JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

ARTICLE

pubs.acs.org/jced

Partition of Substituted Benzenes between Hydrophobic Ionic Liquids and Water: Evaluation of Interactions between Substituents and Ionic Liquids

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ABSTRACT: The partition coefficients (P) of benzene and its various derivatives between hydrophobic ionic liquids and water were determined at 298.2 K. The ionic liquids used are 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([BuMeIm][NTf_2]), 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide ([BuMePyrr][NTf_2]), and 1-butyl-3-methylimidazolium hexafluorophosphate ([BuMeIm][PF_6]). For a given solute, the P value in the [BuMePyrr][NTf_2]/water system is nearly equal to that in the [BuMeIm][NTf_2]/water system. The P values of the alkylated benzenes and the chlorinated ones are slightly smaller in the [BuMeIm][PF_6]/water system than in the [BuMePyrr][NTf_2]/water system, whereas for the derivatives having polar substituents the P values in both the systems are comparable to each other. As compared to 1-octanol, all of the ionic liquids exhibit a higher extraction ability for aniline, benzonitrile, acetophenone, nitrobenzene, and anisole and a lower one for benzoic acid, phenol, and benzyl alcohol. The P values were analyzed by using the regular solution theory, and the contributions of solubility parameters, molar volumes, and solute−solvent specific interactions were evaluated. Each ionic liquid exhibits both the donor and the acceptor properties in the interaction with the polar substituents; the strength of the interaction decreases in the following substituent sequence: $-COOH \geq -OH > -OH$ (aliphatic) $> -NH_2 > -CN > -COCH_3 \geq -NO_2 > -OCH_3 > -Cl$.

INTRODUCTION

Liquid−liquid extraction is one of the most popular separation methods used both in laboratories and industries. A disadvantage of this method is to use lipophilic organic solvents most of which are volatile, flammable, and harmful for the environment. Room temperature ionic liquids have attracted much attention as green solvents because they are almost nonvolatile and their flammability and harmfulness are low. There is an increasing need for the use of ionic liquids as replacements for conventional organic solvents in the liquid−liquid extraction method.[1−3]

The extractability of uncharged compounds is simply governed by the partition coefficients P. Systematic accumulation of the partition coefficient data in various ionic liquid (IL)/water (W) systems is required to characterize the extraction properties of ionic liquids. There are relatively many studies on the $P_{IL/W}$ values of various compounds between 1-butyl-3-methylimidazolium hexafluorophosphate ([BuMeIm][PF_6]) and water.[4−8] However, the views from different workers for the partition behavior in this system are not consistent. Huddleston et al.[4] reported that the $P_{IL/W}$ values in the [BuMeIm][PF_6]/water system show a correlation with those in the 1-octanol (OcOH)/water system, although the former values are in general an order of magnitude lower than the corresponding latter values. Similar results were reported by Inoue et al.[7] Carda-Broch et al.[5] described as follows: for the compounds containing amino groups, the $P_{IL/W} > P_{OcOH/W}$; for the acidic and phenolic compounds, $P_{IL/W} \ll P_{OcOH/W}$; for the neutral compounds and the ionizable compounds with both acidic and basic substituents, $P_{IL/W} \approx P_{OcOH/W}$. Khachatryan et al.[6] described that the $P_{IL/W}$ values of phenols are comparable to their $P_{OcOH/W}$ values. The $P_{IL/W}$ data for other ionic liquids, which were measured for the actual ionic liquid/water two-phase systems, have been reported in only a few studies.[9,10] There are a large number of the $P_{IL/W}$ data calculated from infinite dilution activity coefficients, gas to ionic liquid partition coefficients, and solubilities of dissolved solutes in ionic liquids; Abraham et al. analyzed these partition data by using the Abraham's solvation parameter model.[11−14] They described that ionic liquids have solvation properties quite close to those for polar aprotic organic solvents.

The purpose of this study is to determine experimentally the $P_{IL/W}$ values of uncharged compounds in the ionic liquid/water two-phase systems and to clarify the characteristics of ionic liquids as extraction solvents. The ionic liquids used are three kinds of common hydrophobic salts, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([BuMeIm][NTf_2]), 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide ([BuMePyrr][NTf_2]), and 1-butyl-3-methylimidazolium hexafluorophosphate ([BuMeIm][PF_6]). The partitioning solutes are benzene and its simple substituted derivatives, that is, benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, 1,3,5-trimethylbenzene, chlorobenzene, *o*-dichlorobenzene, *m*-dichlorobenzene, *p*-dichlorobenzene, benzoic acid, phenol, benzyl alcohol, aniline, benzonitrile, acetophenone, nitrobenzene, and anisole. The $P_{IL/W}$ values obtained are analyzed by using the regular solution theory, and the specific interactions between the ionic liquids and the substituent groups are evaluated.

EXPERIMENTAL SECTION

Chemicals. Special grade reagents of [BuMeIm][NTf_2] (mass fraction $w = 1 \cdot 10^{-5}$ for water; $w = 2 \cdot 10^{-7}$ for Li; $w = 1 \cdot 10^{-7}$ for

Received: November 14, 2010
Accepted: February 12, 2011
Published: March 02, 2011

Na; $w = 1 \cdot 10^{-5}$ for F; $w = 1 \cdot 10^{-5}$ for Cl) and [BuMePyrr][NTf$_2$] ($w = 3 \cdot 10^{-6}$ for water; $w < 2 \cdot 10^{-7}$ for Li; $w < 1 \cdot 10^{-7}$ for Na; $w < 1 \cdot 10^{-6}$ for F; $w = 1 \cdot 10^{-6}$ for Cl) were supplied from Kanto Chemicals. [BuMeIm][PF$_6$] was prepared by mixing equal volumes of aqueous solutions of 5 $\text{mol} \cdot \text{dm}^{-3}$ [BuMeIm]Cl (Merck, > 98 % purity) and 6 $\text{mol} \cdot \text{dm}^{-3}$ NaPF$_6$ (Acros Organics, > 98.5 % purity); the ionic liquid phase separated from the aqueous phase was washed five times with deionized water (about 90 % yield). The purity was checked by atomic absorption spectrophotometry for Na$^+$ and ion-selective electrode potentiometry for Cl$^-$ ($w < 4 \cdot 10^{-7}$ for Na; $w < 3 \cdot 10^{-6}$ for Cl). Hexane and heptane (Kanto Chemicals, guaranteed reagent grade) were purified by stirring with fuming sulfuric acid (15 %, diluted with concentrated sulfuric acid) overnight, washing with water for five times, and distilling. Chloroform (Kanto Chemical, guaranteed reagent grade) and diethyl ether (Wako Pure Chemical, spectroscopic grade) were washed three times with water prior to use. Water was distilled and further deionized with a Milli-Q Labo system (Millipore). Other reagents were of guaranteed reagent grade and used without further purification.

