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Utilization of solid-phase microextraction–high-performance liquid chromatography in the determination of aromatic analyte partitioning to imidazolium-based ionic liquid micelles

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ABSTRACT

A solid-phase microextraction (SPME)–high-performance liquid chromatography (HPLC) approach is used, for the first time, to study the partitioning behavior of eight aromatic analytes to three imidazolium-based ionic liquid micelles, namely, 1-hexadecyl-3-methylimidazolium bromide (HDMIm-Br), 1-hexadecyl-3-butylimidazolium bromide (HDBIm-Br), and 1,3-didodecylimidazolium bromide (DDDDIm-Br). The model used to calculate the partition coefficients is improved by determining the accurate critical micelle concentration (CMC) value of the studied IL-micelles, which considers the nature and amount of organic modifier used in the experiments. Proper CMC values in the model improve the quality of the results and decrease the differences between theoretical and experimental intercepts. Surface tensiometry has been utilized to determine the CMC values for the micelles at different acetonitrile contents (1% and 1.5%, v/v). The calculated partition coefficient values for polycyclic aromatic hydrocarbons (PAHs) oscillate between 631 and 5980, whereas aromatic analytes with a lower number of fused rings in their structures suffer non-partitioning to any of the IL-micelles. The obtained partition coefficients to IL-micelles were highest with the DDDDIm-Br IL and were always higher than those obtained with the traditional surfactant cetyltrimethyl ammonium bromide (CTAB).

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1. Introduction

The logarithm of the n-octanol–water partition coefficient (log *P*) is a physicochemical property which is widely used for the prediction of absorption, distribution, metabolism, and even toxicity properties for a number of analytes. Classic direct methods for obtaining log *P* values are the shake-flask method [1] and countercurrent chromatography [2], which have been characterized as being time- and labor-consuming. Indirect methods to determine log *P* are mainly based in the utilization of chromatographic techniques, including thin-layer chromatography [3], high-performance liquid chromatography [4], and micellar electrokinetic chromatography [5]. Alternatively, several methods exist to predict log *P* from solute structure [6].

It is also of great importance to evaluate the interaction of dissolved analytes with aqueous pseudophases such as micelles. The solubility of hydrophobic compounds can be significantly increased by the presence of micelles in solution [7], and this phenomenon has important implications in the development of applications in analytical chemistry [8] as well as in several industrial processes [9]. Obtaining micelle partition coefficients for different classes of analytes (such as drugs or toxic compounds) is of considerable relevance due to the fact that micelles have long been recognized as simple chemical models for biomembranes [10]. Indeed, micelles are structurally more similar to biomembranes than n-octanol. The solubilization of analytes into micelles closely resembles that of lipidic bilayers. The influence of several organic solvents on micelles has been studied to understand the effect of solvent perturbation on biological systems [11]. The traditional direct methods to obtain micelle–water partition coefficients are dialysis, ultradialysis, and centrifugation [12,13].

Ionic liquids (ILs) are non-molecular solvents which are mainly characterized as possessing low melting points, low to negligible vapor pressures, and high thermal stability [14,15]. Their unique solvation properties, coupled to the fact that they can be structurally tailored for specific applications, have resulted in an increasing study of ILs in many areas of fundamental and applied chemistry [16–18]. Around 20 ILs have been confirmed to self-aggregate in aqueous solution [19,20], thereby acting as micelles. Several of these ILs exhibit characteristics of cationic surfactants, which is very interesting given the limitation in the number of traditional

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Fig. 1. Structure of the studied ILs.

cationic surfactants. Due to the fact that there is extreme interest in utilizing ILs as solvents for a variety of applications, it is also of great importance to study the partitioning behavior of dissolved analytes in these aggregate systems.

Solid-phase microextraction (SPME) in combination with gas chromatography (GC) has recently been described as a simple and valid procedure to obtain partition coefficients of several analytes to micelles or IL-aggregates [21–23]. This method is an interesting alternative to determine binding parameters by integrating sample extraction, loading, and transfer into a single step, being much simpler than traditional direct methods. The utilization of SPME allows for the binding equilibria to be effectively undisturbed due to the small amount of analyte extracted by the SPME coating. The main limitation is associated with the gas chromatographic separation in which non-volatile or thermally labile compounds cannot be separated.

The main purpose of this study is to evaluate the partitioning behavior of several analytes (mainly polycyclic aromatic hydrocarbons (PAHs) and functionalized aromatic compounds) to different monocationic imidazolium-based IL micelles by using, for the first time, a SPME approach coupled with high-performance liquid chromatography (HPLC). Moreover, the applied model used to obtain the analyte–aggregate partition coefficients is further improved by establishing the necessity of an accurate critical micelle concentration value of the studied IL-micelle, which takes into account the amount and nature of the organic modifier used.

2. Experimental

2.1. Reagents

The ILs studied included three imidazolium-based ionic liquids, 1-hexadecyl-3-methylimidazolium bromide (HDMIm-Br), 1-hexadecyl-3-butylimidazolium bromide (HDBIm-Br), and 1,3-didodecylimidazolium bromide (DDDDIm-Br). These ILs were synthesized and fully characterized according to previous work [20] and their structures are shown in Fig. 1. Aqueous solutions of these ILs were prepared by dissolving appropriate amounts in deionized water. Deionized water with conductivity of 18.2 MΩs was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA).

