



Octanol/Water Partition Coefficients of Pyridinium-Based Ionic Liquids

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Nine pyridinium-based ionic liquids were synthesised, which include 1-butylpyridinium bromide ([BPYR] [Br]), 1-hexylpyridinium bromide ([HPYR][Br]), 1-octylpyridinium bromide ([OPYR][Br]), 1-hexylpyridinium *bis*(trifluoromethylsulfonyl)imide ([HPYR] [NTf₂]), 1-octylpyridinium *bis*(trifluoromethylsulfonyl)imide ([OPYR][NTf₂]), 1-hexylpyridinium trifluoromethanesulfonate ([HPYR] [TFO]), 1-octylpyridinium trifluoromethanesulfonate ([OPYR][TFO]), 1-hexylpyridinium tetrafluoroborate ([HPYR] [BF₄]), 1-octylpyridinium tetrafluoroborate ([OPYR][BF₄]). The octanol/water partition coefficients (K_{OW}) of these pyridinium-based ionic liquids were determined by shake-flask method. It is found that the pyridinium-based ionic liquids measured in this work are extremely hydrophilic except for [OPYR] [NTf₂]. It is also found that K_{OW} s of [NTf₂] ionic liquids were dependent on the concentration and high ionic liquids concentration in water leads to big K_{OW} .

Keywords: Ionic liquids, Octanol-water partition coefficients, Pyridinium.

INTRODUCTION

Ionic liquids (ILs) are a novel class of room temperature molten salts with melting points near ambient temperature. In recent years, ionic liquids have attracted an increasing attention in the chemical industry for their attractive properties such as negligible vapour pressure, thermomechanical and electrochemical stability, a wide temperature range for liquids, solvating properties for diverse materials, wide electrochemical window. Furthermore, the possible combinations between cations and anions lead to an enormous number of viable ionic liquids.

As one kind of ionic liquids, pyridinium based ionic liquids, whose structures are shown in Fig. 1, have been widely researched for their multiplicate uses. Firstly, they have an active role in chemical reactions and catalysis, which is one of the most important applications of pyridinium based ionic liquids¹⁻⁶. For their capacity of dissolving a variety of solutes, pyridinium based ionic liquids were found effective for extraction processes^{7,8} and widely used as reaction solvent^{9,10}. For the properties of low viscosity and high conductivities pyridinium based ionic liquids were applied in electrolytic media¹¹.

Ionic liquids are called environmental friendly solvents for their negligible vapour pressures, which may reduce the air pollution with respect to the typical volatile organic solvents. Although ionic liquids can lessen the risk of air pollution, a release of ionic liquids from industrial processes into aquatic

environments may lead to water pollution. 1-Octanol/water partition coefficient (K_{OW}) is a key parameter in determining the distribution and fate of compounds in the environment. It basically gives direct information on the hydrophobicity of a compound. Some papers have reported K_{OW} of ionic liquids. Ropel *et al.*¹² reported the K_{OW} of 12 imidazolium-based ionic liquids and found that these ionic liquids will not accumulate or concentrate in the environment for the K_{OW} values are very small. Lee *et al.*¹³ investigated the K_{OW} of 1-butyl-3-methylimidazolium ionic liquids containing either hexafluorophosphate or *bis*(trifluoromethyl)sulfonylamide over a wide range of ionic liquid concentrations and the log K_{OW} value of [bmim][Tf₂N] (2.06) was found to be similar to those of organic solvents such as butyl ethyl ether (2.0), chloroform (2.0) and benzene (2.1). Chapeaux *et al.*¹⁴ predicted K_{OW} for 15 imidazolium, pyridinium and quaternary ammonium ionic liquids using the nonrandom two liquid (NRTL) and electrolyte nonrandom two liquid (eNRTL) excess Gibbs energy models. de los Ríos *et al.*¹⁵ determined K_{OW} of 6 imidazolium-based ionic liquids and the K_{OW} value was used as a key parameter for the selective behaviour of the supported liquid membranes. However, most of the researches focus on imidazolium based ionic liquids and few K_{OW} s data of pyridinium-based ionic liquids were determined by experiment.

