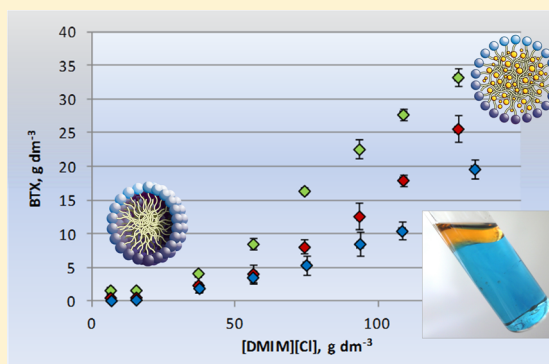


Solubilization of Benzene, Toluene, and Xylene (BTX) in Aqueous Micellar Solutions of Amphiphilic Imidazolium Ionic Liquids

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ABSTRACT: Water-soluble ionic liquids may be considered analogues to cationic surfactants with a corresponding surface activity and ability to create organized structures in aqueous solutions. For the first time, the enhanced solubility of the aromatic hydrocarbons, benzene, toluene, and xylene, in aqueous micellar systems of 1-alkyl-3-methylimidazolium chlorides was investigated. Above a critical micelle concentration, a gradual increase in the concentration of aromatic hydrocarbons in the micellar solution was observed. This phenomenon was followed by means of the molar solubilization ratio, the micellar/water partition coefficient, and the number of solubilize molecules per IL micelle. The molar solubilization ratio for ionic liquid micelles was found to be significantly higher when compared to that of ionic surfactants of similar chain length. The incorporation of the hydrocarbon into the micelle affects also an increase of the aggregation number.



INTRODUCTION

To exemplify the technological relevance of ionic liquids (ILs), the number of patent applications involving these compounds has risen markedly over the past decade (~22% increase yearly from patents.google.com by searching for “ionic liquids” each year since 2000). This interest is a result of the low melting point, high electric conductivity, negligible vapor pressure, tunability, among many other properties.

Due to the inherent charge on the hydrophilic head group and hydrophobic alkyl substituent in the cation and/or anion, a number of ILs have shown to be surface-active (Figure 1).

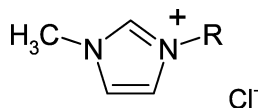


Figure 1. The structure of 1-alkyl-3-methylimidazolium ILs $[C_n\text{MIM}][\text{Cl}]$, where R is the alkyl substituent with chain length C_8 , C_{10} , C_{12} , and C_{14} .

Thereby, they have been shown to self-assemble into micelles in aqueous solutions.^{1–3} Formation of IL micelles in aqueous solutions was recently studied in detail using both experimental and computational methods.^{1–7} Cations and anions have been shown to influence bulk solution properties by factors such as hydrophobicity, degree of association between ion and counterion, and type of counterion.^{5,8}

An important property of aqueous micellar solutions is the ability to increase the solubility of organic solutes with a wide range of polarities and degrees of hydrophobicity.⁹ Although the self-organization of imidazolium ILs has been studied for

some time, very little is actually known about the solubility enhancement of hydrophobic organic solutes in IL micelles. This enhanced solubility in micellar solutions is a result of the partitioning of the compound between water and the micellar phase. The reason for this phenomenon is that the interior of the micelles acts as a hydrophobic environment in which the hydrophobic molecule may be solubilized.¹⁰ The type of interaction occurring between surfactant and solubilize determines the locus of the solubilization phenomenon, for example, at the micellar interface, in between the hydrophilic head groups, between the hydrophilic head group and the first few carbon atoms of the hydrophobic fragment (also commonly referred to as the palisade layer), and finally in the core of the micelle.⁹ Therefore, generally, solutes with polar functional groups are mainly solubilized in the outer region of the micelle, whereas nonpolar compounds are preferentially located in the inner portions of the micelles.¹¹ The locus and extent of solubility enhancement are determined by the type and strength of interaction. For example, nonionic surfactants, due to their lack of charge–charge repulsion, can form much larger micelles, which in turn can be more effective solubility enhancers.

