was then settled for 1 h. It was then stirred for 10 min again and settled for another 2 h. The sample from the [bmim][PF$_6$] phase was analyzed with the Karl Fischer moisture titrator to determine the concentration of water in the [bmim][PF$_6$]. A UV spectrophotometer was used to analyze the sample from the water phase.

Aqueous solutions of each phenolic compound in the concentrations, (10.03 to 45.10) × 10^{-4} mol·L^{-1}, were prepared in 2 mL. These solutions were contacted with 1 mL of [bmim][PF$_6$] in the glass cell at 298.2 K. The sample in the cell was agitated in the same manner as used for measurement of the mutual solubilities of [bmim][PF$_6$] and water. The samples from the ionic liquid were diluted 6 times by methanol. Samples from the water phase were diluted 2.2 times by water. The composition of phenolic compounds in both phases were determined by a UV spectrophotometric method. The detector cell of the UV spectrophotometer was made of quartz, and the optical path length was 1.0 cm. Table 2 lists the wave length values applied to the UV spectrophotometric measurements for each solute in water and methanol solutions.

Table 2. Wavelengths Used to Determine Concentrations of Phenolic Compounds

solute	in water/cm^{-1}	in methanol/cm^{-1}
phenol	273	273
o-cresol	271	274
m-cresol	271	274
p-cresol	277	280
3,5-xylenol	272	272
α-naphthol	293	296

The partition coefficient of a phenolic compound (3) in the [bmim][PF$_6$] (1)/water (2) two-phase system K_3, based on molar concentration, is defined by the following equation:

$$K_3 = \frac{C_3^{(1)}}{C_3^{(2)}} \tag{1}$$

where C_3 is the molar concentration (mol·L^{-1}) of the phenolic compounds. The superscripts (1) and (2) denote the [bmim][PF$_6$] and water phases, respectively. Furthermore, the infinite dilution partition coefficients K_3^{∞} were determined by the extrapolation of K_3 to zero concentration as shown in Figure 2. The values of $K_{x,3}^{\infty}$ based on mole fraction were obtained as

$$K_{x,3}^{\infty} = \frac{x_3^{(1)\infty}}{x_3^{(2)\infty}} = K_3^{\infty}\frac{M_1\rho_2}{M_2\rho_1} \tag{2}$$

where x_i, M_i, and ρ_i are the mole fraction, the molar mass, and the density of compound i, respectively. The concentrations (mol·L^{-1}) are essentially the same as those in (mol·kg^{-1}) at low ionic strength. The subscripts 1 and 2 denote [bmim][PF$_6$] and water, respectively.

Correlation

The regular solution theory[7] was adopted to correlate the experimental results because this theory is applicable to a large variety of mixtures. It is interesting to examine to what extent the theory can be applied to correlate the partition coefficients in the ionic liquid/water two-phase system. Based on the regular solution theory, the infinite dilution activity coefficients of solute (3) in the [bmim][PF$_6$] (1) and water (2) phases can be described as follows:

$$\ln \gamma_3^{(1)\infty} = \frac{V_{\mathrm{m},3}}{RT}[(\delta_1 - \delta_3)^2 + 2l_{13}\delta_1\delta_3] \tag{3}$$

$$\ln \gamma_3^{(2)\infty} = \frac{V_{\mathrm{m},3}}{RT}[(\delta_2 - \delta_3)^2 + 2l_{23}\delta_2\delta_3] \tag{4}$$

where δ_i is the solubility parameter of compound i, $V_{\mathrm{m},3}$ is the molar volume of solute, and l_{ij} is the interaction parameter between compounds i and j. $V_{\mathrm{m},3}$ and δ_3 of phenolic compounds were estimated using the group contribution method by Fedros.[12] The estimated values are slightly larger than those from heat of vaporization data.[13] The slight differences did not influence the correlated results. A group contribution method is useful because it can be applied to a large variety of compounds. These values are listed in Table 3. The solubility parameter of water δ_2 was calculated as $\delta_2 = 47.93$ (J·cm^{-3})$^{1/2}$ from the molar enthalpy[14] of vaporization and molar volume[14] at 298.2 K. When

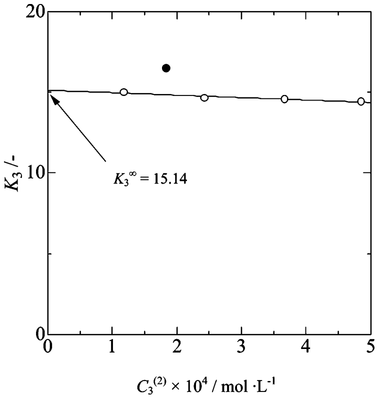


Figure 2. Partition coefficients of phenol between [bmim][PF$_6$]/water system: ○, this work at 298.2 K; ●, ref 3 at 294 K.