In this work, we have synthesised nine pyridinium-based ionic liquids and determined the K_{OW} of these ionic liquids by shake-flask method.

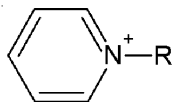


Fig. 1. Structure of pyridinium cation

EXPERIMENTAL

Details of the purities of chemicals and procurement are given in Table-1.

All the ionic liquids are synthesized using reported method^{16,17}. The nine pyridinium-based ionic liquids are 1-butylpyridinium bromide ([BPYR][Br]), 1-hexylpyridinium bromide ([HPYR][Br]), 1-octylpyridinium bromide ([OPYR][Br]), 1-hexylpyridinium *bis*(trifluoromethylsulfonyl)imide ([HPYR][NTf₂]), 1-octylpyridinium *bis*(trifluoromethylsulfonyl)imide ([OPYR][NTf₂]), 1-hexylpyridinium trifluoromethanesulfonate ([HPYR][TFO]), 1-octylpyridinium trifluoromethanesulfonate ([OPYR][TFO]), 1-hexylpyridinium tetrafluoroborate ([HPYR][BF₄]) and 1-octylpyridinium tetrafluoroborate ([OPYR][BF₄]). The structures of these ionic liquids were confirmed using ¹H NMR. All the synthesis progresses are as following:

[BPYR][Br], [HPYR][Br] and [OPYR][Br]: Pyridine was reacted with an excess (10 %) of an alkyl halide (1-bromobutane, 1-bromohexane, or 1-bromooctane) in acetonitrile at 70 °C for 24 h. After cooling to room temperature, the solvent was removed by rotary evaporation. The product was washed with ethyl acetate 3 times and then washed with water and ethyl acetate (1:1) 3 times. After filtered, ethyl acetate and water were removed by rotary evaporation and the resulting product was set under vacuum for 24 h. 1-Alkylpyridinium halide ([BPYR][Br], [HPYR][Br] or [OPYR][Br]) was obtained as a white solid.

[BPYR][Br]: ¹H NMR (500 MHz, CDCl₃, δ): 9.574-9.538 (2H, d, CH_{pyr-o}), 8.525-8.465 (H, t, CH_{pyr-p}), 8.145-8.085 (2H, t, CH_{pyr-m}), 4.965-4.910 (2H, t, N-CH₂), 2.000-1.930 (2H, m, CH₂), 1.385-1.295 (2H, m, CH₂), 0.896-0.844 (3H, t, CH₃).

[HPYR][Br]: ¹H NMR (500 MHz, CDCl₃, δ): 9.635-9.565 (2H, d, CH_{pyr-o}), 8.610-8.550 (H, t, CH_{pyr-p}), 8.235-8.175 (2H, t, CH_{pyr-m}), 5.050-4.980 (2H, t, N-CH₂), 2.115-2.018 (2H, m, CH₂), 1.482-1.233 (6H, m, C₃H₆), 0.883-0.825 (3H, t, CH₃).

[OPYR][Br]: ¹H NMR (500 MHz, CDCl₃, δ): 9.580-9.532 (2H, d, CH_{pyr-o}), 8.595-8.535 (H, t, CH_{pyr-p}), 8.224-8.176 (2H, t, CH_{pyr-m}), 5.040-4.987 (2H, t, N-CH₂), 2.110-2.020 (2H, m, CH₂), 1.438-1.182 (10H, m, C₅H₁₀), 0.890-0.830 (3H, t, CH₃).

[HPYR][NTf₂] and [OPYR][NTf₂]: An excess (10 %) of lithium *bis*(trifluoromethylsulfonyl)imide was reacted with 1-alkylpyridinium halide ([HPYR][Br] or [OPYR][Br]) in water at room temperature for 12 h. Then the product was washed with methylene chloride and water (5:1) until there was no silver bromide found when the product was added in silver nitrate. After filtering and rotary evaporating, the product was set under high vacuum for 24 h 1-alkylpyridinium *bis*(trifluoromethylsulfonyl)imide ([HPYR][Tf₂N] or [OPYR][Tf₂N]) was obtained as a light-yellow liquid.