The solubilization of hydrophobic or partly hydrophobic molecules in aqueous micellar solutions plays an important role in many technological and biotechnological processes. The use of micellar systems in separation science is of increasing importance, for example, in micellar-enhanced ultrafiltration, micellar extraction, micellar liquid chromatography, and

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Table 1. Summary of the Properties of the ILs Used in This Study^a

compound	MW [g/mol]	CMC [mM]	N_{agg}	$\log K_{\text{O/W}}$
[OMIM][Cl]	230.78	234; 220 ¹	23 ± 4 (22) ²⁵	−0.1615
[DMIM][Cl]	258.84	53.8; 59.9 ¹	32 ± 4 (40) ¹⁷	0.6485
[DDMIM][Cl]	286.88	16.1 (± 1.0); 15.5 (± 0.2)	51 ± 3 (58) ¹⁷	1.466
[TDMIM][Cl]	313.95	3.2; 3.4 ¹	60 ± 2 (79) ¹⁷	2.9807

^aThe aggregation numbers (N_{agg}) were determined as part of this research, with literature values given in parentheses with the corresponding reference.

micellar electrokinetic capillary chromatography.¹² Solubilization may also play a vital role during the formulation of products containing water-insoluble ingredients, where micellar solutions can replace the use of volatile organic solvents. Many other applications include micellar catalysis, oil recovery, drug delivery, and so forth.⁹

To this day, much research has been conducted on the micelle formation of ILs in aqueous solutions and various aspects thereof, such as determination of thermodynamic parameters and the effect of chain length, head group, counterion type, and additional substances in the system. However, the scope of literature using ILs as solubilization agents is limited. Dobritz et al. determined the solubility enhancement of acetophenone in water by addition of 1-butyl-3-methylimidazolium tetrafluoroborate by HPLC.¹³ Bica et al. presented the application of aqueous micellar alkylmethylimidazolium chloride solutions as reaction media for Diels–Alder reaction between two water-insoluble substrates, 1,3-cyclohexadiene and *N*-benzylmaleimide, and found that reaction rates in micellar solutions could be significantly increased in comparison to water.¹⁴ Sifaoui et al. determined the micellar solubility of the salicylic acid in didecyldimethylammonium nitrate ([DDA][NO₃])–water, CTAB–water, and mixed aqueous solutions of CTAB and [DDA][NO₃]. The micellar solubility of the salicylic acid in solution of [DDA][NO₃] was similar to that of CTAB–water and CTAB–[DDA][NO₃]–water systems but was doubled when compared to the aqueous solubility.¹⁵ The work by Behera et al.¹⁶ discussed ILs not as a surfactant but as a solute. The solubilization of 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆] was discussed in various aqueous surfactant solutions. The group elucidated that the surfactant type altered the locus of the IL solubilize within the micelle.

Solubilization is also often applied as a tool for the investigations of the micellar solution, especially aggregation number or microscopic viscosity of micelles using, for example, pyrene as a luminescence probe. This tool was used by El Seoud et al. and Wang et al., among others, to investigate the aggregation numbers of alkylmethylimidazolium ILs in water.^{17,18}

The goal of this publication is to elucidate the possibility to use micellar solutions of ILs for the solubilization of benzene, toluene, and xylene (BTX). As was previously shown, *pure* ILs have the ability to extract aromatic compounds from their respective liquid mixtures^{19,20} or absorb them from gaseous streams.^{21,22} To our knowledge, however, the solubility enhancement of aromatic hydrocarbons in IL *micellar* solutions has not been addressed and reported earlier.

Therefore, we aim to examine the relationship between solubilization of BTX aromatics and IL concentrations in the system and the effect of the solute and amphiphile structures on the effectiveness of the process.

METHODS AND MATERIALS

ILs and Hydrocarbons. The ILs 1-methyl-3-octylimidazolium chloride ([OMIM][Cl]), 1-decyl-3-methylimidazolium chloride ([DMIM][Cl]), 1-dodecyl-3-methylimidazolium chloride ([DDMIM][Cl]), and 1-methyl-3-tetradecylimidazolium chloride ([TDMIM][Cl]) were obtained from Merck KGaA, Darmstadt, Germany, with a purity of $\geq 98\%$. ILs were degassed and dried under vacuum (VacuCell VUS-B2 V/VU 22, Czech Republic) of 20 Pa for 24 h at a temperature of 70 °C. The ILs were then stored in a desiccator. The anhydrous hydrocarbons were obtained from Sigma-Aldrich Co. and POCh (Gliwice, Poland) with a purity of $\geq 99.5\%$. The properties of the compounds used in the experiments are shown in Tables 1 and 2. The $\log K_{\text{O/W}}$ values were calculated using our adapted Abraham equation as described by Cho et al.²³

