Effect of Isomers on Partition Coefficients for Phenolic Compounds in the 1-Butyl-3-methylimidazolium Hexafluorophosphate + Water Two-Phase System

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The partition coefficients for five phenolic compounds in the ionic liquid + water two-phase system were measured at 298.2 K by a static method. The ionic liquid focused on in this work was 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]). The effects of isomers for phenolic compounds on the partition coefficients were investigated. The partition coefficients of 2-ethylphenol are larger than those of 3- and 4-ethylphenols. For the phenols with three methyl or methylene groups, the partition coefficients of 2,3,5-trimethylphenol are higher than those of 4-propylphenol. An activity coefficient equation based on a conductor-like screening model was used for the prediction of the partition coefficients. The predicted results are in agreement with the experimental data within the order of magnitude of the partition coefficients. The profiles of the surface charge densities of the phenolic compounds on CH and OH groups for the phenols were used for the investigations of the isomer effects on the partition coefficients.

Introduction

Trace amounts of aromatic compounds in wastewater from manufacturing plants can have significant detrimental effects on water quality because they are toxic to aquatic life. The removal techniques of these compounds from wastewater have been demanded 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] However, the use of organic solvent has the problems associated with toxicity, volatility, and flammability.

Room temperature ionic liquids have been expected as alternative solvents in liquid−liquid extraction for aromatic compounds. The ionic liquids have fundamentally unique properties, very low vapor pressure, the ability to dissolve both ionic and nonionic species and nonflammability. 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 Huddleston et al.[3] Carda-Broch et al.[4] 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. Abraham et al.[5] correlated the partition coefficients of some solutes, such as iodomethane, benzamide, and fluoranthene, and so forth, 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. Extractions of phenolic compounds from the aqueous phase to [bmim][PF_6] phase have been performed over a range of pH by Khachatryan et al.[6] It is also very important for the design of the extraction process to understand the effects of isomers on the partition coefficients in ionic liquid + water two-phase systems.

Herein, the partition coefficients in the [bmim][PF_6] + water two-phase system were measured for the isomers of phenolic compounds at 298.2 K. Furthermore, the infinite dilution partition coefficients were determined by the extrapolation of the partition coefficients to zero concentration of the phenolic compounds. The predictions of the partition coefficients were carried out using an activity coefficient equation based on conductor-like screening model (COSMO),[7] the COSMO−surface activity coefficient (SAC) method.[8] The effects of the isomers on the partition coefficients were investigated from the profiles of the surface charge densities in COSMO-SAC method.

Experimental Section

Materials. The organic synthesis reagent [bmim][PF_6] was supplied by Kanto Kagaku Co., Ltd. The density is 1.37 $g\cdot cm^{-3}$ at 298 K. This ionic liquid is the same as the previous work.[9] The chemicals of 2-ethylphenol, 3-ethylphenol, 4-ethylphenol, 4-propylphenol, and 2,3,5-trimethylphenol were obtained from Kanto Chemical Co., Inc., Japan. They were special grade reagents, and the purities were checked using gas chromatographic analysis by the authors. The peak area percentages of the main compounds were more than 97.0, 96.0, 97.0, 97.5, and 98.0 for 2-ethylphenol, 3-ethylphenol, 4-ethylphenol, 4-propylphenol, and 2,3,5-trimethylphenol, respectively. They were used without further purification. Water was deionized using Milli-Q Labo (Millipore Corporation). The resistivity was (18.0 to 18.2) $M\Omega\cdot cm$.

Apparatus and Procedure. The experimental apparatus and procedure are similar to those in previous work.[9] A glass cell with 10 mL in volume was used for the measurements of the partition coefficients. The temperatures in the cell were controlled by a water bath regulated at (298.2 ± 0.1) K. A magnetic stirrer was used for the agitation of the mixtures in the cell.