The analytes studied were: *o*-cresol (*o*-Cr), *p*-nitrobenzonitrile (*p*-NBN), and biphenyl (BiPh), supplied by Aldrich (Milwaukee, WI, USA); naphthalene (N), acenaphthene (Ace), fluorene (Fl), and phenanthrene (Phe), supplied by Supelco (Bellefonte, PA, USA); and toluene (Tol), supplied by Fisher Scientific (Fair Lawn, NJ, USA). These pure compounds were dissolved in acetonitrile of HPLC-grade (Acros, Morris Plains, NJ, USA) to prepare stock standard solutions with concentration values ranging from 1000 to 20,000 mg L^{-1}, depending on the compound. These standards solutions were stored at 4 °C and used for the preparation of two stock mixture solutions. The first stock mixture solution was prepared containing 10,000 mg L^{-1} of *o*-Cr, 3000 mg L^{-1} of *p*-NBN, and 6000 mg L^{-1} of Tol. The second stock mixture solution was prepared containing 666.7 mg L^{-1} of N and Ace, and 83.3 mg L^{-1} of BiPh, Phe and Fl. These solutions were used in the daily preparation of IL-micelle working standard solutions. The total acetonitrile content in the daily aqueous IL solution was always kept to a constant value of 1% (v/v). Acetonitrile of HPLC-grade was used throughout the study.

2.2. Instrumentation

High-performance liquid chromatographic analysis was carried out on a LC-20A liquid chromatograph (Shimadzu, Japan) with two LC-20AT pumps, a SPD-20 UV/Vis detector, and a DGU-20A_3 degasser. A SPME–HPLC interface unit from Supelco with a 60 μL desorption chamber was also used. All separations were performed using a C_{18} column, (250 mm × 4.6 mm I.D., 5 μm particle size) from Alltech (Deerfield, IL, USA). The separation gradient employed in this study started with 50% acetonitrile, which was linearly increased up to 65% over 15 min, followed by a slow increase to 68% over 25 min, at a flow rate of 1.0 mL min^{-1}. UV detection was accomplished at 254 nm.

A 60-μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) SPME fiber supplied by Supelco was utilized. The fiber was conditioned by exposing it in the SPME–HPLC interface while passing through acetonitrile for 30 min (dynamic mode), according to the instructions given by the manufacturer. A fiber holder (Supelco) for manual sampling was used for SPME analysis.

Extractions were performed in amber glass vials (20 mL) capped with screw caps and PTFE/Butyl septa, obtained from Supelco. The vials were always completely filled to leave no headspace. The agitation for the SPME extractions was performed by using PTFE stir bars and a Barnstead International Super-Nuova stirring plate (Dubuque, IA, USA) at the maximum stirring rate (1200 rpm). Sorption of hydrocarbons can take place on PTFE stir bars, and so they were carefully rinsed after use with acetone, then methanol, then acetonitrile and finally with deionized water to avoid memory effects. The stir bars were daily sonicated for 10 min with acetonitrile.

The desorption process of the fiber in the SPME interface was as follows: it was firstly inserted into the desorption chamber with the six-port injection valve in the "load" position. The chamber was then filled with pure acetonitrile using a 100 μL Hamilton

syringe (Reno, NV, USA), allowing a static desorption to take place. The soaking time for the fiber in the SPME–HPLC interface was always 20 min. Following static desorption, the injection valve was switched to the “injection” position, allowing the mobile phase to pass through the chamber for 5 min. Following each analysis, the fiber was removed and soaked in 15 mL of acetonitrile for 15 min under agitation to make sure no obvious carryover existed.

All of the surface tension measurements were performed using a Fisher Scientific Model 20 Du Nouy Surface Tensiometer (Fair Lawn, NJ, USA) equipped with a platinum–iridium ring having a mean circumference of 6.00 cm. After each measurement, the ring was washed with deionized water and subjected to a high temperature flame to ensure complete removal of residual IL surfactant.

2.3. Procedures

2.3.1. Surface tension measurements

The effect of the acetonitrile content on the critical micelle concentration of the studied IL micelles was verified by surface tensiometry. Concentrated aqueous stock solutions of HDMIm-Br, HDBIm-Br and DDDDIm-Br were first prepared and subsequently diluted with water and the appropriate amount of acetonitrile additive to produce the working standard solution. The studied contents of acetonitrile in the working standard solution were 1% and 1.5% (v/v). All solutions were kept at room temperature for at least 30 min prior to the surface tension measurement. Each surface tension value was measured by duplicate.

