

Solution Thermodynamics of Imidazolium- Based Ionic Liquids and Water

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Introduction

- Using ILs & water as a solvent
 - ILs have high selectivity and diffusion coefficients as extraction solvents
 - Extraction of hydrophilic solute from ILs
 - Cross – contamination
 - Recovery of **ILs** from water
 - Change of physical properties of ILs
 - Requirement of phase behavior of ILs–water

Introduction

- Recovery of biofuels
 - Distillation
 - highly energy consumption process
 - Existing organic solvent (tri-*n*-butyl phosphate, octan-1-ol etc.)
 - flammable, toxic and hazardous
 - Using ILs (ILs + water)
 - Mutual solubility affects the selectivity of BuOH.
 - Lower solubility of ILs in water make the large selectivity

Introduction

- Extraction of metal ion by crown ether
 - Efficiency depends on both the cation and the anion.
 - Difficulty of transporting inorganic anion to organic solvent
 - ILs have high solubility with crown ether and the distribution coefficient
- Hydrophilic products using ILs as a solvent
 - Ionic liquid as a catalyst or solvent
 - Good selectivity and yield
 - Friedel–craft, Diels–Alder, alkylation reaction etc.

General properties of mixture ILs and water

- Miscible or immiscible
 - [bmim][BF₄] is miscible with water at room T but show UCST at low temperature (−8 and 5 °C)
 - “hydrophobic” ILs → immiscibility
 - The mutual solubility can be quite large
- Effect alkyl chain length and anion
 - Halide, ethanoate, nitrate and trifluoroacetate salts
 - totally miscible with water
 - [PF₆], [(CF₃SO₂)₂N] salts
 - Immiscible
 - Large chain length → Decrease solubility

ILs-vapor system

- 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF₆]
- 1-octyl-3-methylimidazolium hexafluorophosphate [C₈mim][PF₆]
- 1-octyl-3-methylimidazolium tetrafluoroborate [C₈mim][BF₄]

ILs-vapor system

Solubility of Water Vapor in Ionic Liquids

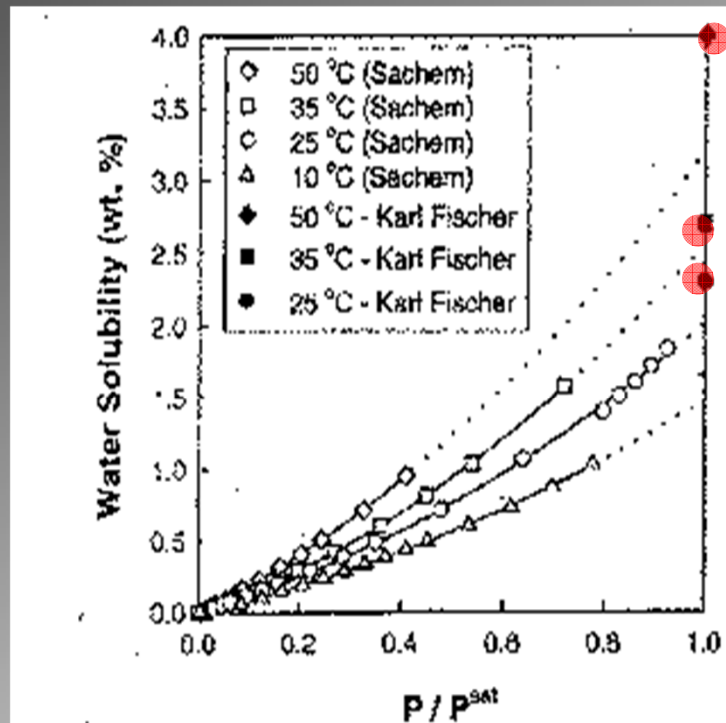


Figure 1. Solubility of Water Vapor in [bmim][PF₆].