Table 2. Physicochemical Data for Tested BTX Aromatics

name	MW [g/mol]	water solubility [mg/dm ³]	$\log K_{\text{O/W}}$
benzene	78.1	1770.0	2.13
toluene	92.1	534.8	2.69
<i>m</i> -xylene	106.2	160.0	3.12–3.20

Solubilization Experiments. The ability of the alkylimidazolium ILs to solubilize hydrocarbons was investigated in 7 cm³ head space vials with silicon/Teflon septa. The IL solutions were placed in the vials, and hydrocarbons were added to each tube in amounts higher than required to saturate the solution. The samples were then agitated for 24 h and centrifuged to allow the phases to separate. The aqueous phase was recovered, and the concentration of hydrocarbons was determined by direct GC analysis. All experiments were performed in triplicate at 25 °C. GC experiments (Perkin–Elmer Clarus 500, Waltham, U.S.A.) with an Elite 5 column, 30 m \times 250 μ m; (Perkin–Elmer, Norwalk, U.S.A.) and FID detector were used. The program was as follows: injector 200 °C, column initial from 60 to 160 °C with a rate of 10 °C per minute, detector temperature 220 °C, and split of 10:1.

Fluorescence Measurements. The steady-state fluorescence quenching technique was used to investigate the aggregation behavior of the ILs in aqueous solutions. Pyrene and *n*-decylpyridinium chloride were used as a fluorescence probe and as a quencher, respectively. The concentration of pyrene was kept constant at 1×10^{-6} M, while the quencher concentration was varied from 1×10^{-5} to 2×10^{-4} M, assuring a Poisson distribution.²⁴ The steady-state fluorescence measurements were carried out with a LS55 luminescence spectrometer (Perkin–Elmer Instruments, U.S.A.). The excitation wavelength was selected to be 335 nm, while the emission spectra were scanned from 350 to 550 nm. The first and third vibronic peaks of pyrene appeared at 372 and 383 nm, respectively. The measurements were conducted at 25 °C.

Theory. The incorporation of a solubilize into a micelle can be described by the following reaction:²⁶



Thus, the equilibrium constant (association constant) is given by the eq 2

$$K_M = \frac{[S_M]}{[S_w][IL_M]} = \frac{[S_T] - [S_w]}{[S_w]([IL] - CMC)} \quad (2)$$

where $[S_T]$ is the total concentration of the solubilize (BTX) in the solution and $[S_M]$ and $[S_w]$ are concentrations of the BTX in the micelles and water, respectively. $[IL_M]$ is equal to $[IL] - CMC$, where $[IL]$ is the concentration of the IL in the solution, and therefore, $[IL_M]$ is the amount of IL incorporated in the micelles.

The number of moles of BTX that can be incorporated into the micelle by 1 mole of IL can be described by the molar solubilization ratio (MSR) as given in the eq 3.

$$MSR = \frac{[S_T] - [S_w]}{[IL] - CMC} \quad (3)$$

The micelle/water partitioning coefficient, which is a ratio of solubilize concentration in the micellar medium to the concentration in water, is given by

$$K_{M/W} = \frac{[S_M]}{[S_w]} = \frac{[S_T] - [S_w]}{[S_w]} \quad (4)$$

Equations 2 and 4 may be combined to give the partition coefficient shown in eq 5.

$$K_{M/W} = K_M([IL] - CMC) \quad (5)$$

Assuming that the total IL concentration is 1 M, the molar partition coefficients may be calculated, as shown in Table 3.

The number of molecules of BTX per IL micelle may be calculated from eq 5, where N_m is the number of BTX molecules per micelle and N_{agg} is the number of IL molecules per micelle.

Table 3. Compilation of the Experimental K_M , MSR, and Molar $K_{M/W}$ Values for the Incorporation of BTX Aromatics in Various Alkylmethylimidazolium Chlorides

	$K_M [M^{-1}]$	MSR	molar $K_{M/W}$	N_m
		[OMIM][Cl]		
benzene	0.026	0.59 (± 0.1)	20.0	13.5
toluene	0.026	0.15 (± 0.02)	20.2	3.5
<i>m</i> -xylene	0.057	0.08 (± 0.01)	42.3	1.9
		[DMIM][Cl]		
benzene	0.04	0.92 (± 0.07)	38.1	29.3
toluene	0.096	0.56 (± 0.07)	90.2	17.8
<i>m</i> -xylene	0.23	0.34 (± 0.05)	212.7	10.9
		[DDMIM][Cl]		
benzene	0.07	1.60 (± 0.15)	69.6	81.6
toluene	0.15	0.91 (0.07)	154.9	46.5
<i>m</i> -xylene	0.48	0.72 (0.07)	473.8	36.9
		[TDMIM][Cl]		
benzene	0.12	2.72 (± 0.11)	119.6	163.2
toluene	0.36	2.09 (± 0.21)	359.2	125.6
<i>m</i> -xylene	0.90	1.36 (± 0.07)	899.9	81.6