2.3.2. Sorption–time profiles and partition coefficients studies

The sorption–time profiles were obtained by immersion of the PDMS/DVB fiber into 20 mL of an aqueous or IL-micelle solution containing the studied analytes for different extraction times (from 15 to 180 min) while stirring at room temperature. The profiles were obtained using working solutions containing a constant concentration of the analytes: 50.71 mg L^{-1} for *o*-Cr, 15.21 mg L^{-1} for *p*-NBN, 30.43 mg L^{-1} for Tol, 4.06 mg L^{-1} for N and Ace, and 507 μg L^{-1} for BiPh, Fl and Phe. The selected concentration values of the ILs for the sorption time profiles were 2.03 mM for HDMIm-Br and HDBIm-Br, and 0.76 mM for DDDDIm-Br. These selected concentrations are at least four times higher than their respective critical micelle concentration (CMC) values in pure aqueous solutions [20].

Partition coefficient determination studies were carried out using different concentration of ILs while fixing the extraction time at 120 min. The concentration of all 8 studied analytes was the same as in the experiments used to generate the sorption–time profiles. The concentration of ILs was varied from 0.15 to 0.76 mM for DDDDIm-Br, from 0.91 to 3.24 mM for HDMIm-Br, and from 0.25 to 2.03 mM for HDBIm-Br. These concentration ranges were always higher than their respective CMC values.

The calibration curves of the eight studied analytes in deionized water were obtained using an extraction time of 120 min, with a total of seven calibration levels.

3. Results and discussion

3.1. Effects of the acetonitrile content on the critical micelle concentration values of the ILs studied

It is well-known that the formation of micelles in water can be affected by the nature of organic additive present in solution [24,25]. In fact, the composition of the aqueous solution can influence the solvaphobic interaction between the aggregates and the organic solvent [26]. The effect of several organic solvents on traditional surfactant systems has been exhaustively studied [24–28]. However, a limited amount of literature has examined the effect of different organic additives on the CMC values of IL micelles [29,30]. Due to the fact that acetonitrile is present in the preparation of working solutions for this partitioning behavior study, it is necessary to examine its effect on the CMC value of the three IL-micelles (HDMIm-Br, HDBIm-Br and DDDDIm-Br) studied.

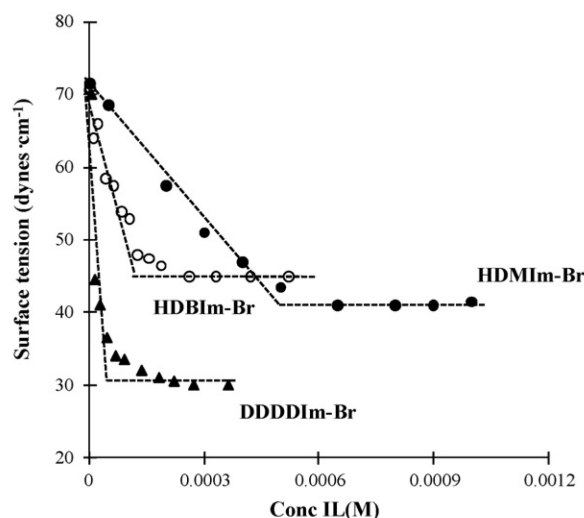

Fig. 2. Surface tension plot illustrating the decrease of the interfacial surface tension for three ILs in 1% (v/v) acetonitrile aqueous solution.

The CMC values of HDMIm-Br, HDBIm-Br and DDDDIm-Br in pure deionized water have been previously measured and reported [20]. In this work, all SPME extractions were conducted in aqueous solution containing the appropriate concentration of IL and 1% (v/v) of acetonitrile. Fig. 2 shows the surface tension plots of the studied ILs in an aqueous solution containing 1% (v/v) of acetonitrile. As depicted in the plots, the surface tension of the solution decreases with the addition of the IL up to a point in which the surface tension levels off and remains constant. The concentration at which this levelling off phenomenon occurs is the CMC. Table 1 shows the changes of the CMC values of the three ILs in various acetonitrile–water mixtures. In the small range studied (0–1.5%, v/v of acetonitrile), DDDDIm-Br and HDMIm-Br present a decrease in the obtained CMC values when using acetonitrile compared with the CMC values obtained in pure water. On the contrary, the HDBIm-Br shows a slight increase in the CMC values. The effect that the acetonitrile content has on the formation of IL micelles is relatively complex and can be influenced by many factors. The increase of the CMC value for the traditional anionic surfactant SDS when increasing the acetonitrile content in solution has been attributed to an increased solvation of surfactant monomers by acetonitrile, which explains that a greater amount of surfactant is needed to form the micellar assembly [31]. Nevertheless, such increasing effect is only noticeable when working with acetonitrile contents higher than 3% (v/v).

This work is mainly focused in the determination of partition coefficients for several analytes to IL-micelles. Therefore, the use of CMC values (Table 1) for each IL surfactant system that takes into account the role of acetonitrile is a means to more accurately characterize the extraction system. The importance of obtaining an accurate CMC value to calculate partition coefficients by SPME will be discussed in Section 3.4.

3.2. SPME–HPLC in an aqueous medium

The eight analytes selected for this study include functionalized aromatic compounds and PAHs. These analytes were chosen to specifically probe their interactive capabilities with the IL micelles.

Table 1
Effects of the acetonitrile content (%, v/v) on the critical micelle concentration (CMC) of several IL-micelles.