Partition Experiments in Ionic Liquid/Water Systems. The ionic liquids were saturated with water at (298.2 ± 0.2) K, and the densities were measured at that temperature with an oscillating U-tube density meter (Anton Paar, DMA35n) calibrated with pure water; the densities were $(1.4311 \pm 0.0009)\ \text{g} \cdot \text{cm}^{-3}$ for water-saturated [BuMeIm][NTf$_2$], $(1.3919 \pm 0.0005)\ \text{g} \cdot \text{cm}^{-3}$ for water-saturated [BuMePyrr][NTf$_2$], and $(1.3550 \pm 0.0001)\ \text{g} \cdot \text{cm}^{-3}$ for water-saturated [BuMeIm][PF$_6$] from 5 to 8 measurements for each. The water-saturated ionic liquid and an ionic liquid-saturated water were placed in a stoppered glass tube, together with an aromatic compound whose concentration was adjusted to $(7 \cdot 10^{-4}$ to $1 \cdot 10^{-2})\ \text{mol} \cdot \text{dm}^{-3}$ against the volume of the ionic liquid phase. Here, the volume of the viscous ionic liquid phase was accurately evaluated from the mass by using the density described above, and the volume ratio of the ionic liquid phase to the aqueous phase was adjusted to 1/10. When the solute was benzoic acid, phenol, or aniline, the pH of the aqueous solution was preadjusted to (1.0 to 2.3), (3.3 to 7.1), or (7.0 to 11.6), respectively, with hydrochloric acid or an aqueous NaOH solution to suppress the dissociation or protonation of the solute; the pH dependence of the $P_{\text{IL/W}}$ value obtained was confirmed to be negligibly small in the pH range. 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 phase separation by centrifugation, the concentration of the solute in the aqueous phase was measured in the following manner. For benzoic acid, benzyl alcohol, or aniline, the concentration in the aqueous phase was determined spectrophotometrically ($\lambda_{\max} = 273.2$ nm, $\varepsilon = (969.1 \pm 0.7)\ \text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for benzoic acid; $\lambda_{\max} = 256.6$ nm, $\varepsilon = (185.0 \pm 0.4)\ \text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for benzyl alcohol; $\lambda_{\max} = 279.5$ nm, $\varepsilon = (1346 \pm 1)\ \text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for aniline). For phenol, an aliquot of the aqueous phase was transferred into another glass tube, and the concentration was determined spectrophotometrically after the pH was adjusted to about 13 with the addition of an aqueous NaOH solution ($\lambda_{\max} = 286.2$ nm, $\varepsilon = (2.49 \pm 0.04) \cdot 10^3\ \text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for phenolate). When the solute was benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, 1,3,5-trimethylbenzene, chlorobenzene, *o*-dichlorobenzene, *m*-dichlorobenzene, or *p*-dichlorobenzene, an aliquot of the aqueous phase was transferred into another stoppered glass tube, and hexane (the volume was 1/10 of that of the aqueous phase) was added into the tube. The two-phase mixture was stirred with a magnetic stirrer for 1 h to completely extract the solute from the aqueous phase into hexane. The solute concentration in the hexane phase was determined spectrophotometrically ($\lambda_{\max} = 254.5$ nm, $\varepsilon = (171 \pm 7)\ \text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for benzene; $\lambda_{\max} = 261.0$ nm, $\varepsilon = (226 \pm 2)\ \text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for toluene; $\lambda_{\max} = 262.4$ nm, $\varepsilon = (256 \pm 1)\ \text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for *o*-xylene; $\lambda_{\max} = 264.0$ nm, $\varepsilon = (259 \pm 2)\ \text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for *m*-xylene; $\lambda_{\max} = 266.0$ nm, $\varepsilon = (421 \pm 3)\ \text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for *p*-xylene; $\lambda_{\max} = 265.0$ nm, $\varepsilon = (202.7 \pm 0.8)\ \text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for 1,3,5-trimethylbenzene; $\lambda_{\max} = 264$ nm, $\varepsilon = (223 \pm 2)\ \text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for chlorobenzene; $\lambda_{\max} = 269.8$ nm, $\varepsilon = (321 \pm 6)\ \text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for *o*-dichlorobenzene; $\lambda_{\max} = 270.2$ nm, $\varepsilon = (346 \pm 5)\ \text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for *m*-dichlorobenzene; $\lambda_{\max} = 273.0$ nm, $\varepsilon = (448 \pm 6)\ \text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for *p*-dichlorobenzene). In the case of benzonitrile, the concentration in the aqueous phase was determined similarly, but chloroform was used instead of hexane ($\lambda_{\max} = 270.6$ nm, $\varepsilon = (816.7 \pm 0.5)\ \text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$). In the case of acetophenone, nitrobenzene, or anisole, the solute in the aqueous phase was extracted with heptane in a similar manner to that for benzene, and so forth ($\lambda_{\max} = 277.4$ nm, $\varepsilon = (865 \pm 5)\ \text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for acetophenone; $\lambda_{\max} = 251.0$ nm, $\varepsilon = (8.74 \pm 0.05) \cdot 10^3\ \text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for nitrobenzene; $\lambda_{\max} = 270.6$ nm, $\varepsilon = (1.96 \pm 0.03) \cdot 10^3\ \text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for anisole). Since these compounds were only partially extracted into heptane, the concentrations in the aqueous phase before extraction were calculated from the concentrations in the heptane phase by using their partition coefficients between heptane and water. In all of the cases, the solute concentration in the ionic liquid phase was calculated based on the mass balance, and the $P_{\text{IL/W}}$ value was calculated as the ratio of the molar concentration in the ionic liquid phase to that in the aqueous phase. Each $P_{\text{IL/W}}$ value was determined as a mean value from six measurements at 5- to 10-fold different initial concentrations of the solute; the lack of the concentration dependence of the $P_{\text{IL/W}}$ value was confirmed.