[HPYR][NTf₂]: ¹H NMR (500 MHz, CDCl₃, δ): 8.860-8.805 (2H, d, CH_{pyr-o}), 8.525-8.465 (H, t, CH_{pyr-p}), 8.085-8.015

(2H, t, CH_{pyr-m}), 4.620-4.550 (2H, t, N-CH₂), 2.040-1.950 (2H, m, CH₂), 1.422-1.234 (6H, m, C₃H₆), 0.895-0.805 (3H, t, CH₃).

[OPYR][NTf₂]: ¹H NMR (500 MHz, CDCl₃, δ): 8.870-8.810 (2H, d, CH_{pyr-o}), 8.535-8.475 (H, t, CH_{pyr-p}), 8.100-8.010 (2H, t, CH_{pyr-m}), 4.630-4.550 (2H, t, N-CH₂), 2.071-1.948 (2H, m, CH₂), 1.490-1.160 (10H, m, C₅H₁₀), 0.800-0.825 (3H, t, CH₃).

[HPYR][TFO] and [OPYR][TFO]: An excess (10 %) of potassium trifluoromethanesulfonate was reacted with 1-alkylpyridinium halide ([HPYR][Br] or [OPYR][Br]) in acetonitrile at room temperature for 12 h. After filtering and removal of acetonitrile by rotary evaporation, the product was washed with methylene chloride 1 time. After filtering, the product was washed with methylene chloride and water (5:1) until there was no silver bromide found when the product was added in silver nitrate. After filtering and rotary evaporating, the product was set under high vacuum for 24 h 1-alkylpyridinium *bis*(trifluoromethylsulfonyl)imide ([HPYR][TFO] or [OPYR][TFO]) was obtained as a white solid.

[HPYR][TFO]: ¹H NMR (500 MHz, CDCl₃, δ): 9.005-8.955 (2H, d, CH_{pyr-o}), 8.520-8.460 (H, t, CH_{pyr-p}), 8.105-8.035 (2H, t, CH_{pyr-m}), 4.715-4.635 (2H, t, N-CH₂), 2.040-1.950 (2H, m, CH₂), 1.421-1.217 (6H, m, C₃H₆), 0.944-0.795 (3H, t, CH₃).

[OPYR][TFO]: ¹H NMR (500 MHz, CDCl₃, δ): 8.870-8.810 (2H, d, CH_{pyr-o}), 8.535-8.475 (H, t, CH_{pyr-p}), 8.100-8.030 (2H, t, CH_{pyr-m}), 4.635-4.555 (2H, t, N-CH₂), 2.054-1.942 (2H, m, CH₂), 1.436-1.177 (10H, m, C₅H₁₀), 0.905-0.815 (3H, t, CH₃).

[HPYR][BF₄] and [OPYR][BF₄]: An excess (10 %) of sodium tetrafluoroborate was reacted with 1-alkylpyridinium halide ([HPYR][Br] or [OPYR][Br]) in acetonitrile at room temperature for 12 h. After filtering and removal of acetonitrile by rotary evaporation, the product was washed with methylene chloride 1 time. After filtering, the product was washed with methylene chloride and water (5:1) until there was no silver bromide found when the product was added in silver nitrate. After filtering and rotary evaporating, the product was set under high vacuum for 24 h 1-alkylpyridinium tetra-fluoroborate ([HPYR][BF₄] or [OPYR][BF₄]) was obtained as a white solid.

[HPYR][TFO]: ¹H NMR (500 MHz, CDCl₃, δ): 8.875-8.880 (2H, d, CH_{pyr-o}), 8.555-8.455 (H, t, CH_{pyr-p}), 8.100-8.000 (2H, t, CH_{pyr-m}), 4.650-4.570 (2H, t, N-CH₂), 2.025-1.920 (2H, m, CH₂), 1.410-1.199 (6H, m, C₃H₆), 0.883-0.771 (3H, t, CH₃).