IL	Percent of acetonitrile content (v/v)	CMC ± SD[a] (mM)	ST[b] at CMC (dynes cm^{-1})	ST[b] drop (dynes cm^{-1})
HDBIm-Br	0	0.080[c]	43[c]	23[c]
	1	0.128 ± 0.019	43	28
	1.5	0.171 ± 0.024	43	29
HDMIm-Br	0	0.760[c]	41[c]	30[c]
	1	0.480 ± 0.066	41	31
	1.5	0.490 ± 0.062	41	31
DDDDIm-Br	0	0.100[c]	28[c]	42[c]
	1	0.042 ± 0.015	30	42
	1.5	0.044 ± 0.014	30	42

[a] Calculated error of the CMC value.
[b] Surface tension (ST).
[c] Obtained from Ref. [20].

Table 2
Figures of merit of the calibration curves obtained in Milli-Q water by SPME–HPLC.

Analytes	Slope ± error (×10^3)	Linear range (μg L^{-1})	Linearity (*R*)
o-Cr	1.209 ± 0.071	500–50,000	0.991
p-NBN	60.3 ± 3.7	150–15,000	0.992
Tol	10.44 ± 0.26	300–30,000	0.998
N	0.644 ± 0.041	40–4,000	0.992
BiPh	9.59 ± 0.62	50–500	0.990
Ace	0.745 ± 0.045	400–4,000	0.993
Fl	13.51 ± 0.64	50–500	0.996
Phe	23.82 ± 0.94	50–500	0.996

The sorption–time profiles in water were obtained to determine the equilibration time of each analyte to allow for the generation of calibration curves and subsequent measurement of partition coefficients [21–23,32]. The extraction system was considered to have attained equilibration when the amount of an analyte sorbed by the fiber stopped increasing, and it was monitored in terms of chromatographic response. Compounds with low molecular weight (e.g., N) reached equilibrium in less than 40 min while compounds like BiPh, Fl, and Ace reached equilibrium in around 90–120 min. Phe required around 150 min. For small molecules such as *o*-Cr, *p*-NBN, and BiPh, equilibration was observed in around 15 min. An extraction time of 120 min was then chosen for the entire study to ensure that most the analytes reached equilibration and to avoid long extraction times.

Calibration curves of each analyte in deionized water were obtained at the selected extraction time (120 min) at 20 °C. The figures of merit of the calibration curves including slope, linearity, and linear range, are shown in Table 2. The obtained correlation coefficients (*R*) varied from 0.990 to 0.998.

3.3. Analyte sorption behavior in IL-micelle solutions

The sorption–time profiles of all eight analytes were also obtained in IL-micelle solutions to prove that the selected equilibration time in water was still valid. According to previous work, a dramatic decrease in the equilibration time was observed for the extraction of several PAHs when using the nonionic surfactant polyoxyethylene-10-lauryl ether (POLE) [32], and for a group of phenols when sodium dodecylsulfate (SDS) was used [23]. In this study, analytes with smaller molecular weights containing less fused rings, such as *o*-Cr and Tol, experienced no obvious differences in the equilibration times in aqueous solution compared to the three IL-micelle solutions. The differences became more distinct for analytes having higher molecular weight and a larger fused ring system. For example, Ace reached equilibration in about 90 min in aqueous solution while 50–60 min was required for the three IL-micelle solutions. This effect on the equilibration time can be observed in Fig. 3A and B. In the case of Fl, an equilibration time of 110 min was observed in aqueous solution and decreased to 70 min in the presence of the IL-micelle solution. For Phe, equilibration was achieved in 70 min when using IL micelles. In all the cases, it was adequate to use an extraction time of 120 min to ensure equilibration for all analytes in the ILs studied.

The extraction efficiency for analytes with higher molecular weights or a larger number of fused rings decreased dramatically using IL-based micellar media. This effect on the extraction efficiency can also be observed from Fig. 3B. A threefold decrease in extraction efficiency can be observed for Ace, Fl and Phe in all three IL-micelle solutions. This is due to the fact that these analytes partition more into the IL-micelle which provides less free analyte to be extracted by the SPME fiber coating.

In the case of Tol, *o*-Cr, and *p*-NBN there is little noticeable difference in the extraction efficiency between the aqueous solu-

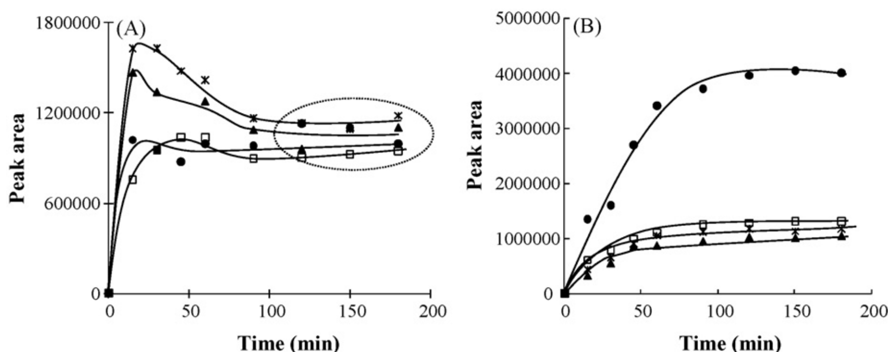

Fig. 3. Sorption time profiles for *p*-NBN (A) and Ace (B) in (●) aqueous media, (▲) HDMIm-Br media, (*) HDBIm-Br media, and (□) DDDDIm-Br media.