$$N_m = \frac{([S_T] - [S_w])N_{agg}}{[IL] - CMC} \quad (6)$$

RESULTS AND DISCUSSION

Previously, we have shown that the group of alkylmethylimidazolium chlorides ([OMIM][Cl], [DMIM][Cl], [DDMIM][Cl], and [TDMIM][Cl], among others) is capable of forming micelles in aqueous solution.¹ To extend this area of research, we determined the effectiveness of these micellar aggregates to increase the solubility of water-insoluble compounds. BTX hydrocarbons were selected as a number of publications have previously shown that these compounds have the affinity to interact with ILs in a variety of scenarios.^{27,28} An exemplary solubilization of aromatic hydrocarbons in aqueous mixtures of [OMIM][Cl] and [DMIM][Cl] is shown in Figure 2.

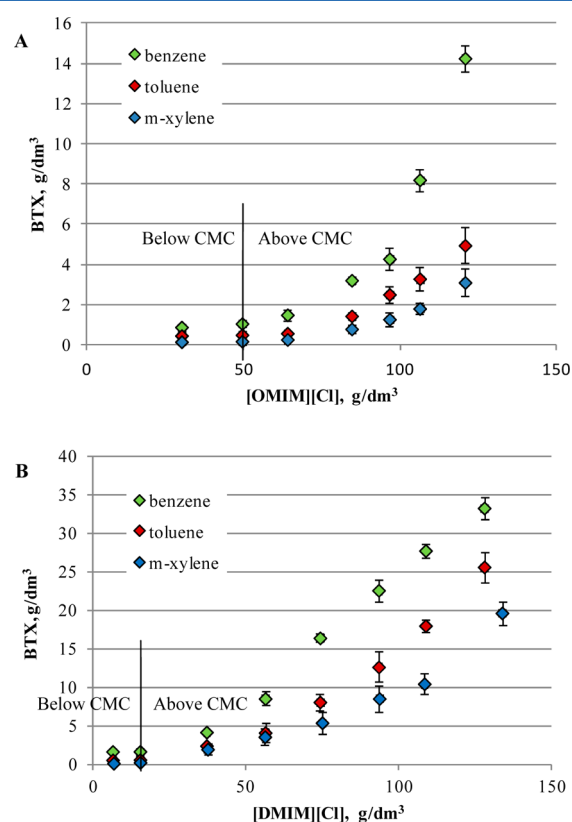


Figure 2. Solubilization of aromatic hydrocarbons (benzene, toluene, *m*-xylene) in various concentrations of (A) [OMIM][Cl] and (B) [DMIM][Cl]

The concentration on the *x*-axis represents the amount of IL introduced into the sample. The lowest concentration of each IL was chosen so as to be below the CMC, and the next was at the CMC, which was previously determined by this group.¹ The measured concentration of the BTX aromatics of these two samples was the same as the maximum water solubility of the corresponding compounds, as shown in Table 2. Above the CMC of the IL, the concentration of the BTX aromatics in the system was observed to continually increase with respect to the IL concentration, thereby indicating the BTX solubility enhancement in water. The highest increase in solubility was observed for benzene followed by toluene and then *m*-xylene.

As shown in Figure 3, comparing the solubilization of hydrocarbons in solutions of ILs with various chain lengths, it

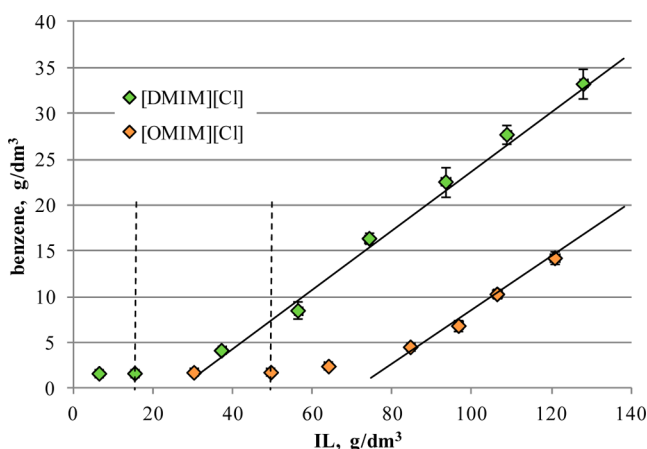


Figure 3. Comparison of the benzene solubilization in various concentrations of ILs [OMIM][Cl] and [DMIM][Cl].

was observed that the elongation of the alkyl chain of the disubstituted imidazolium cation results in an increased solubility. The observed enhanced solubilization by the ILs with the longer substituents is related to a lower CMC and higher aggregation number, shown in Table 1.