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Table 1. Wavelengths λ of Ultraviolet Spectrophotometer Analysis in Water and Methanol

solute	λ (H_2O)/nm	λ (MeOH)/nm
2-ethylphenol	271	274
3-ethylphenol	271	274
4-ethylphenol	276	279
4-propylphenol	276	279
2,3,5-trimethylphenol	279	282

The concentrations of the phenolic compounds in [bmim][PF_6] and water phases were determined by an ultraviolet spectrophotometer (V-550, JASCO, Japan). A detector cell of the ultraviolet spectrophotometer was made of quartz,and the optical path length was 1.0 cm.

Initially, the aqueous solutions of the phenolic compounds in 2 mL were prepared in the concentrations, $(10.0 \text{ to } 83.1)\cdot 10^{-4}$ $\text{mol}\cdot\text{L}^{-1}$. The aqueous solutions were contacted with 1 mL of [bmim][PF_6] in the glass cell at 298.2 K. The mixtures in the cell were agitated for 10 min and then settled for 1 h. Furthermore, it was then stirred for 10 min again and settled for 2 h. The samples in [bmim][PF_6] and water phases were taken using a syringe for the analysis of the concentrations of the phenolic compounds. The samples in the [bmim][PF_6] phase were diluted six times by methanol. The additional water was used for the preparations of the 2.2 times dilute solutions of the samples in the water phase. These samples for the [bmim][PF_6] and water phases were analyzed by the ultraviolet spectrophotometer for the determinations of the concentrations of the phenolic compounds. Table 1 lists the wavelengths used for the determinations of the concentrations of the phenolic compounds.

The partition coefficient for phenolic compound (3) in the [bmim][PF_6] (1) + water (2) system, K_3, is defined using the molar concentrations by the following equation:

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

where C_3 is the molar concentration in $\text{mol}\cdot\text{L}^{-1}$ of the phenolic compound. The superscripts (1) and (2) mean the [bmim][PF_6] and water phases, respectively. In this work, the partition coefficient in eq 1 was converted to that based on mole fraction for comparisons between results from the experimental and the theoretical approaches described in the next section. The partition coefficient based on the mole fraction $K_{x,3}$ can be obtained from that based on the molar concentration K_3 given as follows:

$$K_{x,3} = \frac{x_3^{(1)}}{x_3^{(2)}} = K_3\frac{M^{(1)}\rho^{(2)}}{M^{(2)}\rho^{(1)}} \tag{2}$$

where x is the mole fraction. The M and ρ are the molar mass in $\text{kg}\cdot\text{mol}^{-1}$ and density in $\text{mol}\cdot\text{L}^{-1}$ of the liquid phases obtained from the following equations:

$$\begin{aligned} M^{(1)} &= M_1x_1^{(1)} + M_2x_2^{(1)} \\ M^{(2)} &= M_1x_1^{(2)} + M_2x_2^{(2)} \end{aligned} \tag{3}$$

$$\begin{aligned} \rho^{(1)} &= \rho_1x_1^{(1)} + \rho_2x_2^{(1)} \\ \rho^{(2)} &= \rho_1x_1^{(2)} + \rho_2x_2^{(2)} \end{aligned} \tag{4}$$

where the subscripts 1 and 2 mean [bmim][PF_6] and water, respectively. The mutual solubility data for [bmim][PF_6] + water system[10] were used as the mole fractions in eqs 3 and 4.

Prediction. The COSMO-SAC method[8] is used for the prediction of thermodynamic properties from the surface charge densities on molecules by quantum calculations, using the COSMO model.[7] In this work, the surface charge densities of the [bmim] cation and [PF_6] anion were obtained from the COSMO calculations by Gaussian 03W software.[10] For the phenolic compounds and water, the surface charge densities are available from the software of COSMO base version C2.1.[11] The details of COSMO-SAC method are given in the literature.[8]

The activity coefficient of component i, γ_i, in the mixture is obtained by the following equation.