Some partition coefficients in the organic solvent (heptane, chloroform, or diethyl ether)/water systems were also determined in a similar manner to that for the ionic liquid/water systems.

Partition Experiments in [BuMeIm][NTf$_2$]/Heptane Systems. A two-phase mixture of heptane and a [BuMeIm][NTf$_2$] solution (saturated with heptane) containing $(4 \cdot 10^{-3}$ to $3 \cdot 10^{-2})\ \text{mol} \cdot \text{dm}^{-3}$ phenol or acetophenone was stirred for 1 h in a stoppered glass tube at (298.2 ± 0.2) K. Here, the volume ratio of the ionic liquid solution to heptane was adjusted to 1/3, and the dissolution of the ionic liquid into heptane was neglected. The solute concentration in the heptane phase was determined spectrophotometrically ($\lambda_{\max} = 270.6$ nm, $\varepsilon = (2019 \pm 5)\ \text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ for phenol; the data of $\lambda_{\max}$ and ε for acetophenone in heptane are above-described). The water content of the ionic liquid phase was $(2.4 \pm 0.4) \cdot 10^{-4}$ in mass fraction.

Determinations of Solubility of Hexane in Ionic Liquids. To determine the solubility parameters of the ionic liquids, the solubilities of hexane in the ionic liquids were measured as follows. The ionic liquids were saturated with hexane at (298.2 ± 0.2) K. The ionic liquid phase was transferred into a stoppered glass tube together with heptane, where the volume ratio of the ionic liquid phase to heptane was 1/3. The tube was stirred with a magnetic stirrer for 1 h. By this operation, more than 99 % of hexane in the ionic liquid phase was extracted into the heptane phase. The concentration of hexane in the heptane phase was

Table 1. Partition Coefficients of Benzene and Its Substituted Derivatives in Various Solvent (S)/Water (W) Systems at 298.2 K

	solute	log $P_{S/W}$						
		S = [BuMeIm][NTf$_2$]	[BuMePyrr][NTf$_2$]	[BuMeIm][PF$_6$]	heptane	1-octanol	chloroform	diethyl ether
1	benzene	2.344 ± 0.006	2.326 ± 0.006	2.22 ± 0.02 2.15[c]	2.29[d]	2.13[h]	2.80[g]	2.60 ± 0.01
2	toluene	2.70 ± 0.02 2.04 (295 K)[b]	2.72 ± 0.02	2.48 ± 0.01 2.38[c], 2.00 (295 K)[b]	2.85[e]	2.69[h]	3.41[g]	3.05 ± 0.02
3	*o*-xylene	3.048 ± 0.004	3.050 ± 0.007	2.773 ± 0.007	3.39[e]	3.12[g]		
4	*m*-xylene	3.06 ± 0.01	3.069 ± 0.007	2.775 ± 0.007	3.54[e]	3.20[g]		
5	*p*-xylene	3.067 ± 0.004	3.05 ± 0.01	2.78 ± 0.01	3.45[e]	3.15[g]		
6	1,3,5-trimethylbenzene	3.34 ± 0.01	3.48 ± 0.02	3.09 ± 0.01	4.082 ± 0.005	3.42[g]		
7	chlorobenzene	2.82 ± 0.01	2.78 ± 0.02	2.588 ± 0.009	2.92[d]	2.84[h]	3.46[g]	
8	*o*-dichlorobenzene	3.20 ± 0.02	3.12 ± 0.02	2.96 ± 0.02	3.37[d]	3.40[i]		
9	*m*-dichlorobenzene	3.203 ± 0.009	3.05 ± 0.01	2.88 ± 0.01	3.53[d]	3.53[i]		
10	*p*-dichlorobenzene	3.140 ± 0.009	3.088 ± 0.009	2.921 ± 0.007	3.53[d]	3.52[i]		
11	benzoic acid[a]	1.19 ± 0.01	1.11 ± 0.01	1.159 ± 0.005 1.72[c]	−1.16 ± 0.03	1.87[h]	0.46[j]	1.89[k]
12	phenol[a]	1.333 ± 0.003	1.369 ± 0.004	1.218 ± 0.008 1.20[c]	−0.90[f]	1.46[h]	0.36[j]	1.64[k]
13	benzyl alcohol	0.94 ± 0.03	0.866 ± 0.008	0.84 ± 0.02	−0.70[f]	1.10[h]	0.862 ± 0.009	0.917 ± 0.006
14	aniline[a]	1.55 ± 0.01	1.564 ± 0.009	1.545 ± 0.008 1.57[c]	−0.03[e]	0.90[h]	1.42[j]	0.85[g]
15	benzonitrile	1.987 ± 0.004	1.964 ± 0.003	2.010 ± 0.001	0.90[g]	1.56[h]	2.71[g]	1.88 ± 0.02
16	acetophenone	1.99 ± 0.02	1.917 ± 0.004	1.924 ± 0.009	1.129 ± 0.009	1.58[h]	2.79[g]	1.75[l]
17	nitrobenzene	2.257 ± 0.004	2.207 ± 0.007	2.245 ± 0.005	1.476 ± 0.009	1.85[h]	2.93[g]	2.27 ± 0.01
18	anisole	2.32 ± 0.01	2.332 ± 0.003	2.220 ± 0.007	2.125 ± 0.004	2.11[h]	3.12[g]	2.46[m]

[a] In a neutral form. [b] Ref 9. [c] Ref 5. [d] Ref 16. [e] Ref 17. [f] Ref 18. [g] Ref 15. [h] Ref 19. [i] Ref 20. [j] Ref 21. [k] Ref 22. [l] Ref 23. [m] Ref 24.

determined by gas chromatography (Shimadzu GC-14B with Shimadzu HiCap-CBP1-M25-025 fused silica capillary column and a flame ionization detector) using methanol as an internal standard; temperature conditions were 423 K for the injector and 333 K for the column and detector. The solubilities of hexane determined from three measurements for each ionic liquid were (0.27 ± 0.02) $\text{mol}\cdot\text{dm}^{-3}$ in [BuMeIm][NTf$_2$], (0.25 ± 0.02) $\text{mol}\cdot\text{dm}^{-3}$ in [BuMePyrr][NTf$_2$], and (0.078 ± 0.004) $\text{mol}\cdot\text{dm}^{-3}$ in [BuMeIm][PF$_6$].