The initial observation of the higher enhanced solubility of benzene compared to that of toluene and *m*-xylene is due to the additional methyl groups in the aromatic ring, which may reduce the ability of the micelle to solubilize the hydrocarbons. This phenomenon may be further clarified by discussing the correlation with their water solubility. Benzene has a comparatively higher water solubility, and therefore, the highest solubilization was observed for this compound. However, the concentration gradient of BTX aromatics inside and outside of the micelles should be taken into account. Therefore, as the concentration outside of the micelle is increased, the concentration inside of the micelle increases correspondingly. To remove this dependency, we calculated the concentration inside of the micelle with respect to the quantity in water. The concentration outside is always constant, that is, at maximum water solubility, and inside is the difference between the total and the water solubility, as shown in eq 2. The concentration of BTX inside of the micelle, eq 3, was plotted versus the amount of IL incorporated into the micelles, as shown in Figure 4.

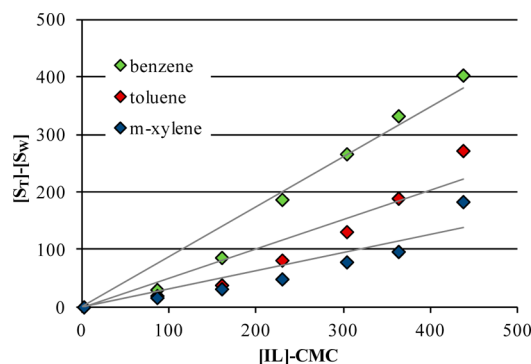


Figure 4. Exemplary plots of $[S_T] - [S_W]$ against $[IL] - CMC$ of BTX in [DMIM][Cl], where the MSR is the slope, according to eq 2.

From the slopes of the graph, the average MSRs were calculated and are presented in Table 3. In addition, the K_M and the molar $K_{M/W}$ were calculated from eqs 2 and 5, respectively. The results are also given in Table 3.

Comparing the MSR of toluene (Tables 3 and 4), we found it is higher for IL micellar solutions than for various surfactant solutions. For example, the MSRs of BTX determined for aqueous cetyltrimethylammonium bromide (CTAB) were found to be lower (0.79) than those for [TDMIM][Cl] (2.09) and similar to those for [DDMIM][Cl] (0.91). This indicates a higher solubility enhancement in IL solutions in comparison to quaternary ammonium bromides. Moreover, the MSR is of similar magnitude to gemini cationic surfactants, possessing two alkyl chains of equal length and therefore with a much lower CMC than [DDMIM][Cl]. Interestingly, the MSR was also observed to be higher than that for the anionic surfactant sodium dodecylsulphate (SDS; MSR of 0.25, compared to 0.91 for [DDMIM][Cl]), even though SDS has a lower CMC, a higher N_{agg} of 60, and anionic surfactants are considered better solubilizing agents than cationic compounds.²⁹ The observed higher partitioning of BTX aromatics into the micelle is due to the additional $\pi \cdots \pi$ interaction of BTX with the imidazolium ring. This results in a higher localized concentration of the BTX aromatics close to the micellar interface. This in turn creates a higher chemical potential difference between the outside of the micelle and the micellar core and thus provides the driving force to push the BTX aromatics inside.

When analyzing the $K_{M/W}$ for the various BTX aromatics, it can be seen that the order of BTX aromatics solubilization appears to be now reversed as *m*-xylene partitions stronger into the micelle than the smaller benzene. The justification for this observation is related to the $\log K_{O/W}$ (as presented in Table 2) and, therefore, the hydrophobicity. Thus, *m*-xylene, which has the highest hydrophobicity of the compounds investigated, also has the largest molar $K_{M/W}$.