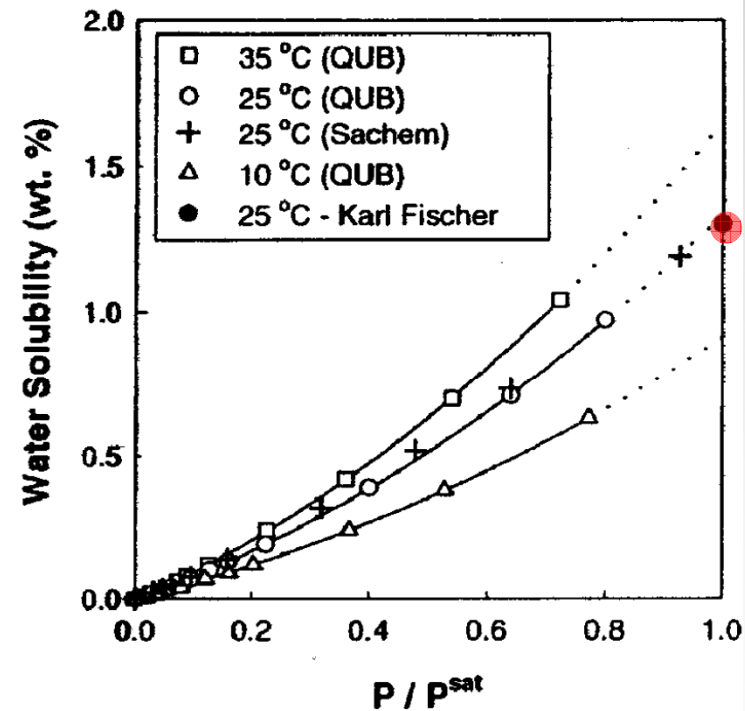


Figure 2. Solubility of Water Vapor in [C₈mim][PF₆].

ILs-vapor system

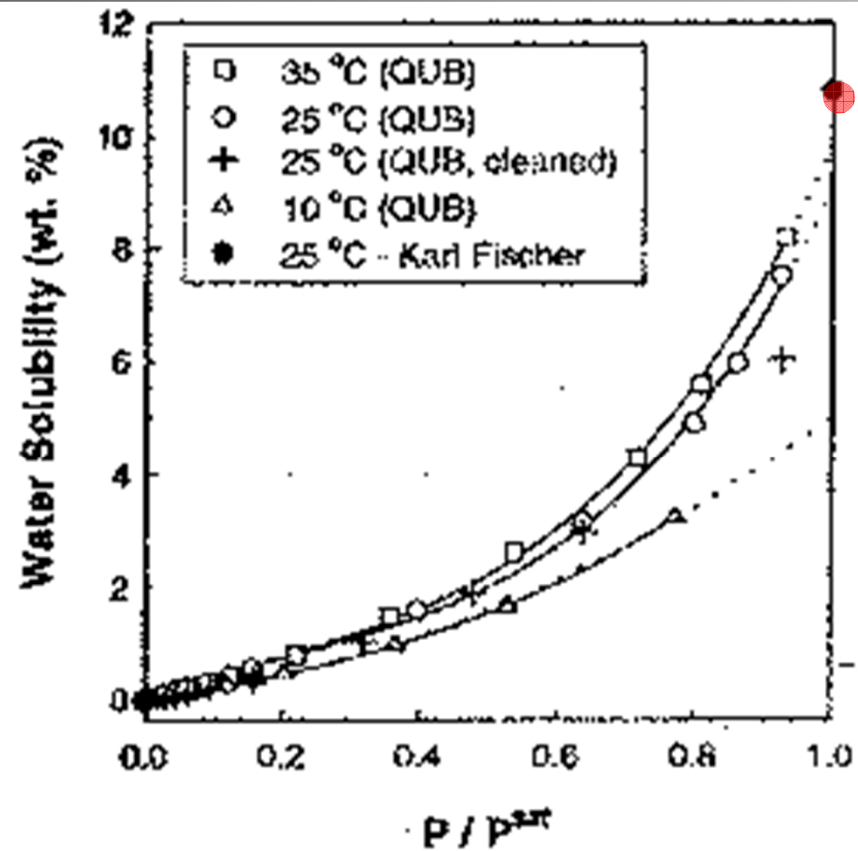


Figure 3. Solubility of Water Vapor in $[\text{C}_6\text{mim}][\text{BF}_4]$.