RESULTS

The $P_{IL/W}$ values are summarized in Table 1. For a given solute, the $P_{IL/W}$ value in the [BuMeIm][NTf$_2$]/water system is almost equal to that in the [BuMePyrr][NTf$_2$]/water system. In general, an aromatic solvent has considerably different extraction property from an aliphatic one when they have similar molar volumes.[15] However, the $P_{IL/W}$ values for the aromatic and aliphatic ionic liquids ([BuMePyrr][NTf$_2$] and [BuMeIm][NTf$_2$], respectively) clearly show that the aromaticity of the cation has little contribution to the extraction property of the ionic liquid. Although the $P_{IL/W}$ values in the [BuMeIm][PF$_6$]/water system are also close to those in the [BuMeIm][NTf$_2$]/water system, the values for the alkylated or chlorinated benzenes are slightly smaller in the former system than in the latter one.

The partition coefficients between some organic solvents and water are also shown in Table 1, where the organic solvents are heptane, 1-octanol, chloroform, and diethyl ether.[16−24] For the alkylated or chlorinated benzenes, the partition coefficients are generally smaller for the ionic liquids than for the organic solvents, that is, chloroform > heptane ≥ 1-octanol ≥ ionic liquids. On the other hand, the partition coefficient of aniline is larger for the ionic liquids than for the organic solvents, that is, ionic liquids > chloroform > 1-octanol ≈ diethyl ether > heptane. For the other solutes having polar functional groups, the partition coefficients decrease in the following solvent sequences: diethyl ether ≈ 1-octanol > ionic liquids ≥ chloroform > heptane for the protic compounds (benzoic acid, phenol, and benzyl alcohol); chloroform > ionic liquids ≈ diethyl ether > 1-octanol ≥ heptane for the aprotic compounds (benzonitrile, acetophenone, nitrobenzene, and anisole). From the above, the ionic liquids have relatively high affinity for the compounds having polar functional groups, whereas they are not good solvents for the hydrophobic alkylated or chlorinated benzenes.

Assuming additivity of the substituent effects on the log P value, the contributions of substituents −X (the substituent constants), $\pi(-\text{X})$, were calculated from the data in Table 1:

$$\pi(-\text{X}) = \log P(\text{RX}) - \log P(\text{RH}) \qquad (1)$$

where $P(\text{RX})$ and $P(\text{RH})$ denote the partition coefficient of a substituted derivative RX and that of the parent compound RH, respectively. For example, $\pi(-\text{Cl})$ = log P(chlorobenzene) − log P(benzene) or 0.5·{log P(dichlorobenzene) − log P(benzene)}; π(aliphatic −OH) = log P(benzyl alcohol) − log P(toluene). The $\pi(-\text{X})$ values are summarized in Table 2. The values of $\pi(-\text{Cl})$, which were obtained from different chlorinated benzenes, are in good agreement with each other, supporting the additivity assumption. The same is true for the $\pi(-\text{CH}_3)$ values. In all of the ionic liquid/water systems, the values of

Table 2. Contributions of Substituents (−X) to Logarithmic Partition Coefficients of Substituted Benzenes at 298.2 K

substituent	$\pi(X)_{S/W}$						
	S = [BuMeIm][NTf$_2$]	[BuMePyrr][NTf$_2$]	[BuMeIm][PF$_6$]	heptane	1-octanol	chloroform	diethyl ether
$-CH_3$	0.35 ± 0.01[a]	0.37 ± 0.01[a]	0.28 ± 0.01[a]	0.58 ± 0.03[a]	0.51 ± 0.05[a] 0.56[d]	0.61	0.45
$-Cl$	0.43 ± 0.03[b]	0.40 ± 0.04[b]	0.35 ± 0.02[b]	0.60 ± 0.04[b]	0.69 ± 0.03[b] 0.71[d]	0.66	
$-COOH$	−1.15	−1.22	−1.06	−3.45	−0.26 −0.32[d]	−2.34	−0.71
$-OH$	−1.01	−0.96	−1.00	−3.19	−0.67[d]	−2.44	−0.96
$-OH$ (aliphatic)[c]	−1.76	−1.85	−1.64	−3.55	−1.59 −1.64[d]	−2.55	−2.13
$-NH_2$	−0.79	−0.76	−0.68	−2.32	−1.23[d]	−1.38	−1.75
$-CN$	−0.36	−0.36	−0.21	−1.39	−0.57[d]	−0.09	−0.72
$-COCH_3$	−0.35	−0.41	−0.30	−1.16	−0.55	−0.01	−0.85
$-NO_2$	−0.09	−0.12	0.02	−0.81	−0.28[d]	0.13	−0.33
$-OCH_3$	−0.02	0.01	0.00	−0.17	−0.02	0.32	−0.14

[a] Average value of $\pi(-CH_3)$ values calculated for toluene, *o*-xylene, *m*-xylene, *p*-xylene, and 1,3,5-trimethylbenzene. [b] Average value of $\pi(-Cl)$ values calculated for chlorobenzene, *o*-dichlorobenzene, *m*-dichlorobenzene, and *p*-dichlorobenzene. [c] Obtained by subtracting the log *P* value of toluene from that of benzyl alcohol. [d] Ref 15.