In addition, with increasing chain length of the IL, we observed a higher N_m , for example, for toluene, the N_m increased from 3.5 for [OMIM][Cl] to 126.5 for [TDMIM][Cl]. The observed tendency can be related to the higher aggregation number of each micellar system. Aggregation numbers were determined as part of this research and are presented in Table 1. An exemplary fluorescence spectrum of [TDMIM][Cl] is shown in Figure 5. As the number of molecules forming a micelle increases, the volume of the micelle also increases. Thereby, the number of BTX molecules that may either interact with the surface of the micelle or reside inside of the core rises correspondingly. In fact, with the addition of the BTX aromatics to the inside of the micelle, a swelling and a consequential increase in the N_{agg} (e.g., [TDMIM][Cl] 60 ± 2 with no toluene to 76 ± 2 with toluene) is observed.

According to Nagarajan et al., at low MSRs, the BTX aromatic may be located close to the micelle–water interface. However, as the MSR increases above 1 (as it does for our ILs), the BTX aromatics will have already sorbed to the surface of the micelles and therefore may diffuse toward the core.³⁶ This is in agreement with our previous observation on the importance of $\pi \cdots \pi$ interactions of the BTX with the IL.

CONCLUSIONS

The solubilization of the aromatic hydrocarbons (benzene, toluene, and *m*-xylene) in aqueous mixtures of various 1-alkyl-

Table 4. Compilation of Literature Data for MSR, CMC, $K_{M/W}$, and N_m Values of Various Surfactant BTX Combinations

solubilize	surfactant	$K_{M/W}$	MSR	CMC [mM]	N_m
benzene	cetyl-trimethylammonium bromide (CTAB)		1.39 ³⁰		
<i>p</i> -xylene			0.95 ³⁰		
<i>m</i> -xylene			0.88 ³⁰		
<i>o</i> -xylene			0.95 ³⁰		
toluene		1378 ³¹	0.79 ³⁰	1.12 ³¹	
	sodium dodecylsulphate (SDS)	130 ³²	0.25 ³²	8, ³² 7.82 ³¹	
	octylphenol-poly(ethylene glycol ether (TX-114)	4943 ³¹		0.26 ³¹	
	bis(quaternary ammonium bromide) 12–10–12 ^a		2.13 ³²	0.7 ³²	
	bis(quaternary ammonium bromide) 12–6–12		2.40 ³²	1.3 ³²	
	bis(quaternary ammonium bromide) 12–2–12		3.50 ³²	1.1 ³²	
	dodecylammonium trifluoroacetate				6.9 ³³
benzene	1- dodecanesulfonic acid			7.8 ³⁴	0.726 ³⁴
toluene					1.23 ³⁴
benzene	polyoxyethylene (20) sorbitan monolaurate (Tween 20)	1823 ± 8.5 ³⁵		0.049 ³⁵	
toluene		5755.4 ± 21.8 ³⁵			
benzene	polyoxyethylene (80) sorbitan monolaurate (Tween-80)	2650.4 ± 36.6 ³⁵		0.01 ³⁵	
toluene		8780.4 ± 14.1 ³⁵			

^aBis(quaternary ammonium bromide) 12–10–12, where 12 is the chain length on the ammonium and 10 is the length of the spacer between the two ammonium centers.

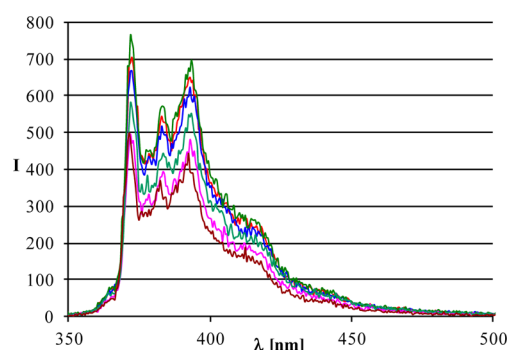


Figure 5. Exemplary fluorescence intensity with varying quantity of pyrene quencher in [TDMIM][Cl] micelles.

3-methylimidazolium chlorides was investigated. Comparing the molar solubilization ratio (MSR) of the BTX aromatics with typical ionic surfactants of similar chain length, the ILs presented a significantly higher MSR. The observed enhanced solubility in the IL micelles is thought to be due to the additional $\pi\cdots\pi$ interactions between the imidazolium head group and the aromatic solubilize. With elongation of the chain length of the IL, an increased number of BTX molecules inside of the micelle (N_m) was determined, which can be a direct result of the higher aggregation number of the corresponding IL micelles (N_{agg}).

The significantly higher MSR of the aromatic compounds in the IL micellar systems can justify their application in, for example, micellar separation processes or micellar catalysis, among others.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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