$$\ln \gamma_i = \frac{A_i}{a_{\text{eff}}}\sum_{\sigma_m} p_i(\sigma_m)[\ln \Gamma(\sigma_m) - \ln \Gamma_i(\sigma_m)] + \ln \gamma_i^{\text{C}} \tag{5}$$

where A_i is the surface area of component i, a_{eff} is the standard segment surface area, $p_i(\sigma_m)$ is the probability of finding a segment with charge density σ_m in component i, $\Gamma(\sigma_m)$ is the segment activity coefficient with charge density σ_m, and $\Gamma_i(\sigma_m)$ is the segment activity coefficient with charge density σ_m in component i. The superscript C means the combinatorial contribution from the differences of the molecular sizes and shapes. To calculate the segment activity coefficients, two parameters, c_{hb} and σ_{hb}, are necessary. These are the constant and the cutoff value for the hydrogen bonding interactions, respectively. The values of these parameters proposed by Lin and Sandler[8] were used as $a_{\text{eff}} = 7.5$ Å^2, $c_{\text{hb}} = 0.0084\ e\cdot\text{Å}^{-2}$, and $\sigma_{\text{hb}} = 3.581\cdot 10^5\ \text{kJ}\cdot\text{mol}^{-1}\cdot\text{Å}^{-4}\cdot e^{-2}$. The Staverman–Guggenheim equation[12,13] was adopted for the calculations of the combinatorial term in this work. The molecular volume and surface area parameters in Staverman–Guggenheim equation were obtained from the normalization of the molecular volume and surface area by the COSMO calculations to a standard volume, 66.69 Å^3, and surface area, 79.53 Å^2, in the literature.[8] From the liquid–liquid equilibrium relationship, the partition coefficients of the phenolic compound (3) in the [bmim][PF_6] (1) + water (2) two-phase system are given by the following equation.

$$K_{x,3} = \frac{x_3^{(1)}}{x_3^{(2)}} = \frac{\gamma_3^{(2)}}{\gamma_3^{(1)}} \tag{6}$$

Equations 5 and 6 were used for the calculations of the infinite dilution partition coefficients of the phenolic compounds in the [bmim][PF_6] + water phase system. The mole fraction of the phenolic compound was set to zero for the calculations of the activity coefficients in eq 5. The mutual solubility data[9] for the [bmim][PF_6] + water system were used as the mole fractions in the each phase. The ionic liquid [bmim][PF_6] is treated as a neutralized molecule in this work.

Results and Discussion

The experimental results of the partition coefficients for the phenolic compounds in the [bmim][PF_6] + water system are shown in Table 2. The uncertainties of the partition coefficients are estimated as ± 0.4, 0.4, 0.3, 0.4, and 0.6 for 2-, 3-, and 4-ethylphenol, 4-propylphenol, and 2,3,5-trimethylphenol, respectively, from the repeatabilities of the concentrations in the [bmim][PF_6] and water phases. Figures 1 and 2 give the initial concentration dependences on the partition coefficient for the ethylphenol and propylphenol isomers, respectively. For ethylphenol isomers, the partition coefficients of 2-ethylphenol are higher than those for 3- and 4-ethylphenols. The values for 3-ethylphenol are almost the same as those for 4-ethylphenol.

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

solute	$10^4\ C_{3,0}^{(2)a}$ / mol·L^{-1}	$10^4\ C_3^{(2)}$ / mol·L^{-1}	$10^4\ C_3^{(1)}$ / mol·L^{-1}	K_3
2-ethylphenol	10.0	1.00	75.9	76.0
	20.1	2.09	159.2	76.4
	30.1	3.08	239.1	77.7
	40.1	4.19	323.1	77.1
3-ethylphenol	10.1	0.31	17.3	55.8
	20.1	0.70	39.8	56.9
	30.1	1.04	57.9	55.7
	40.2	1.36	75.5	55.5
4-ethylphenol	16.5	1.60	85.3	53.3
	33.1	2.46	133.5	54.2
	66.2	3.24	177.3	54.8
4-propylphenol	58.2	2.24	279.5	124.8
	66.5	2.55	322.1	126.3
	74.8	2.82	358.3	127.1
	83.1	3.14	397.4	126.6
2,3,5-trimethylphenol	25.2	0.763	137.6	180.3
	28.8	0.876	159.4	182.0
	32.4	0.971	175.5	180.7
	36.0	1.089	197.4	181.3

[a] $C_{3,0}^{(2)}$ is initial molar concentration of phenolic compound in water phase.