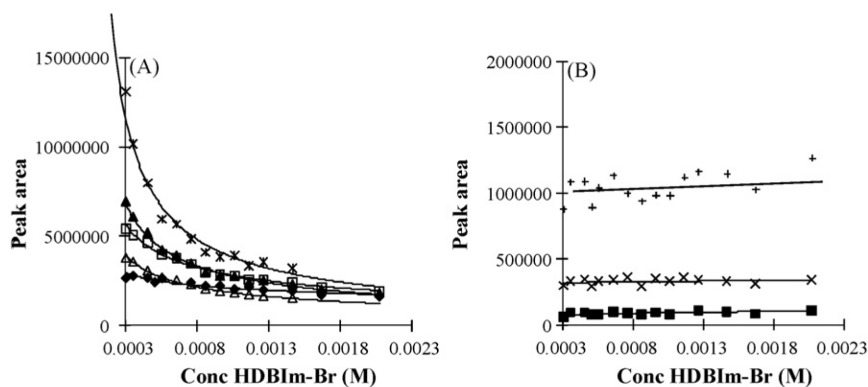

Fig. 4. Effect of the HDBIm-Br concentration on the extraction efficiency of eight analytes that (A) suffer partitioning into the IL-micelle, (*) Phe, (▲) Fl, (□) BiPh, (△) Ace, (♦) N; or (B) do not suffer partitioning to the IL-micelle, (+) *p*-NBN, (×) Tol, and (■) *o*-Cr.

tion and the IL-micelle media when working at extraction times higher than 50 min (see Fig. 3A), indicating that there is a slight or non-partitioning behavior of these analytes into the IL micelles. Interestingly, it was also observed that the extraction efficiency in the IL-micelle solution was much higher than that in pure water for small molecules when extracted with short extraction times. The most significant case was observed for *p*-NBN and *o*-Cr in the HDBIm-Br IL solution. In the case of *p*-NBN, the maximum extraction efficiency was reached at 15 min with a value two times higher than that of pure water in the same extraction period. As the extraction time increased, the extraction efficiency decreased. This behavior is similar to the "salting-out effect" observed with chaotropic salts. However, the mechanism of IL additives as kosmotropic or chaotropic agents is still not well understood [33,34] and is the focus of future investigations in our group.

3.4. Determination of analyte partition coefficients to IL-micelles by SPME–HPLC

The decrease of the free analyte concentration in a micellar solution when increasing the IL concentration is due to a partitioning of the analyte between the micelles and the aqueous phase. There are several partitioning equilibria to be considered when introducing a SPME fiber coating into an aqueous IL-micelle solution containing analytes. The analytes present in solution can partition onto the fiber and into the IL-micelles. It is assumed that the analytes retained onto the fiber coating originate from the aqueous phase whereas the analytes bound to the aggregate remain in solution. IL-micelles, as aqueous entities, do not partition to the fiber coating, at least, not in the form of micelles. However, some sorption of ILs monomers to the coating can take place. When working with IL concentrations higher than the CMC, it must be considered that the concentration of monomers of ILs in solution is always equal to the CMC, not matter how high the IL concentration in solution is increased. In other words, the possible presence of IL-monomers in the coating is always the same and independent on the IL concentration in solution. Furthermore, it must be also considered that the CMC values of the selected ILs are quite low, and so it is expected that the small amount of IL monomers present in the coating are not significantly altering the polymeric characteristics of the PDMS/DVB coating. In this sense, a small amount of free analyte in the aqueous phase is going to be available for the SPME fiber coating when analyzing hydrophobic analytes that bind and partition to the IL-micelles due to the fact that the majority of the analyte will remain in solution binding to the IL-micelles.

The partition coefficient of an analyte in the presence of an IL-micelle solution can be defined as the relationship between its concentrations in the micellar and in the aqueous phases [21–23]. Based on this assumption, the following equation can be derived [22,35] when introducing a SPME fiber in the system:

$$\frac{1}{C_{\mathrm{W,m}}} = \frac{1}{C_{\mathrm{total,m}}} + \frac{K_{\mathrm{M,m}}}{C_{\mathrm{total,m}}} C_{\mathrm{M}} \quad (1)$$

where $C_{\mathrm{W,m}}$ is the free concentration of analyte in water (measured by SPME); C_{M} corresponds to the overall IL-micellar concentration in solution which is calculated by subtracting the CMC value from the total IL concentration ($C_{\mathrm{M}} = C_{\mathrm{total,IL}} - \mathrm{CMC}$); $C_{\mathrm{total,m}}$ is the total analyte concentration; and $K_{\mathrm{M,m}}$ is the analyte-IL micelle partition coefficient which can be determined by plotting $1/C_{\mathrm{W,m}}$ versus C_{M}. $K_{\mathrm{M,m}}$ is defined as the ratio of the analyte concentration in the micellar phase M ($C_{\mathrm{M,m}}$) to that in water ($C_{\mathrm{W,m}}$), and it is expressed in L mol^{-1} if $C_{\mathrm{M,m}}$ is expressed in mol/mol and $C_{\mathrm{W,m}}$ in mol L^{-1} [22,35].

