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Ionic Liquids/Water Distribution Ratios of Some Polycyclic Aromatic Hydrocarbons

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By using the shake-flask procedure, the distribution ratios (D) at infinite dilution and 298.1 K of 15 polycyclic aromatic hydrocarbons (PAHs) between room-temperature ionic liquids, 1-alkyl-3-methylimiazolium hexafluorophosphates ([C_nMIM][PF_6], $n = 4$ and 8), and water were determined. The log D values are in the range of 3.34−4.36, which increased very slowly with the molar mass of PAHs.

Introduction

Room-temperature ionic liquids (ILs) are gaining wide recognition as potential environmental benign solvents. Some unique properties of ILs such as the negligible vapor pressure, low flammability, tuneable viscosity, and the miscibility in water and other organic solvents merit their consideration as an alternative recyclable medium for synthesis, catalysis, and separation.[1,2] ILs were recently considered as attractive water-immiscible phases for liquid−liquid extraction of target substances; however, the very limited physicochemical data such as the distribution ratios of solutes between ILs and water has delayed their application.

Dai et al.[3] studied the extraction of Sr^{2+} from an aqueous phase into disubstituted imidazolium hexafluorophosphates and 1,1,1-trifluo-N-[(trifluoromethyl)sulfonyl]methanesulfonamide ILs by dicyclohexano-18-crown-6, and it was found that distribution ratios (D) values in ILs with 1,1,1-trifluo-N-[(trifluoromethyl)sulfonyl]methanesulfonamide are much larger than those with hexafluorophosphates. Later, the D values of Na^+, Cs^+, and Sr^{2+} in 1-alkyl-3-methylimiazolium hexafluorophosphates ([C_nMIM][PF_6], $n = 4$, 6, and 8)/water with crown ethers as extractant were reported.[4,5] Heavy metal ions such as Cd^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Cu^{2+}, Ag^+, and Fe^{3+} and actinides in the [C_4MIM][PF_6]/water system with various organic and inorganic extractants[6−8] were also determined. Visser et al.[9] prepared a series of task-specific ILs by appending urea-, thiourea-, and thioether-substituted alkyl groups to imidazoles and determined the D values of Hg^{2+} and Cd^{2+} between the task-specific ILs and water.

ILs have also been applied to extract organic compounds from aqueous solutions. The *D* values of a series of organic compounds in [C_4MIM][PF_6]/water system were determined, and it was reported that the D values in octanol/water are in general an order of magnitude higher than those in [C_4MIM][PF_6]/water.[10] While Abraham et al.[11] calculated and determined the D values for some organic compounds in ILs/water systems, Carda-Broch et al.[12] investigated in detail the solvent properties of [C_4MIM][PF_6] and determined the [C_4MIM][PF_6]/water and [C_4MIM][PF_6]/heptane distribution ratios for a set of 40 compounds, including organic acids, organic bases, amino acids, antioxidants, and neutral compounds.

The D values of these above target compounds in the ILs/water system reported in reference were determined using the traditional procedure, i.e., aliquots of ILs (1−3 mL) were mixed with aqueous solutions and vortexed for the prescribed time, then the mixtures were centrifuged to separate the two phases, and the compounds in the two phases were determined by radio analysis,[9] atomic absorption,[7] or high-performance liquid chromatography (HPLC)[12] measurement. Finally the distribution ratio was calculated according to the concentration ratio between the two phases. However, this method suffered from the fact that it is impossible to determine the distribution ratio of very hydrophobic compounds such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) by this procedure.

Currently, the shake-flask and slow-stirring methods are widely applied to determine the distribution coefficient in octanol/water systems (K_{ow}).[13−16] The slow-stirring method has been shown to be applicable for the determination of K_{ow} values of very hydrophobic compounds, as slow stirring can prevent the formation of microemulsion of octanol in the water phase. In the shake-flask procedure, however, microemulsion of octanol forms in the water phase and thus prevents the reliable determination of compounds with large K_{ow} values.[13]

In this present study, the distribution ratio at infinite dilution (D) of some PAHs between [C_nMIM][PF_6] ($n = 4$ and 8) and water were determined. Since the IL phase and the water phase can be separated easily after mixing and shaking, the shake-flask procedure was adopted in this study.