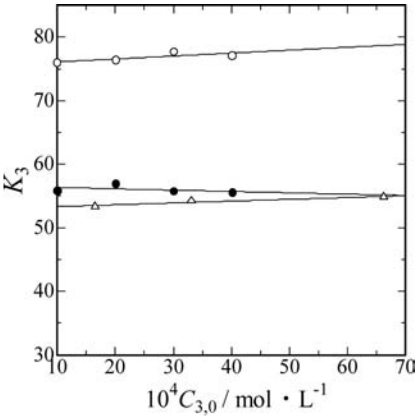

Figure 1. Partition coefficients for ethylphenol isomers in the [bmim][PF$_6$] + water system at 298.2 K: ○, 2-ethylphenol; ●, 3-ethylphenol; △, 4-ethylphenol.

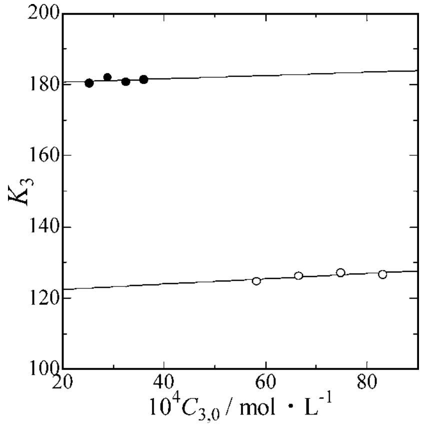

Figure 2. Partition coefficients for 4-propylphenol and 2,3,5-trimethylphenol in the [bmim][PF$_6$] + water system at 298.2 K: ○, 4-propylphenol; ●, 2,3,5-trimethylphenol.

Table 3. Experimental and Predicted Results of Infinite Dilution Partition Coefficients for the Phenolic Compound (3) in the [bmim][PF$_6$] (1) + Water (2) System at 298.2 K

solute	$K_{3,\mathrm{exp}}^{\infty}$	$\ln K_{x,3,\mathrm{exp}}^{\infty}$	$\ln K_{x,3,\mathrm{calc}}^{\infty}$	dev.[a]
2-ethylphenol	75.6	2.86	2.06	0.80
3-ethylphenol	56.5	2.74	1.89	0.85
4-ethylphenol	53.0	2.71	1.87	0.83
4-propylphenol	120.9	3.07	2.26	0.81
2,3,5-trimethylphenol	179.6	3.24	2.64	0.60

[a] dev. = $|\ln K_{x,3,\mathrm{exp}}^{\infty} - \ln K_{x,3,\mathrm{calc}}^{\infty}|$.

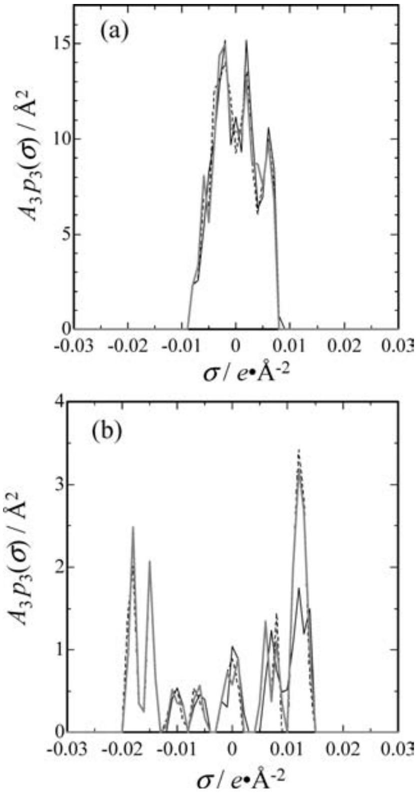

Figure 3. Profiles of surface charge densities on (a) CH and (b) OH groups for ethylphenol molecules: black line, 2-ethylphenol; dashed line, 3-ethylphenol; gray line, 4-ethylphenol.