Table 3. Molar Volumes and Solubility Parameters of Phenolic Compounds at 298.2 K[12]

solute	$V_{m,3}$/cm^3·mol^{-1}	δ_3/(J·cm^{-3})$^{1/2}$
phenol	84.4	25.24
o-cresol	98.9	24.31
m-cresol	98.9	24.31
p-cresol	98.9	24.31
3,5-xylenol	113.4	23.60
α-naphthol	153.6	23.85

Table 4. Mutual Solubilities of [bmim][PF$_6$] and Water System at 298.2 K

	[bmim][PF$_6$] in water		water in [bmim][PF$_6$]	
	mass fraction	mole fraction	mass fraction	mole fraction
this work	0.019	1.28 × 10^{-3}	0.023	0.26
literature[3]	0.014	1.13 × 10^{-3}	0.018	0.21

Table 5. Partition Coefficients for Phenolic Compounds (3) in [bmim][PF$_6$] (1)/Water (2) System at 298.2 K[a]

solute	$C_{3,0}^{(2)} \times 10^4$ mol·L^{-1}	$C_3^{(2)} \times 10^4$ mol·L^{-1}	$C_3^{(1)} \times 10^4$ mol·L^{-1}	K_3 –
phenol	10.20	1.177 ± 0.03	17.7 ± 0.8	15.0 ± 0.3
	20.40	2.423 ± 0.04	35.5 ± 0.3	14.7 ± 0.1
	30.60	3.668 ± 0.05	53.5 ± 0.4	14.6 ± 0.3
	40.80	4.853 ± 0.02	70.0 ± 0.8	14.4 ± 0.2
o-cresol	10.03	0.634 ± 0.04	17.7 ± 1.4	28.0 ± 0.3
	20.05	1.329 ± 0.05	37.6 ± 0.9	28.3 ± 0.4
	30.08	2.012 ± 0.02	56.7 ± 0.3	28.2 ± 0.1
	40.10	2.645 ± 0.02	75.0 ± 2.0	28.3 ± 0.5
m-cresol	10.10	0.581 ± 0.01	18.9 ± 0.6	32.5 ± 0.4
	20.20	1.216 ± 0.00	38.9 ± 0.2	32.0 ± 0.1
	30.30	1.829 ± 0.002	57.5 ± 0.6	31.5 ± 0.3
	40.40	2.471 ± 0.02	77.6 ± 0.7	31.4 ± 0.3
p-cresol	11.30	0.677 ± 0.01	21.0 ± 0.4	31.1 ± 1.1
	22.60	1.455 ± 0.07	45.9 ± 1.5	31.6 ± 0.8
	33.80	2.130 ± 0.07	69.3 ± 0.9	32.5 ± 1.4
	45.10	3.121 ± 0.58	99.9 ± 16.3	32.0 ± 1.0
3,5-xylenol	10.38	0.342 ± 0.02	18.7 ± 0.4	54.7 ± 2.1
	20.75	0.679 ± 0.04	38.5 ± 1.8	56.7 ± 1.0
	31.13	0.983 ± 0.04	59.1 ± 2.1	60.1 ± 0.2
	41.50	1.263 ± 0.004	79.6 ± 0.7	63.0 ± 0.7
α-naphthol	16.90	0.112 ± 0.01	34.4 ± 1.2	307.6 ± 23.4
	25.35	0.176 ± 0.01	54.4 ± 0.3	309.9 ± 20.5
	33.80	0.233 ± 0.002	71.9 ± 0.6	308.0 ± 0.5

[a] $C_{3,0}^{(2)}$ is the molar concentration of the solute in aqueous solution before measurement.

Table 6. Partition Coefficients of Phenolic Compounds in the [bmim][PF$_6$]/Water and 1-Octanol/Water Systems at 298.2 K

	ln K_3^{∞}/–	
solute	[bmim][PF$_6$]/water	1-octanol/water[15]
phenol	2.72 ± 0.01	3.36
o-cresol	3.33 ± 0.01	4.49
m-cresol	3.63 ± 0.03	4.47
p-cresol	3.43 ± 0.03	4.51
3,5-xylenol	3.94 ± 0.02	5.41
α-naphthol	5.72 ± 0.05	6.86

the mutual solubilities of [bmim][PF$_6$] and water are negligible, the infinite dilution partition coefficients are given by

$$K_{x,3}^{\infty} = \frac{\gamma_3^{(2)\infty}}{\gamma_3^{(1)\infty}} \tag{5}$$

The following linear relationship ln $K_{x,3}^{\infty}$ and the solubility parameter of the solutes δ_3 can be derived from eqs 3 to 5:

$$\frac{RT}{V_{m,3}} \ln\ K_{x,3}^{\infty} = (\delta_2^{\ 2} - \delta_1^{\ 2}) + 2\{(1 - l_{13})\delta_1 - (1 - l_{23})\delta_2\}\delta_3 = \alpha + \beta\delta_3 \tag{6}$$