Experimental Section

Materials. A mixed PAHs standard solution containing the 16 American Environmental Protection Agency (EPA) priority PAHs (shown in Table 1) was purchased from AccuStandard Inc. (New Haven, CT). 1-Methylimidazole (99%), 1-chlorobutane (99%), 1-chloroctane (99%), and

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Table 1. Fluorescence Detection Wavelength (FL) and the Determined Ionic Liquids/Water Distribution Ratios (log D) (Mean ± Standard Deviation, 3 Measurements) at Infinite Dilution at 298.1 K of Some PAHs

	FL (nm)			log D	
compounds	excitation	emission	log K_{ow}[a]	$[C_4MIM][PF_6]$/water	$[C_8MIM][PF_6]$/water
naphthalene	218	357	3.24 to 3.40	3.34 ± 0.06	3.51 ± 0.07
acenaphthylene	218	357	4.33	ND[b]	ND
acenaphthene	226	359	4.07	3.71 ± 0.07	3.86 ± 0.16
fluorene	226	359	4.18	3.82 ± 0.15	3.97 ± 0.19
phenanthrene	250	350	4.46 to 4.64	4.06 ± 0.12	4.14 ± 0.07
anthracene	250	425	4.55 to 4.79	4.15 ± 0.10	4.12 ±0.33
fluoranthene	234	440	5.12 to 5.31	4.20 ± 0.13	4.23 ± 0.17
pyrene	234	440	5.0 to 5.18	4.21 ± 0.11	4.21 ± 0.20
benz[*a*]anthracene	286	405	5.74 to 6.04	4.22 ± 0.15	4.17 ± 0.14
chrysene	286	405	5.63 to 5.94	4.22 ± 0.14	4.23 ± 0.18
benzo[*b*]fluoranthene	250	420	5.78	4.31 ± 0.17	4.26 ± 0.18
benzo[*k*]fluoranthene	250	420	5.86 to 6.28	4.30 ± 0.20	4.22 ± 0.19
benzo[*a*]pyrene	294	460	5.91 to 6.28	4.32 ± 0.18	4.32 ± 0.16
dibenz[a,h]anthracene	298	420	6.5	4.30 ± 0.21	4.23 ± 0.18
benzo[ghi]perylene	298	420	5.95 to 6.38	4.31 ± 0.22	4.30 ± 0.18
indenol[1,2,3cd]pyrene	246	490	7.04	4.36 ± 0.17	4.31 ± 0.18

[a] References 16, 20, and 21. [b] Not detected.

hexafluorophosphoric acid (60 (m/m)% solution in water) were obtained from Acros Organics. HPLC-grade methanol and acetonitrile were purchased from Scharlace Chemie SA, Barcelona, Spain. All other chemicals were of analytical grade (Beijing Chemicals Corporation, Beijing, China), and ultrapure water (EASYpure LF) was used throughout.

Appratus and Procedure. The synthesis and some physicochemical properties of $[C_nMIM][PF_6]$ ($n = 4$ and 8) ILs were described in our previous study.[17] Briefly, $[C_nMIM]Cl$ ($n = 4$ and 8) was prepared by adding equal amounts (0.2 mol) of 1-methylimidazole and 1-chlorobutane or 1-chloroctane to a round-bottomed flask fitted with a reflux condenser and reacting for 48 h at 343 K. $[C_nMIM][PF_6]$ ($n = 4$ and 8) mixtures were prepared by slowly adding hexafluorophosphoric acid (0.13 mol) to each of their corresponding chlorides (0.1 mol) in 100 mL of water. After stirring for 12 h, the lower liquid portion was washed with water until the washings were no longer acidic. The ILs were cleaned up with Al_2O_3 and dried under a vacuum at 353 K. The obtained two ILs were colorless viscous liquids, and the determined density (293.1 K) and viscosity (298.1 K) were 1.37 g/mL and 393 mPa·s for $[C_4MIM][PF_6]$ and 1.20 g/mL and 710 mPa·s for $[C_8MIM][PF_6]$, respectively. The chloride and water content were 107 mg/L and 920 mg/kg for $[C_4MIM][PF_6]$ and 102 mg/L and 366 mg/kg for $[C_8MIM][PF_6]$, respectively.

ILs and water were presaturated with each other by adding 50 mL of IL and 900 mL of water in a 1000-mL flask and shaking occasionally for 48 h at (298.1 ± 0.2) K. Then the two phases were separated and collected. Following the presaturation, the D value of PAHs in the IL−water system were determined between the water-saturated IL and the IL-saturated water. To a 500-mL flask were added 4 mL of water-saturated IL and 0.02 mg each of PAHs (100 μL of 200 mg/L mixed PAHs standard), and then 400 mL of IL-saturated water was added. After shaking and mixing, the mixtures were kept at (298.1 ± 0.2) K with occasional shaking for 48 h. Then, the IL and the aqueous phases were separated. The PAHs concentration in the IL phase can be determined directly. For determining the PAHs concentration in the aqueous phase, the aqueous phase was extracted twice and each time with 30 mL of dichloromethane. The extractants were combined, the dichloromethane solvent was removed under a gentle stream of nitrogen, and the residue was dissolved by adding methanol to obtain a total volume of 5 mL for the $[C_4MIM][PF_6]$/water system and 1 mL for the $[C_8MIM][PF_6]$ system, respectively.