[OPYR][TFO]: ¹H NMR (500 MHz, CDCl₃, δ): 8.885-8.830 (2H, d, CH_{pyr-o}), 8.540-8.480 (H, t, CH_{pyr-p}), 8.110-8.040 (2H, t, CH_{pyr-m}), 4.675-4.585 (2H, t, N-CH₂), 2.050-1.945 (2H, m, CH₂), 1.442-1.144 (10H, m, C₅H₁₀), 0.885-0.805 (3H, t, CH₃).

There are many methods to determine the K_{ow} values, such as the shake-flask method, the slow-stirring method, the generator-column method, the chromatograph method, *etc.* As a tradition method the shake-flask method was used in this work. This method¹⁸ was used for determining K_{ow} of halogen benzoic acids. A diagram of the experimental apparatus is shown in Fig. 2. The apparatus consisted of a 40 mL, 90 mm tall glass vial containing a 2 mm diameter glass tubing which was used for taking sample from water-rich.

1-Octanol and water are not completely immiscible. At 25 °C, the solubility of water in octanol is approximately 0.275 mol/L¹⁹ and the solubility of 1-octanol in water is 7.5 × 10⁻⁵

TABLE-1
PURITIES OF CHEMICALS USED IN THE EXPERIMENT

No.	Name	Purity (%)	Company
1	Lithium bis(trifluoromethylsulfonyl)imide	98	Alfa Aesar
2	Potassium trifluoromethanesulfonate	98	Alfa Aesar
3	1-Bromobutane	98	Tianjin Guangfu Technology Development Co. Ltd, China
4	1-Bromohexane	98	Tianjin Guangfu Technology Development Co. Ltd, China
5	1-Bromooctane	98	Tianjin Guangfu Technology Development Co. Ltd, China
6	Methylene chloride	99.5	Tianjin Guangfu Technology Development Co. Ltd, China
7	Acetonitrile	Reagent	Tianjin Guangfu Technology Development Co. Ltd, China
8	Ethyl acetate	99.5	Tianjin Guangfu Technology Development Co. Ltd, China
9	Sodium tetrafluoroborate	98	Tianjin Guangfu Technology Development Co. Ltd, China
10	Octanol	Reagent	Tianjin Guangfu Technology Development Co. Ltd, China

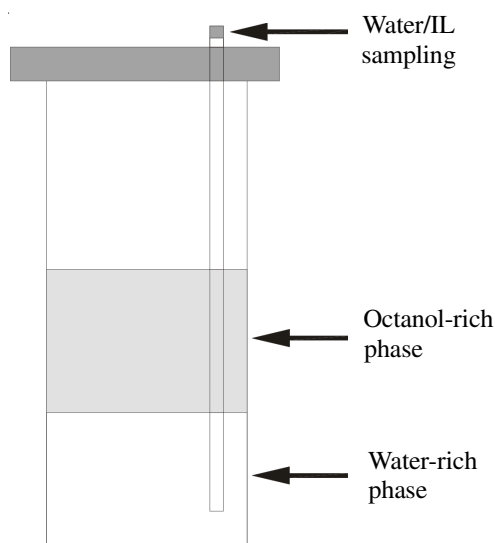


Fig. 2. Diagram of the experimental apparatus

mol/L²⁰. Therefore the water was presaturated with 1-octanol and 1-octanol was presaturated with water first. 10 mL 1-octanol-ionic liquid "stock" solution, consisting of 1-octanol presaturated with water and a known amount of ionic liquid was added to the vial. 10 mL water that had been presaturated with 1-octanol was added to the vial. Then the glass tubing was sealed by teflon to prevent 1-octanol and water evaporation. The vial was shook in constant temperature shaker (WE-1, Ounuo co. Tianjin, China) slowly to prevent the emulsion at room temperature 25 ± 0.1 °C for 12 h. Then the sample was stood for 24 h at 25 ± 0.1 °C to separate the two phases. The sample was withdrawn from the water-rich phase using a syringe. Concentration of ionic liquid in water-rich phase was measured using an ultraviolet spectrophotometer (U-3010, Hitachi Ltd., Tokyo, Japan), which has a sensitivity of ± 0.0001 absorbance units. The above process was repeated 3 times for each ionic liquid at a concentration and the average data was recorded as the result. And for each ionic liquid K_{ow} is determined at 3 concentrations.