$\pi(-Cl)$ and $\pi(-CH_3)$ are positive, indicating that −Cl and $-CH_3$ have hydrophobic contributions. This is the same as in the general organic solvent (heptane, 1-octanol, and chloroform)/water systems. The π values for −Cl and $-CH_3$ in the ionic liquid/water systems are close to each other (0.3 to 0.5) and somewhat smaller than those in the normal organic solvent/water systems (0.5 to 0.7). This means that the hydrophobic contributions of these substituents are slightly smaller in the ionic liquid/water systems than in the organic solvent/water systems. The $\pi(-X)$ values of the other substituents are generally negative in both the ionic liquid/water and normal organic solvent (heptane, 1-octanol, chloroform, and diethyl ether)/water systems, indicating the hydrophilic contributions. The absolute value depends greatly on the kinds of solvents and substituents.

■ DISCUSSION

Evaluation of Log $P_{IL/w}$ Values by Regular Solution Theory. By applying the regular solution theory for a mixture of components A and B,[25] the activity (*a*) of A is expressed as

$$\ln a_A = \ln \varphi_A + (V_A {\varphi_B}^2/RT)(\delta_B - \delta_A)^2 + \varphi_B(1 - V_A/V_B) \quad (2)$$

where φ, δ, and *V* represent volume fraction, solubility parameter, and molar volume, respectively. The standard state for the activity a_A is pure liquid of A. The molar volumes of [BuMeIm][NTf$_2$], [BuMePyrr][NTf$_2$], and [BuMeIm][PF$_6$] are 291.6 $cm^3 \cdot mol^{-1}$,[26] 302.6 $cm^3 \cdot mol^{-1}$,[26] and 207.8 $cm^3 \cdot mol^{-1}$,[27] respectively. The solubility parameters of these ionic liquids were determined from the solubilities of hexane in the ionic liquids by using eq 2, where the literature values were used for the molar volume and solubility parameter of hexane (131.6 $cm^3 \cdot mol^{-1}$ and 14.9 $MPa^{1/2}$).[28] The solubility parameters calculated are 22.4 $MPa^{1/2}$ for [BuMeIm][NTf$_2$], 22.5 $MPa^{1/2}$ for [BuMePyrr][NTf$_2$], and 23.9 $MPa^{1/2}$ for [BuMeIm][PF$_6$]. These values are comparable to some literature values, for example, 21.3 $MPa^{1/2}$ for [BuMeIm][NTf$_2$], 21.1 $MPa^{1/2}$ for [BuMePyrr][NTf$_2$], and 25.1 $MPa^{1/2}$ for [BuMeIm][PF$_6$].[29]

Applying eq 2 to a system of immiscible solvents S1 and S2 containing a solute A, the following equation is derived:

$$\begin{aligned}\ln(\varphi_{A,S1}/\varphi_{A,S2}) = {} & \varphi_{S2}(1 - V_A/V_{S2}) - \varphi_{S1}(1 - V_A/V_{S1}) \\ & + (V_A/RT)\{\varphi_{S2}(\delta_A - \delta_{S2}) \\ & + \varphi_{S1}(\delta_A - \delta_{S1})\}\{\varphi_{S2}(\delta_A - \delta_{S2}) \\ & - \varphi_{S1}(\delta_A - \delta_{S1})\}\end{aligned} \quad (3)$$

When the concentration of A in each phase is sufficiently low, both φ_{S1} and φ_{S2} are nearly 1, and the volume fraction ratio, $\varphi_{A,S1}/\varphi_{A,S2}$, is equal to the partition coefficient in molarity scale, $P_{S1/S2}$:

$$\begin{aligned}\log P_{S1/S2} = {} & (V_A/2.303RT)\{RT(1/V_{S1} - 1/V_{S2}) \\ & + (\delta_{S2} + \delta_{S1} - 2\delta_A)(\delta_{S2} - \delta_{S1})\}\end{aligned} \quad (4)$$

This equation is based on the assumptions that the interaction forces act between the centers of the molecules and that the solute−solvent interaction is governed by nonspecific dispersion forces. However, specific and local interactions between the solvents and the functional groups of the solute, which are independent of the solute molar volume, are not considered. We introduced an additional energy term *E* for such specific solute−solvent interactions:[30,31]

$$\begin{aligned}\log P_{S1/S2} = {} & (V_A/2.303RT)\{RT(1/V_{S1} - 1/V_{S2}) \\ & + (\delta_{S2} + \delta_{S1} - 2\delta_A)(\delta_{S2} - \delta_{S1})\} \\ & + (E_{A,S1} - E_{A,S2})/2.303RT\end{aligned} \quad (5)$$

where $E_{A,S1}$ and $E_{A,S2}$ represent the energies for specific interactions of the solute A with the solvent S1 and S2, respectively. In general, the Hildebrand solubility parameters are determined from vaporization energies which include contributions from all of the intermolecular forces such as London dispersion, dipole−dipole, and hydrogen bond interactions. However, the δ_A value in eq 5 should include mainly

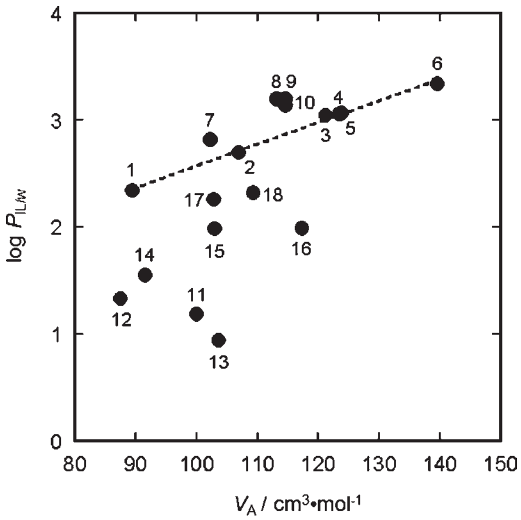

Figure 1. Partition coefficients between [BuMeIm][NTf$_2$] and water of benzene and its substituted derivatives as a function of the solute molar volume. The numbers of solutes correspond to those in Table 1. The regression line is drawn for a group of benzene and its alkylated derivatives.

the contribution from nonspecific dispersion forces because the contributions from other specific interactions are included in the $E_{A,S1} - E_{A,S2}$ term.[32] According to the Hansen's parameters,[33] all of the benzene derivatives used in this study have similar values of the dispersion component of the solubility parameter (18 MPa$^{1/2}$ to 20 MPa$^{1/2}$).