The partition coefficients of 2,3,5-trimethylphenol are higher than those for those for 4-propylphenol. The infinite dilution partition coefficients are obtained from the extrapolations of the relationship between the initial concentrations and the partition coefficients of the phenolic compounds as shown in Figures 1 and 2. The values of the infinite dilution partition coefficients are listed in Table 3. The predicted results of the partition coefficients are also listed in Table 3. The deviations between the experimental and the predicted results are lower than the unity for all phenolic compounds. It means that the predicted results are in agreement with the experimental results within the order of magnitude of their partition coefficients.

The effects of isomers on the partition coefficients can be explained from the profiles of the surface charge densities on CH and OH groups for phenolic compounds as shown in Figures 3 and 4. As shown in Figure 3, the profiles of the surface charge densities on the CH groups are almost the same for 2-, 3-, and 4-ethylphenols. On OH groups, the surface charge densities for 2-ethylphenol at (0.01 to 0.015) $e\cdot$Å^{-2} are much smaller than those for 3- and 4-ethylphenol. In eq 5, the activity coefficient in the mixture is derived from the surface charge density of the phenols. The results in Figure 3 explain that the differences of the activity coefficients and partition coefficients for the ethylphenol isomers are from the differences of the surface charge densities on OH groups. Figure 4 shows that the profiles for 4-propylphenol and 2,3,5-trimethylphenol give considerable differences on both CH and OH groups. For CH group, the highest peak for 4-propylphenol is located at $-0.0025\ e\cdot$Å^{-2},

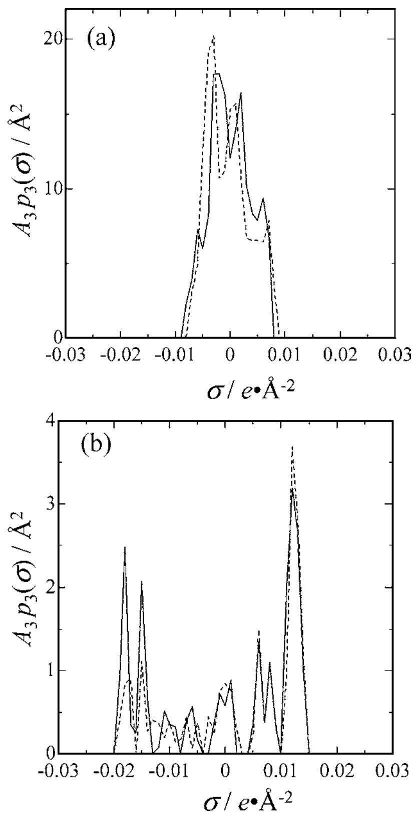

Figure 4. Profiles of surface charge densities on (a) CH and (b) OH groups for 4-propylphenol and 2,3,5-trimethylphenol molecules: black line, 4-propylphenol; dashed line, 2,3,5-trimethylphenol.

which is more positive than the case of 2,3,5-trimethylphenol. The surface charge densities at (-0.02 to -0.015) $e \cdot$Å^{-2} for 4-propylphenol are higher than those for 2,3,5-trimethylphenol. It is found that the partition coefficients for 4-propylphenol and 2,3,5-trimethylphenol are affected by the differences of the surface charge densities on not only OH but also CH groups.

Conclusion

The partition coefficients of the phenolic isomers between [bmim][PF$_6$] and water two-phase systems were investigated from the experimental and calculation approaches. For the ethylphenol isomers, the partition coefficients of 2-ethylphenol are larger than those for 3- and 4-ethylphenols. For the phenols with three methyl groups, the partition coefficients of 2,3,5-trimethylphenol are larger than those of 4-propylphenol. In the prediction model, the profiles of the surface charge densities on CH and OH groups for the phenolic compounds explain the effects of the isomers on the partition coefficients. It is thought that the partition coefficients result from the differences of the surface charge densities on the OH group for 2-, 3-, and 4-ethylphenols and on CH and OH groups for the 4-propylphenol and 2,3,5-trimethylphenol.

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