Results and Discussion

Table 4 lists the mutual solubilities of [bmim][PF$_6$] and water at 298.2 K. The experimental data in this work are in good agreement with literature data.[3] The experimental results of the partition coefficients for phenol; *o*-, *m*-, and *p*-cresols; 3,5-xylenol; and α-naphthol are listed in Table 5. The partition coefficients of phenol are almost independent of the concentration of phenol in the water phase. The results of phenol are also shown in Figure 2 for comparison with literature data.[3] The experimental data in this work are in fair agreement with the literature data though the experimental temperatures are slightly different. The K_3 values of the cresol isomers are also independent of the composition of the cresol isomers in the water phase as presented in Table 5. The values are around twice those of phenol. The difference in K_3 among the cresol isomers is not so large. The partition coefficients of 3,5-xylenol increase with increasing $C_3^{(2)}$ and are larger than those of the cresol isomers. It is found that the K_3 values of α-naphthol do not change with concentration in the water phase, the same as found for phenol and the cresol isomers. The values are much larger than those of phenol, the cresol isomers and 3,5-xylenol. Table 5 shows that the K_3 values increase in the following order: phenol < cresol isomers < 3,5-xylenol < α-naphthol. This phenomena can be explained by the hydrophobicity of the solutes related to the addition of a methyl or phenyl group.

The experimental data in this work are compared with partition coefficient data[15] from the 1-octanol/water system as listed in Table 6. Table 6 shows that the partition coefficients for phenolic compounds in the [bmim][PF$_6$]/water system follow a similar pattern to those in the 1-octanol/water system.

In eq 6, the values of α and β were evaluated by the plotting the left-hand side against δ_3 and were determined as −101.5 and 10.14, respectively. The solubility parameter for [bmim][PF$_6$] was determined from α as δ_1 = 48.98 (J·cm^{-3})$^{1/2}$ with δ_2 = 47.93 (J·cm^{-3})$^{1/2}$. The interaction parameter l_{23} shown in eq 4 can be evaluated by using the infinite dilution activity coefficient data of phenolic compounds (3) in water (2). They are available for phenol, the cresol isomers, and 3,5-xylenol in the literature.[10] The values of l_{23} range from −0.005 to −0.010, so that the average value of −0.0073 for phenol, the cresol isomers, and 3,5-xylenol was used as the interaction parameter for phenolic compounds/water pairs in this work. The value of

Table 7. Infinite Dilution Partition Coefficients for Phenolic Compound (3) in the [bmim][PF_6] (1)/Water (2) System at 298.2 K

solute	$\ln K^{\infty}_{x,3,\mathrm{exp}}/-$[a]	$\ln K^{\infty}_{x,3,\mathrm{calc}}/-$	$\sigma/\%$[b]
phenol	5.16 ± 0.01	5.25	2.0
o-cresol	5.77 ± 0.01	5.77	0.03
m-cresol	6.08 ± 0.03	5.77	5.0
p-cresol	5.87 ± 0.03	5.77	2.0
3,5-xylenol	6.39 ± 0.02	6.29	2.0
α-naphthol	8.17 ± 0.05	8.68	6.0

[a] $\ln K^{\infty}_{x,3,\mathrm{calc}} = \frac{V_{\mathrm{m},3}}{RT}(-101.5 + 10.14\delta_3)$. [b] $\sigma = \frac{|\ln K^{\infty}_{x,3,\mathrm{exp}} - \ln K^{\infty}_{x,3,\mathrm{calc}}|}{\ln K^{\infty}_{x,3,\mathrm{exp}}} \times 100$.

β in eq 6 was used to determine the interaction parameter l_{13}. The value was −0.089. Table 7 compares the experimental data and the correlated results of the infinite dilution partition coefficients of phenolic compounds in the [bmim][PF_6]/water two-phase system. The correlated results are in good agreement with the experimental results for all phenolic compounds, although it is difficult to distinguish the difference among the cresol isomers.

Conclusion

The partition coefficients of the phenolic compounds (phenol; *o*-, *m*-, and *p*-cresols; 3,5-xylenol; and α-naphthol) in the 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6])/water two-phase system were measured using an UV spectrophotometric method at 298.2 K. The infinite dilution partition coefficients were obtained by the extrapolation of those data to zero concentration. The values increase by addition of a methyl or phenyl group as phenol < cresol isomers < 3,5-xylenol < α-naphthol. From the comparison with the data in the 1-octanol/water system, the values of partition coefficients in the [bmim][PF_6]/water system show a similar tendency.

The infinite dilution partition coefficients were correlated by using the regular solution theory. The intermolecular parameter for the solute and water pairs was evaluated from the data of infinite dilution activity coefficients of the solutes in water. The solubility parameter of [bmim][PF_6] and the interaction parameters for [bmim][PF_6] and solute pairs were determined from the linear relationship between the infinite dilution partitions and the solubility parameters of the solutes. The correlated results show good agreement with the experimental data.

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