As seen from eq 5, the partition coefficient is a function of the solute molar volume. The plot of log $P_{IL/W}$ and V_A for the benzene derivatives in the [BuMeIm][NTf$_2$]/water system is shown in Figure 1, where the molar volumes of the solutes are cited from the literature.[28,33] A linear relationship between log $P_{IL/W}$ and V_A is observed for a group of benzene (solute No. 1) and its alkylated derivatives (solute No. 2 to 6). The same was true for the other ionic liquids, [BuMePyrr][NTf$_2$] and [BuMeIm][PF$_6$]. The alkylated benzenes not only have similar solubility parameter values (18.8 MPa$^{1/2}$ for benzene; 18.2 MPa$^{1/2}$ for toluene; 18.4 MPa$^{1/2}$ for *o*-xylene; 18.0 MPa$^{1/2}$ for *m*-xylene, *p*-xylene, and 1,3,5-trimethylbenzene) but also have no specific interactions, such as hydrogen bonding, with the solvents. In such a case, a linear relation between log $P_{IL/W}$ and V_A is expected from eq 5. From the slopes of the linear relations observed for the three ionic liquid/water systems, the empirical solubility parameter of water, δ_W, was calculated to be (34.5 ± 0.3) MPa$^{1/2}$. This δ_W value is close to the literature values, for example, 33.3 MPa$^{1/2}$,[34] 35.9 MPa$^{1/2}$,[35] and 36.2 MPa$^{1/2}$.[31] It can be concluded that the partition behavior of the alkylated benzenes in the ionic liquid/water systems are mostly governed by dispersion forces and explained by the regular solution theory. Chlorinated benzenes have somewhat larger $P_{IL/W}$ values than that expected from the relation between log $P_{IL/W}$ and V_A for the alkylated benzenes. The reason cannot be explained by the regular solution theory, but similar results are observed for other organic solvent/water systems such as heptane/water and 1-octanol/water.

According to eq 5, the result that the $P_{IL/W}$ values of the alkylated or chlorinated benzenes in the [BuMeIm][PF$_6$]/water system are slightly smaller than in the [BuMeIm][NTf$_2$]/water and [BuMePyrr][NTf$_2$]/water systems is explained in terms of the larger solubility parameter of [BuMeIm][PF$_6$]. The solubility parameters of [BuMeIm][NTf$_2$] and [BuMePyrr][NTf$_2$] are close to the value of 1-octanol (21.0 MPa$^{1/2}$).[33] Owing to this, the partition coefficients of the alkylated benzenes and the chlorinated ones in these [NTf$_2$]-based ionic liquid/water systems are comparable to those in the 1-octanol/water system. However, the slopes of the linear relationship between log P and V_A are smaller in the ionic liquid/water systems than in the 1-octanol/water system, resulting in the smaller values of $\pi(-\mathrm{Cl})$ and $\pi(-\mathrm{CH_3})$ for the former systems. This is caused by the fact that the molar volume of the solvent (V_{S1} in eq 5) is considerably larger for the ionic liquids (ca. 300 cm^3·mol^{-1}) than for 1-octanol (157.7 cm^3·mol^{-1}).[33]

In a given ionic liquid/water system, the log $P_{IL/W}$ value of *o*-dichlorobenzene is almost equal to that of *p*-dichlorobenzene, although these dichlorobenzenes have considerably different dipole moments (2.53 D for *o*-dichlorobenzene and 0 D for *p*-dichlorobenzene).[28] This fact indicates that the dipole moment of the solute is not an important factor affecting the solute partitioning between the ionic liquid and water. It appears that the dipole−dipole interaction between the solute and the solvent molecules in the aqueous phase is largely compensated by that in the ionic liquid phase. The $P_{IL/W}$ values of the benzene derivatives having polar substituents are much smaller than those expected from the linear relationships for the alkylated benzenes. This is attributed to the specific interactions, such as hydrogen bonding, of the polar substituents with water in the aqueous phase.

Interactions between Polar Substituents and Ionic Liquids. For quantitative evaluation of the specific interactions between the ionic liquids and the polar substituents, we consider the partition between ionic liquids and heptane (Hep), because heptane (as opposed to water) has no specific interaction with the solutes. The $P_{IL/Hep}$ values can be calculated from the following relation:

$$\log P_{IL/Hep} = \log P_{IL/W} - \log P_{Hep/W} \qquad (6)$$

Strictly speaking, the $P_{IL/Hep}$ values calculated in this way are the partition coefficients between water-saturated ionic liquid and water-saturated heptane. The solubility (in mass fraction) of water is 1.4·10^{-2} in [BuMeIm][NTf$_2$],[9] 1.17·10^{-2} in [BuMePyrr][NTf$_2$],[36] 2.3·10^{-2} in [BuMeIm][PF$_6$],[9] and 9.1·10^{-5} in heptane.[37] We compared the $P_{[BuMeIm][NTf_2]/Hep}$ values of phenol and acetophenone calculated from eq 6 with those experimentally determined between dry [BuMeIm][NTf$_2$] and heptane; log $P_{IL/Hep}$ (wet) = 2.23 for phenol and 0.86 for acetophenone; log $P_{IL/Hep}$ (dry) = 2.128 ± 0.003 for phenol and 0.894 ± 0.002 for acetophenone. The differences in the log $P_{IL/Hep}$ values between the water-saturated system and the dry system are 0.1 or less, indicating that the effect of water in the ionic liquid phase on the solute partitioning is sufficiently small.