ILs-vapor system

◀ Factor to influence the solubility of water ▶

- Anion ([C8mim][PF₆], [C8mim][BF₄])
 - Van der Waals volume [PF₆] : 68 Å³ [BF₄] : 48 Å³
 - High charge density for smaller anion
 - ▶ large solubility of water
- Temperature
 - Lower temperature Higher solubility
- Alkyl chain
 - Increasing the length of alkyl chain length decrease the solubility of water
- Chloride impurities

ILs-vapor system

◀ Factor to influence solubility ▶

- Water – Water interaction

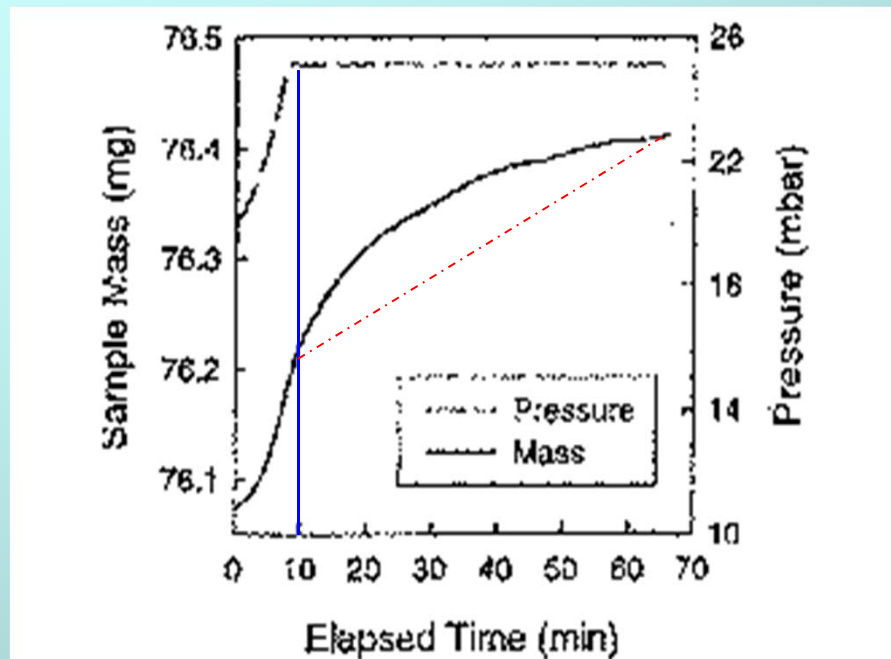


Figure 4. Solubility of Water Vapor in [bmim][PF₆] as a Function of Time at 25 °C and 25 mbar.

LLs –vapor

- Henry's constant & Infinite-Dilution Activity Coefficients

$$\phi_1 \cdot y_1 \cdot P = \gamma_1 \cdot x_1 \cdot f_1^o$$

$$P = \gamma_1 \cdot x_1 \cdot P_1^{sat}$$

$$H_1(T, P) \equiv \lim_{x_1 \rightarrow 0} \frac{f_1^L}{x_1}$$

$$H_1(T) = \lim_{x_1 \rightarrow 0} \gamma_1 \cdot P_1^{sat}$$

or

$$\gamma_1^\infty = \frac{H_1(T)}{P_1^{sat}}$$

Organic solvents - water vapor

TABLE 1: Henry's Law Constants, H_1 , and Infinite Dilution Activity Coefficients, γ^∞ , for Water in [C₅mim][BF₄], [bmim][PF₆] and [C₈mim][PF₆] (the error in γ^∞ is consistent with that given for H_1)

T (°C)	P^{sat} (bar)	[C ₅ mim][BF ₄]		[bmim][PF ₆]		[C ₈ mim][PF ₆]	
		H_1 (bar)	γ^∞	H_1 (bar)	γ^∞	H_1 (bar)	γ^∞
10	0.012	0.033 ± 0.014	2.65	0.09 ± 0.02	6.94	0.11 ± 0.03	8.62
25	0.031	0.055 ± 0.006	1.76	0.17 ± 0.02	5.36	0.20 ± 0.03	6.51
35	0.055	0.118 ± 0.014	2.13	0.25 ± 0.04	4.45	0.30 ± 0.02	5.87
50	0.122			0.45 ± 0.05	3.73		

TABLE 2: Literature Values for Henry's Law Constants, H_1 , and Infinite Dilution Activity Coefficients, γ^∞ , for Water in Various Organic Solvents

T (°C)	P^{sat} (bar)	Methanol ²³		Ethanol ²³		2-Propanol ²³		Acetone ²³	
		H_1 (bar)	γ^∞	H_1 (bar)	γ^∞	H_1 (bar)	γ^∞	H_1 (bar)	γ^∞
10	0.012								
15	0.017					0.10	5.88		
25	0.031	0.13	4.19	0.10	3.23				
35	0.055	0.09	1.64					0.34	6.18
45	0.096	0.17	1.77			0.34	3.54	0.54	5.63
50	0.122	0.40	3.28						
55	0.157	0.27	1.72			0.53	3.38	0.83	5.29