In order to obtain the analyte–micelle partition coefficient, $K_{\mathrm{M,m}}$, the chromatographic response of the studied analytes was measured at different IL concentrations while keeping the rest of the experimental conditions constant. Fig. 4 shows the change of the extraction efficiency for each analyte when increasing the concentration of the HDBIm-Br micelles. More specifically, Fig. 4A shows the decrease of the peak area for the five PAHs included in this study. It is observed that there is a dramatic decrease in the extraction efficiency for Phe, Fl, and BiPh while only a slight decrease for N and Ace is observed with increasing the IL surfactant concentration. This indicates a stronger partitioning between Phe, Fl, and BiPh with the HDBIm-Br micelles compared to that of N and Ace. The observed decrease in extraction efficiency cannot be linked to the presence of IL-monomers in the fiber coating, because such decrease in the extraction efficiency is dependent on the IL concentration.

However, other analytes (*p*-NBN, Tol and *o*-Cr) did not show variation in their chromatographic response when the IL concentration was increased, as shown in Fig. 4B. This behavior suggests that these three analytes do not exhibit appreciable partitioning to the IL-micelles. The same trend and behavior of these analytes were also observed in the HDMIm-Br and DDDDIm-Br IL micellar solutions.

Table 3 lists the obtained partition coefficient values, intercepts, and the correlations coefficients corresponding to these plots, all calculated with CMC values obtained in 1% (v/v) of acetonitrile or in pure water. According to Eq. (1), the obtained intercepts should be close to the theoretical value which is the inverse of the total concentration of the analyte. In this study, the correlations between the theoretical and the experimental intercepts were statistically significant at the 95% confidence level for all the three studied ILs when using the revised CMC value obtained with 1% (v/v) of acetonitrile. Considering each IL, the agreement between the intercepts had correlation coefficients (R) of 0.94, 0.96 and 0.99 for HDBIm-Br, HDMIm-Br and DDDDIm-Br, respectively. When using the original CMC values calculated in pure water, there is also a statistical signif-

Table 3
Obtained partition coefficients ($K_{M,m}$) and intercepts when plotting $1/C_{W,m}$ versus C_M for the studied IL-micelles and analytes using both revised and non-revised CMC data.

IL	Analyte	Theoretical intercept	n[a]	Using revised CMC (1% acetonitrile v/v)			Using original CMC (pure water)		
				Experimental intercept ± SD[b]	$K_{M,m}$ (M^{-1}) ± SD[c]	R	Experimental intercept ± SD[b]	$K_{M,m}$ (M^{-1}) ± SD[c]	R
HDBIm-Br	N	31,527	14	31,780 ± 940	631 ± 32	0.985	31,040 ± 970	625 ± 32	0.985
	BiPh	304,142	14	249,000 ± 14,000	2021 ± 51	0.996	226,000 ± 16,000	2000 ± 59	0.995
	Ace	37,980	13	26,400 ± 2,400	2435 ± 90	0.993	25,400 ± 2,500	2461 ± 94	0.992
	Fl	327,811	15	288,000 ± 34,000	2840 ± 120	0.989	253,000 ± 37,000	2820 ± 120	0.989
	Phe	351,479	12	194,000 ± 62,000	5980 ± 260	0.991	125,000 ± 73,000	5870 ± 290	0.988
HDMIm-Br	N	31,527	14	32,900 ± 2,500	985 ± 52	0.984	40,000 ± 2,500	1017 ± 61	0.979
	BiPh	304,142	12	226,000 ± 46,000	2270 ± 100	0.989	366,000 ± 39,000	2400 ± 110	0.990
	Ace	37,980	9	18,000 ± 10,000	5250 ± 300	0.988	50,300 ± 6,200	6140 ± 260	0.994
	Fl	327,811	11	374,000 ± 52,000	4420 ± 140	0.995	672,000 ± 83,000	4720 ± 290	0.983
	Phe	351,479	9	339,000 ± 60,000	4920 ± 170	0.996	620,000 ± 100,000	5560 ± 370	0.985
DDDDIm-Br	N	31,527	14	37,700 ± 1,600	1190 ± 110	0.949	39,500 ± 1,700	1210 ± 140	0.932
	BiPh	304,142	14	249,000 ± 20,000	2400 ± 150	0.977	278,000 ± 16,000	2490 ± 140	0.982
	Ace	37,980	14	26,200 ± 6,000	5910 ± 360	0.979	35,400 ± 5,100	6130 ± 340	0.981
	Fl	327,811	13	281,000 ± 42,000	5060 ± 310	0.980	349,000 ± 37,000	5260 ± 320	0.981
	Phe	351,479	10	250,000 ± 38,000	4262.9 ± 332.7	0.976	301,000 ± 23,000	4610 ± 240	0.989

[a] n is the number of IL concentration levels.
[b] SD is the error of the experimental intercept.
[c] SD is the error of the $K_{M,m}$ for n IL concentration levels (slope error × $C_{total,m}$).

icant correlation at the 95% confidence level between the intercepts, however, the independent correlations (R) are worse. The obtained values were 0.85, 0.95 and 0.98 for HDBIm-Br, HDMIm-Br and DDDDIm-Br, respectively. By using the revised CMC values, the intercept values are much closer to the theoretical intercept values for all three IL surfactant systems. In addition, the correlations of the plots obtained in the determination of the partitioning coefficients for HDBIm-Br and HDMIm-Br are increased by up to 1.2%. However, the correlations are very similar in the case of DDDDIm-Br when using both CMC values.