The standard Gibbs free energy of transfer of a solute A from heptane to a solvent S, $\Delta G°_{Hep\rightarrow S}(A)$, is equal to $-2.303RT$ log $P_{S/Hep}(A)$. Therefore, the contribution of a substituent −X to $\Delta G°_{Hep\rightarrow S}(RX)$ is given by

$$\Delta G°_{Hep\rightarrow S}(-X) = -2.303RT\{\log P_{S/Hep}(RX) - \log P_{S/Hep}(RH)\} \qquad (7)$$

The $\Delta G°_{Hep\rightarrow S}(-X)$ values are summarized in Table 3. Applying eq 5 to eq 7, the $-\Delta G°_{Hep\rightarrow S}(-X)$ value is expressed as

Table 3. Contributions of Substituents (−X) to Standard Gibbs Free Energies of Transfer from Heptane to Solvents (S) at 298.2 K

substituent[a]	$\Delta G^\circ_{\mathrm{Hep}\to\mathrm{S}}(-\mathrm{X})/\mathrm{kJ}\cdot\mathrm{mol}^{-1}$						
	S = [BuMeIm][NTf$_2$]	[BuMePyrr][NTf$_2$]	[BuMeIm][PF$_6$]	water	1-octanol	chloroform	diethyl ether
$-CH_3$	1.3	1.2	1.7	3.3	0.4	−0.3	0.6
−Cl	1.0	1.2	1.4	3.4 (2.32)[b]	−0.5	−0.2	
−COOH	−13.1	−12.8	−13.6	−19.7	−18.2	−6.3	−15.6
−OH	−12.4	−12.7	−12.5	−18.2 (−19.35)[b]	−14.4	−4.3	−12.7
−OH (aliphatic)	−10.2	−9.7	−10.9	−20.3 (−25.95)[b]	−11.2	−5.7	−8.1
$-NH_2$	−8.7	−8.9	−9.4	−13.2	−6.2	−5.4	−3.3
−CN	−5.9	−5.9	−6.7	−7.9	−4.7	−7.4	−3.8
$-COCH_3$	−4.6	−4.3	−4.9	−6.6	−3.5	−6.6	−1.8
$-NO_2$	−4.2	−4.0	−4.8	−4.6 (−8.60)[b]	−3.0	−5.4	−2.8
$-OCH_3$	−0.8	−1.0	−0.9	−0.9	−0.8	−2.8	−0.1

[a] On a benzene ring except for −OH (aliphatic). [b] Standard Gibbs free energy of hydration of a substituent (ref 38).

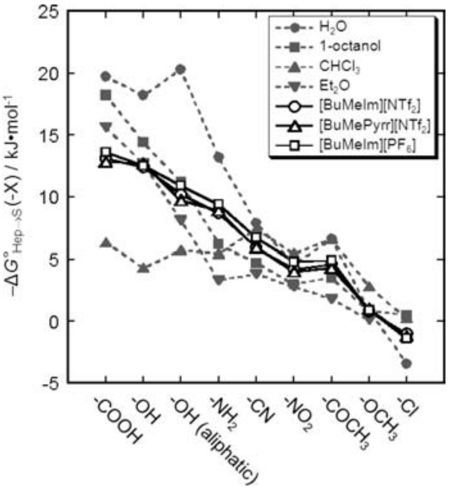

Figure 2. Graphical presentation of the contributions of substituents to the standard Gibbs free energies of transfer from heptane to other solvents.

follows:

$$
\begin{aligned}
-\Delta G^\circ_{\mathrm{Hep}\to\mathrm{S}}(-\mathrm{X}) = {} & V_{\mathrm{RX}}\{RT(1/V_{\mathrm{S}} - 1/V_{\mathrm{Hep}}) \\
& + (\delta_{\mathrm{Hep}} + \delta_{\mathrm{S}} - 2\delta_{\mathrm{RX}})(\delta_{\mathrm{Hep}} - \delta_{\mathrm{S}})\} \\
& - V_{\mathrm{RH}}\{RT(1/V_{\mathrm{S}} - 1/V_{\mathrm{Hep}}) \\
& + (\delta_{\mathrm{Hep}} + \delta_{\mathrm{S}} - 2\delta_{\mathrm{RH}})(\delta_{\mathrm{Hep}} - \delta_{\mathrm{S}})\} \\
& + \{(E_{\mathrm{RX,S}} - E_{\mathrm{RX,Hep}}) \\
& - (E_{\mathrm{RH,S}} - E_{\mathrm{RH,Hep}})\} \qquad (8)
\end{aligned}
$$

When $\delta_{\mathrm{RX}} \approx \delta_{\mathrm{RH}}$, $E_{\mathrm{RX,S}} \gg E_{\mathrm{RX,Hep}}$, and $E_{\mathrm{RH,S}} \gg E_{\mathrm{RH,Hep}}$, eq 8 is transformed into

$$
\begin{aligned}
-\Delta G^\circ_{\mathrm{Hep}\to\mathrm{S}}(-\mathrm{X}) = {} & V_{-\mathrm{X}}\{RT(1/V_{\mathrm{S}} - 1/V_{\mathrm{Hep}}) \\
& + (\delta_{\mathrm{Hep}} + \delta_{\mathrm{S}} - 2\delta_{\mathrm{RH}})(\delta_{\mathrm{Hep}} - \delta_{\mathrm{S}})\} + E_{-\mathrm{X,S}} \qquad (9)
\end{aligned}
$$

Where $V_{-\mathrm{X}}$ and $E_{-\mathrm{X,S}}$ equal to $V_{\mathrm{RX}} - V_{\mathrm{RH}}$ and $E_{\mathrm{RX,S}} - E_{\mathrm{RH,S}}$, respectively. For the polar substituents studied, absolute values of the first term on the right side of eq 9 are about 0.3 kJ·mol^{-1} or less when S = the ionic liquids, chloroform, and diethyl ether; about 2 kJ·mol^{-1} or less when S = water and 1-octanol. Therefore, the $-\Delta G^\circ_{\mathrm{Hep}\to\mathrm{S}}(-\mathrm{X})$ value is generally governed by the $E_{-\mathrm{X,S}}$ value and can be regarded as a measure of the strength of the specific interaction between a substituent −X and a solvent S. Indeed, when S = water, the $\Delta G^\circ_{\mathrm{Hep}\to\mathrm{S}}(-\mathrm{X})$ values are comparable to the standard Gibbs free energies of hydration of the substituents (the values[38] are included in Table 3), and a positive correlation is found between these free energies.