K_{ow} is defined as:

$$K_{ow} = \frac{C^o}{C^w} \quad (1)$$

where C^o and C^w are extremely dilute concentrations of the test compound in water and 1-octanol phases. ionic liquids will have a greater tendency to dissociate in the water-rich phase. Due to the difficulty of this measurement, K_{ow} is reported as¹²:

$$K_{ow} = \frac{[MX]^o + [M^+]^o}{[MX]^w + [M^+]^w} \quad (2)$$

where $[MX]^o$ and $[MX]^w$ are concentrations of ionic liquid in 1-octanol and water phases; $[M^+]^o$ and $[M^+]^w$ are concentrations of cation in 1-octanol and water phases.

In this work K_{ow} is reported as:

$$K_{ow} = \frac{[MX]_0^o \times V^o - ([MX]^w + [M^+]^w) \times V^w}{([MX]^w + [M^+]^w) \times V^o} \quad (3)$$

where V^w and V^o are the volume of water and 1-octanol phases; $[MX]_0^o$ is the concentration of ionic liquid in 1-octanol phase when it was added to the vial.

In this work, because $V^w = V^o = 10$ mL, eqn. 3 can be simplified as:

$$K_{ow} = \frac{[MX]_0^o - ([MX]^w + [M^+]^w)}{[MX]^w + [M^+]^w} \quad (4)$$

RESULTS AND DISCUSSION

The values of K_{ow} for the nine ionic liquids are listed in Table-2. The maximum absorbance (λ_{max}) of the nine pyridinium-based ionic liquids in water is 259 nm. The correlation coefficients (R^2) of standard curves are also given in Table-2 and the result shows that the standard curves are all quite precise. K_{ow} is determined at different concentrate, therefore the concentrate ranges of ionic liquids in water/(mol/L) are shown in Table-2. The K_{ow} values were influenced by the concentrate of ionic liquids and the K_{ow} ranges of ionic liquids are presented in Table-2 as well.

The results indicate that the pyridinium-based ionic liquids measured in this work are extremely hydrophilic except for [OPYR][NTf₂]. The K_{ows} of ionic liquids are determined by both cation and anion. For the cation influence: K_{ows} increase with the carbon number of -R, which can be seen from Fig. 3. For the anion influence: NTf₂ > TFO > BF₄ > Br, which is shown in Fig. 4.