Using the two sets of CMC values, the partition coefficients for a given analyte to a given IL micelle differ from 0.9% to 14.4%. Given these results, it is important to use the proper CMC value (depending on the specific experimental conditions) to ensure accurate results when determining the partition coefficients.

As shown in Table 3, the partition coefficients for Fl, Ace and Phe are all significantly higher than the partition coefficients for N and Biph in all three ILs. Considering the structure of the five selected PAHs, Fl, Ace, and Phe are relatively more hydrophobic than N and BiPh. The presence of long alkyl chain substituents on the imidazolium head group allows for stronger interaction with the analytes, which justifies the trend obtained.

3.5. Partition coefficient comparison between SPME–GC and SPME–HPLC

A previous SPME–GC study of several IL-micelles [21] was accomplished with no consideration of the influence of acetonitrile content on the CMC value and therefore on the calculation of the partition coefficients. The prior GC study was carried out using aqueous solutions with an acetonitrile content of 1.5% (v/v). Table 4 includes the changes attained in the previously reported partition coefficients as well as in the obtained intercepts and the correlations for three of those ILs. It can be observed that there is a significant improvement in the obtained correlation coefficients of the plots for all of the ILs studied when the revised CMC value is used in the calculations. In general, the revised partition coefficients present a slight increase for most of the analytes in all studied

Table 4
Partition coefficients values obtained by SPME–GC [21] and their revision by using accurate CMC data.

IL	Analyte	Theoretical intercept	Using revised CMC (1.5% acetonitrile, v/v)			Using original CMC (pure water) [21]		
			Experimental intercept	$K_{M,m}$ (M^{-1}) ± SD	R	Experimental intercept	$K_{M,m}$ (M^{-1}) ± SD	R
HDBIm-Br	Nonane	7.19×10^5	3.85×10^5	2282 ± 96	0.994	1.05×10^5	2282 ± 96	0.994
	1,2-Dichlorobenzene	3.05×10^5	3.50×10^5	905 ± 19	0.993	3.12×10^5	881 ± 19	0.998
	Naphthalene	1.69×10^6	1.76×10^6	1023 ± 22	0.998	1.53×10^6	989 ± 28	0.996
	Ethyloctanoate	8.91×10^5	8.72×10^5	1767 ± 47	0.997	6.65×10^5	1704 ± 67	0.992
	Methyldecanoate	9.47×10^5	8.10×10^5	5670 ± 200	0.995	2.05×10^5	5230 ± 350	0.982
	Acenapthylene	1.83×10^6	1.98×10^6	2148 ± 66	0.996	1.46×10^6	2075 ± 75	0.994
	Fluorene	1.13×10^6	1.06×10^6	3490 ± 110	0.995	5.38×10^5	3360 ± 150	0.990
HDMIm-Br	Nonane	7.19×10^5	4.71×10^5	1865 ± 69	0.993	1.39×10^5	1670 ± 120	0.975
	1,2-Dichlorobenzene	3.05×10^5	3.50×10^5	758 ± 29	0.993	2.78×10^5	700 ± 23	0.995
	Naphthalene	1.69×10^6	1.69×10^6	859 ± 30	0.994	1.28×10^6	772 ± 45	0.984
	Ethyloctanoate	8.91×10^5	9.65×10^5	1497 ± 47	0.995	6.02×10^5	1356 ± 61	0.990
	Methyldecanoate	9.47×10^5	1.28×10^6	4680 ± 150	0.995	1.26×10^5	4230 ± 180	0.992
	Acenapthylene	1.83×10^6	1.88×10^6	2244 ± 86	0.994	8.63×10^5	1990 ± 120	0.984
	Fluorene	1.13×10^6	1.35×10^6	3280 ± 140	0.992	4.13×10^5	2920 ± 160	0.986
DDDDIm-Br	Nonane	7.19×10^5	2.21×10^5	5390 ± 490	0.961	1.43×10^5	5140 ± 540	0.950
	1,2-Dichlorobenzene	3.05×10^5	6.17×10^5	1390 ± 110	0.964	5.98×10^5	1390 ± 110	0.964
	Naphthalene	1.69×10^6	1.68×10^6	784 ± 63	0.958	1.64×10^6	763 ± 62	0.957
	Ethyloctanoate	8.91×10^5	7.93×10^5	1249 ± 85	0.971	7.62×10^5	1209 ± 92	0.964
	Methyldecanoate	9.47×10^5	6.14×10^5	5110 ± 380	0.976	5.14×10^5	4880 ± 420	0.969
	Acenapthylene	1.83×10^6	1.74×10^6	2480 ± 190	0.969	1.63×10^6	2400 ± 190	0.966
	Fluorene	1.13×10^6	1.13×10^6	2980 ± 210	0.975	1.04×10^6	2870 ± 210	0.974

Table 5
Comparison of several partition coefficients of a group of analytes to IL-micelles and traditional cationic surfactant CTAB obtained by SPME–GC using a PA fiber and by SPME–HPLC using a PDMS/DVB fiber.