Figure 2 shows a graphical representation of the $-\Delta G^\circ_{\mathrm{Hep}\to\mathrm{S}}(-\mathrm{X})$ values for different S and −X (polar substituents and −Cl), where the substituents on the abscissa are aligned in the sequence of decreasing electron acceptor ability estimated from theoretical calculations and the $E_{\mathrm{T}}^{\mathrm{N}}$ parameters.[39,40] Protic functional groups, particularly −COOH and −OH, have strong electron acceptor ability. The electron donor solvents such as 1-octanol and diethyl ether have larger $-\Delta G^\circ_{\mathrm{Hep}\to\mathrm{S}}(-\mathrm{X})$ values (i.e., stronger interactions) for these substituents than for the other substituents. Water also shows a similar tendency in the interaction with the substituents. In addition, the interaction of water is generally stronger than that of 1-octanol and diethyl ether; this is particularly remarkable for the substituents having strong electron donor ability such as −OH (aliphatic), $-NH_2$, and $-COCH_3$, owing to the electron acceptor ability of water. Chloroform, which is a typical electron acceptor solvent, shows stronger or equally strong interactions with −CN, $-COCH_3$, $-NO_2$, $-OCH_3$, and −Cl, as compared to water. The ionic liquids all show the interaction which decreases in the following substituent sequence: −COOH ≥ −OH > −OH (aliphatic) > $-NH_2$ > −CN > $-COCH_3$ ≥ $-NO_2$ > $-OCH_3$ > −Cl. This sequence is similar to those observed for 1-octanol and diethyl ether, indicating that the ionic liquids have electron donor properties. The interaction of the acidic substituents, −COOH and −OH, is generally weaker with the ionic liquids than with 1-octanol and diethyl ether. However, the ionic liquids have a higher affinity with $-NH_2$ and polar aprotic substituents than 1-octanol and diethyl ether. For the polar aprotic substituents, the interaction with the ionic liquids is as strong as that with chloroform. These results suggest that the ionic liquids can act as electron acceptors as well as donors. The component cation and anion of the ionic liquids are expected to act as an electron acceptor and a donor, respectively. According to our results, the ionic liquids are stronger in the electron acceptor ability and weaker in the electron donor ability, as compared to 1-octanol. Such a view is almost consistent with that reported by Carda-Broch et al.[5] in the solvation parameter analysis for [BuMeIm][PF$_6$]. The interactions of the ionic liquids with most of the substituents are weaker than those of water.

The $-\Delta G^\circ_{\mathrm{Hep}\rightarrow\mathrm{S}}(-\mathrm{X})$ values with the three ionic liquids are close to each other, indicating that these ionic liquids are similar in the interaction with all of the substituents. When viewing the details of the $\Delta G^\circ_{\mathrm{Hep}\rightarrow\mathrm{S}}(-\mathrm{X})$ values, it is seen that the affinity with a polar substituent is generally slightly higher for [BuMeIm][PF_6] than for [BuMeIm][NTf_2] and [BuMePyrr][NTf_2]. [BuMeIm][PF_6] is considered to be a little stronger as both an electron donor and an acceptor than the other two ionic liquids. This may suggest that the donor and acceptor abilities of the ionic liquid correspond to the degree of ion dissociation; the effective ionic concentrations of the ionic liquids are reported to be 3.3 $\mathrm{mol \cdot dm^{-3}}$, 2.3 $\mathrm{mol \cdot dm^{-3}}$, and 1.8 $\mathrm{mol \cdot dm^{-3}}$ for [BuMeIm][PF_6], [BuMePyrr][NTf_2], and [BuMeIm][NTf_2], respectively.[41]

■ CONCLUSION

In the ionic liquid/water two-phase systems, the partition behavior of alkylated benzenes can be accounted for by the regular solution theory; the ionic liquids behave like normal molecular solvents, where an ion pair corresponds to a solvent molecule. The same is almost true for chlorinated benzenes. 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 the [NTf_2]-based ionic liquids, are close to that of 1-octanol. However, the contributions of the substituents $-CH_3$ and $-Cl$ to the logarithmic partition coefficient values are somewhat smaller for the ionic liquid/water systems than for the 1-octanol/water system, owing to the greater molar volumes of the ionic liquids than that of 1-octanol. The partitioning of the benzene derivatives having polar substituents in the ionic liquid/water systems are 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 was evaluated by determining the contribution of the substituent to the standard Gibbs free energy of transfer from heptane to the solvent. It was found that each ionic liquid has both the properties as an electron donor and an acceptor. The ionic liquids are stronger acceptors and weaker donors than 1-octanol. As a result, the ionic liquids exhibit a higher extraction ability for aniline, benzonitrile, acetophenone, nitrobenzene, and anisole and a lower one for benzoic acid and phenol.

[BuMeIm][NTf_2] and [BuMePyrr][NTf_2] are almost the same in the solubility parameter, the molar volume, and the specific interaction with the substituents. Therefore, they have very similar extraction properties for all of the aromatic compounds studied. It can be concluded that the aromaticity of the cation has little contribution to the extraction property. On the other hand, [BuMeIm][PF_6] has a slightly larger solubility parameter and a slightly stronger specific interaction with polar substituents than [BuMeIm][NTf_2]. The partition coefficients of the alkylated or chlorinated benzenes are a little lower for [BuMeIm][PF_6] than for [BuMeIm][NTf_2], owing to the difference in the solubility parameters of these ionic liquids. The partition coefficients of the benzene derivatives having polar substituents are almost the same for [BuMeIm][PF_6] and [BuMeIm][NTf_2], because the effect of the solubility parameter is compensated by that of the specific interaction.

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Funding Sources

This research was financially supported by a Grant-in-Aid for Scientific Research (No. 22550070) from the Ministry of Education, Culture, Sports, Science and Technology of Japan and a Grant for Environmental Research Projects (No. 093155) from the Sumitomo Foundation.

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