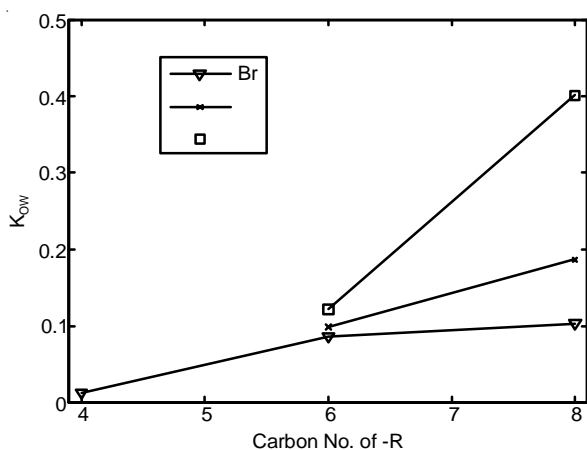
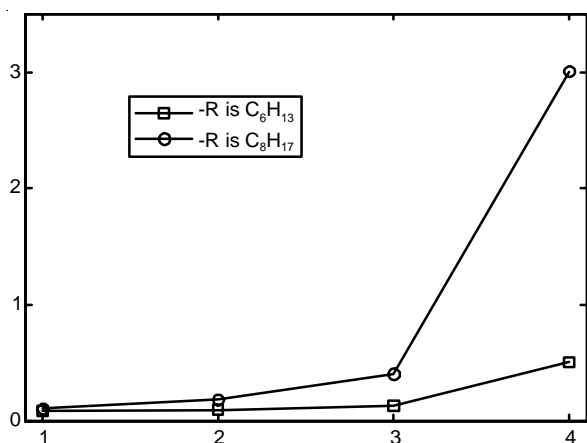
It is found that the K_{ows} of [TNf₂] ionic liquids were dependent upon concentration, which is shown clearly in Table-3. The K_{ows} of [OPYR][NTf₂] and [HPYR][NTf₂] are all changes with ionic liquids concentration in water. High ionic liquids concentration in water leads to big K_{ow} . For [OPYR][NTf₂], K_{ow} changes from 2.0 to 4.1 when ionic liquids concentration changes from 4.38×10^{-5} to 1.04×10^{-4} mol/L. For [HPYR][NTf₂], K_{ow} changes from 0.32 to 0.72 when ionic liquids concentration changes from 1.01×10^{-4} to 3.11×10^{-4} mol/L.

TABLE-2
 RESULTS OF THE K_{OW} S DETERMINATION

Compounds	K_{OW}	K_{OW} range	Concentration ranges of ILs in water (mol/L)	λ_{max} in water (nm)	R^2
[BPYR][Br]	0.014	0.011-0.018	1.27×10^{-4} – 5.08×10^{-4}	259	0.9998
[HPYR][Br]	0.087	0.073-0.102	1.04×10^{-4} – 4.17×10^{-4}	259	0.9999
[OPYR][Br]	0.10	0.10-0.11	9.04×10^{-5} – 3.76×10^{-4}	259	0.9999
[HPYR][BF ₄]	0.098	0.093-0.1039	1.04×10^{-4} – 4.32×10^{-4}	259	0.9995
[OPYR][BF ₄]	0.19	0.12-0.23	9.79×10^{-5} – 3.92×10^{-4}	259	0.9996
[HPYR][TFO]	0.12	0.11-0.14	8.52×10^{-5} – 3.56×10^{-4}	259	0.9998
[OPYR][TFO]	0.40	0.39-0.42	5.28×10^{-4} – 2.13×10^{-4}	259	1.0000
[HPYR][NTf ₂]	0.50	0.32-0.72	1.00×10^{-4} – 3.12×10^{-4}	259	0.9998
[OPYR][NTf ₂]	3.0	2.0-4.1	4.34×10^{-5} – 1.04×10^{-4}	259	1.0000

 TABLE-3
 INFLUENCE OF IONIC LIQUIDS CONCENTRATION IN WATER ON THE K_{OW} S DETERMINATION

[OPYR][NTf ₂]		[HPYR][NTf ₂]	
Concentration ranges of ILs in water (mol/L)	K_{OW}	Concentration ranges of ILs in water (mol/L)	K_{OW}
4.38×10^{-05}	2.0	1.01×10^{-04}	0.32
6.70×10^{-05}	2.9	1.84×10^{-04}	0.45

Fig. 3. Influence of -R on the 1-octanol/water partition coefficient (K_{OW})Fig. 4. Influence of anion on the 1-octanol/water partition coefficient (K_{OW})

Conclusion

In this work, nine pyridinium-based ionic liquids were synthesized. Then the K_{OW} of these nine pyridinium-based ionic liquids were determined by shake-flask method. It is found that pyridinium-based ionic liquids measured in this work are extremely hydrophilic except for [OPYR][NTf₂]. The K_{OW} s of ionic liquids are both determined by cation and anion. For

the cation influence: K_{OW} s increase with the carbon number of -R. For the anion influence: NTf₂ > TFO > BF₄ > Br. It is also found that the K_{OW} s of [NTf₂] ionic liquids were dependent on concentration. High ionic liquids concentration in water leads to big K_{OW} .

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