Analyte	HDMIm-Br		HDBIm-Br		DDDDIm-Br		CTAB
	GC[a]	HPLC	GC[a]	HPLC	GC[a]	HPLC	GC[b]
N	772 ± 45	985 ± 52	989 ± 28	631 ± 32	763 ± 62	1190 ± 110	725 ± 15
Fl	2920 ± 160	4420 ± 140	3360 ± 150	2840 ± 120	2870 ± 210	5060 ± 310	1532 ± 28
BiPh	–	2270 ± 100	–	2021 ± 51	–	2400 ± 150	–
Ace	–	5250 ± 300	–	2435 ± 90	–	5910 ± 360	1308 ± 23
Phe	–	4920 ± 170	–	5980 ± 260	–	4260 ± 330	1663 ± 37

–: Non-studied.
[a] From Ref. [21] (non-corrected the CMC data).
[b] From Ref. [22] (non-corrected the CMC data).

ILs. However, the most significant improvement is observed in the experimental intercepts. For the HDMIm-Br IL, the correlation (R) between the theoretical intercept and the experimental intercept was 0.72 without correction of the CMC value and improves to 0.98 after correcting for the added acetonitrile. For the HDBIm-Br IL, R improves to 0.98 from a previous value of 0.90. In the case of the DDDDIm-Br IL, the improvement is not as significant as the correlation coefficient improves to 0.89 from 0.87.

In order to carry out a comparison between the obtained values for some PAHs by SPME–HPLC and previous values obtained by SPME–GC [21,22], using ILs-micelles or traditional cationic surfactants, Table 5 includes some comparative data. It must be highlighted that for each IL micelle system, the partition coefficients of N and Fl obtained by GC and HPLC are remarkably similar despite the fact that different fibers and desorption conditions were used. There are not statistical significant differences between both sets of values for N and Fl using HPLC or GC at the 95% confidence level.

In the previous study of IL-micelles and SPME–GC, it was found that some aliphatic hydrocarbons, phenols, esters and several PAHs presented higher partition coefficients to HDBIm-Br followed by HDMIm-Br and DDDDIm-Br [21]. In contrast, the following order was found in this HPLC study: DDDDIm-Br > HDMIm-Br > HDBIm-Br for PAHs like N, Fl, BiPh and Ace. On contrary, for Phe the trend was the same as in the GC study.

A comparison of the partition coefficients for the same analytes obtained by SPME–GC with the traditional cationic surfactant cetyltrimethyl ammonium bromide (CTAB) reveals that the analytes partition stronger to the IL-based micelles. The extent of partitioning is most obvious for large PAHs (e.g., Fl, Ace, Phe). The possible reason for the enhanced partitioning may lie with the fact that the three imidazolium-based cationic surfactants can interact with analytes by both hydrophobic interaction as well as π–π interaction. These results can also justify the superior extractability of heavy PAHs from sediment samples when using IL-micelles as an extractive system compared to CTAB [36].

4. Conclusions

The partitioning behavior of eight analytes was studied in three imidazolium-based IL micellar media using a micellar SPME–HPLC approach. This is the first report that describes a SPME–HPLC method to determine partition coefficients to micelles in an aqueous solution. Partition coefficients were determined with lower error when using corrected CMC values taking into account the concentration of the acetonitrile content. An accurate determination of the CMC, which considers the amount of organic solvent present in solution, is reflected in a more accurate partition coefficient determination.

Among the eight compounds studied, small molecules including Tol, *p*-NBN and *o*-Cr exhibited no partitioning or slight partitioning to the three studied IL micelles. Considering the structure of the analyte, the partition coefficients of Ace, Phe and Fl to IL micelles were significantly higher than that of N and BiPh. The IL DDDDIm-Br gave, in general, the highest partition coefficients for the studied PAHs. The partition coefficients of selected analytes to three IL micelles obtained by micellar SPME–GC and SPME–HPLC method are remarkably similar, showing the applicability for both techniques in partition coefficient determination. In addition, it was shown that the studied analytes exhibited stronger partitioning to the IL-based micelles than to the traditional cationic surfactant CTAB.

The micellar SPME–HPLC method has proven to be another valid method to determine partition coefficients for various IL-micelles. Compared with the SPME–GC method, the SPME–HPLC method is relatively time consuming due to longer fiber desorption and possible higher carryover. However, polycyclic aromatic hydrocarbons, pesticides, biomolecules and other non-volatile or thermally labile compounds are more effectively monitored by HPLC, which has more application in different fields of study as well as a large number of separation modes. The results and understanding gained from this work can be applied as an experimental foundation in choosing appropriate IL micelles for the selective extraction of analytes from various matrices in addition to designing solvent systems in which partitioning of an analyte/substrate to a micellar catalyst is desired.

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