The PAH concentrations in IL and aqueous phases were determined by direct injection of 20 μL of the above prepared solutions into the HPLC system and quantified by external standard method. The HPLC equipment used was an Agilent 1100LC including a gradient (BinPump) pump, a UV/Vis (VWD) detector set at 254 nm wavelength, and a fluorescence (FLD) detector. The excitation and the emission wavelength of the fluorescence detector were set as shown in Table 1. HPLC separation of PAHs was conducted by using a C_{18} analytical column (Inertsil ODS-P, 250 mm × 4.6 mm inside diameter, 5 μm particles, GL Sciences, Inc., Japan) and a mixture of acetonitrile and water as mobile phase at a flow rate of 1.0 mL/min. The gradient profile was 55 (v/v)% acetonitrile for (0−5) min, increase to 60 (v/v) % acetonitrile during (5−13) min and keep to 20 min, then increase to 80 (v/v)% acetonitrile during (20−25) min, 90 (v/v) % acetonitrile during (25−28) min, and 100 (v/v)% acetonitrile during (28−30) min. The 100 (v/v)% acetonitrile was kept to 70 min and decreased to 55 (v/v)% acetonitrile in 5 min.

In HPLC determination, blank ILs gave many matrix peaks when detected by a UV detector, but this was much improved by using a fluorescence detector. As the concentrations of PAHs are relatively high, all the studied PAHs (except acenaphthylene) can be easily identified and quantified. The concentrations of naphthalene, acenaphthene, and fluorine were quantified based on the peak area obtained with the UV detection, while the other PAHs were quantified based on the peak area of fluorescence detection.

The distribution ratio at infinite dilution of a PAH between $[C_nMIM][PF_6]$ ($n = 4$ and 8) and water (D, dimensionless) was calculated from the ratio of its concentration (mg/L) in the IL phase (C_{IL}) to that in the aqueous phase (C_{aq})

$$\mathrm{D} = C_{IL}/C_{aq}$$

Three separate measurements for the D values were made by using the above-described procedures. Reported values of log D are the arithmetic average of the three independent measurements, and the standard deviation of these replicate measurements was taken to be the estimate of the uncertainty in the reported mean value.

Results and Discussion

Table 1 shows the measured log D values of 15 PAHs in the $[C_4MIM][PF_6]$/water and the $[C_8MIM][PF_6]$/water systems at infinite dilution at 298.1 K as well as their log K_{ow} values. As can be seen, the log D values of low molar mass PAHs, including naphthalene, acenaphthene, and fluorene in the $[C_4MIM][PF_6]$/water system are lower than that in the $[C_8MIM][PF_6]$/water system, while there are no significant differences between the values in these two systems for the other studied PAHs. The log D value of fluoranthene in the $[C_4MIM][PF_6]$/water system determined in this study (4.20 ± 0.13) is very close to the value (4.22) theoretically calculated by Abraham et al.[11] According to their calculated result, the log D value of fluoranthene in the $[C_6MIM][PF_6]$/water system is 3.75. This is lower than our experimentally determined values in the $[C_4MIM][PF_6]$/water system (4.20 ± 0.13) and $[C_4MIM][PF_6]$/water system (4.23 ± 0.17). This result is reasonable and is due to the unusual behavior of $[C_6MIM][PF_6]$ which has the highest polarity of these three homologues.[5,18]

Table 1 also indicates that, in contrast to the log K_{ow}, which increased significantly with the molar mass of PAHs, the log D value for $[C_nMIM][PF_6]$/water ($n = 4$ and 8) increased very slowly with molar mass for the high molecular PAHs. Thus, while the D value for $[C_nMIM][PF_6]$/water ($n = 4$ and 8) is almost the same as the K_{ow} for naphthalene, the D values are in general 1−3 orders of magnitude lower than the K_{ow} values for high molar mass PAHs. This is not in agreement with the result of Huddleston et al.,[6] who reported that the distribution ratios in the $[C_4MIM][PF_6]$/water system are in general an order of magnitude lower than those in octanol/water. However, our results are reasonable as the polarity of $[C_4MIM][PF_6]$ was reported to be in the same region of lower alcohols such as methanol and ethanol,[11,19] and generally the solubility of PAHs in ethanol decreased with the increasing of molar mass. For example, the solubility of anthracene in ethanol (15 g/L) is much less than that of naphthalene (77 g/L). Therefore, it is expected that the change of PAHs solubility in $[C_nMIM][PF_6]$ ($n = 4$ and 8) should have a similar tendency as in ethanol, and the increase of D in the $[C_nMIM][PF_6]$ ($n = 4$, 8)/water system should not be as significant as K_{ow}.

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