T (°C)	P^{sat} (bar)	Benzene ²²		Carbon Tetrachloride ²²		Cyclohexane ²²	
		H_1 (bar)	γ^∞	H_1 (bar)	γ^∞	H_1 (bar)	γ^∞
10	0.012	6	500	25	2083	78	6500
15	0.017						
25	0.031	10	323	37	1194	97	3129
35	0.055	13	236	46	836	105	1909
45	0.096						
50	0.122						
55	0.157						

ILs-Liquid

TABLE 5: Liquid-Liquid Equilibrium Results for Water with [C₈mim][BF₄], [bmim][PF₆], or [C₈mim][PF₆] at Ambient Conditions

ionic liquid	IL in aqueous phase		water in IL phase	
	wt. %	mol fraction	wt. %	mol fraction
[C ₈ mim][PF ₆]	0.7 ± 0.1	3.50 × 10 ⁻⁴	1.3 ± 0.5	0.20
[bmim][PF ₆]	2.0 ± 0.3	1.29 × 10 ⁻³	2.3 ± 0.2	0.26
[C ₈ mim][BF ₄]	1.8 ± 0.5	1.17 × 10 ⁻³	10.8 ± 0.5	0.63

TABLE 7: Liquid-Liquid Equilibrium Results for Water and [bmim][PF₆] at Various Temperatures

T (°C)	IL in aqueous phase		water in IL phase	
	wt. %	mol fraction	wt. %	mol fraction
25	2.0 ± 0.3	1.29 × 10 ⁻³	2.3 ± 0.2	0.26
35	2.2 ± 0.2	1.40 × 10 ⁻³	2.7 ± 0.3	0.30
50	2.7 ± 1.3	1.74 × 10 ⁻³	4.0 ± 0.3	0.40

ILs-Liquid

◀ Factor to influence solubility ▶

- Shorter alkyl chain, smaller anion
 - ▶ large solubility
- Temperature
 - ▶ At high temperature, mutual solubility is large

LLE of Water – organic compounds

TABLE 6: Liquid-Liquid Equilibrium Results for Water and Various Organics at Ambient Conditions

organic	org. in aqueous phase		water in org. phase	
	wt. %	mol fraction	wt. %	mol fraction
Benzene	0.176 ³¹	3.9×10^{-4}	0.066 ²²	2.20×10^{-3}
Toluene	0.052 ³²	1.0×10^{-4}	0.045 ³⁰	2.80×10^{-3}
Carbon Tetrachloride	0.08 ³²	9.4×10^{-5}	0.010 ²²	8.60×10^{-4}
Cyclohexane	0.006 ³³	1.3×10^{-5}	0.007 ²²	3.40×10^{-4}
<i>n</i> -Butanol ³⁴	7.38	1.9×10^{-2}	20.3	0.51
Cyclohexanol ³⁴	3.77	7.1×10^{-3}	12.1	0.43
<i>n</i> -Pentanol ³⁴	1.92	3.8×10^{-3}	9.0	0.34
<i>n</i> -Hexanol ³⁴	0.56	1.0×10^{-3}	6.7	0.29
<i>n</i> -Octanol ³⁴	0.051	7.0×10^{-4}	3.5	0.21
<i>n</i> -Decanol ³⁴	3.7×10^{-3}	4.2×10^{-6}	4.0	0.27
<i>n</i> -Dodecanol ³⁴	2.3×10^{-4}	2.3×10^{-7}	1.4	0.13

Recovery IL from water

- Adsorption of IL from Aqueous phase
 - For removal of Ionic liquids in Aqueous phase
 - Using Activated carbon

TABLE 8: Percent of [bmim][PF₆] Remaining in Water Using Activated Carbon (± 3%)

mass of AC/ initial mass of contaminant	[bmim][PF ₆] 2 day eq. time UV-vis	2 day eq. time ICP-OES	2 week eq. time	Toluene ²⁷
0.060				25.4
0.061				28.9
0.076				33.1
0.078				20.9
0.182				18.2
0.294	99			
1.31	82	80		
2.17			88	
3.37	56	46		
4.29			64	
5.31	21	15		
5.75	6			
7.21	2			
9.99			0.15	

Conclusion

- ILs is available for extracting solvents
- Mutual solubility with water is affected by species of ILs and their substances
- Relatively high solubilities of ionic liquids in water induce another environmental problem
- Removal of ILs will be especially important