

Note

Near-infrared spectroscopic method for the sensitive and direct determination of aggregations of surfactants in various media

Chieu D. Tran*, Shaofang Yu

Department of Chemistry, Marquette University, P.O. Box 1881, Milwaukee, WI 53201, USA

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Abstract

A new cmc determination method based on a NIR spectroscopic technique has been developed. Comparing to other cmc determination methods, this NIR method is universal, sensitive, nonintrusive and nonadditive; namely, it can be used for the direct measurements of cmc of normal micelles as well as reversed micelles, without adding any dye or fluorescent probe. cmc values of various surfactants including CTAB, SDS, Triton X-100, Brij-35, Brij-700, Tween-20, SB-12, SB3-10 determined by this method agree very well with those determined by other methods. Additionally, the method can be used for the sensitive and direct determination of cmc values of various nonionic surfactants in room-temperature ionic liquids including $[\text{BMIm}]^+[\text{PF}_6]^-$ and $[\text{EMIm}]^+[\text{Tf}_2\text{N}]^-$. The preliminary results presented here clearly demonstrate that it is possible to use the NIR technique not only to characterize aggregation of surfactants in RTILs but also to determine kinetics and to identify products of reactions in RTILs as well as in microreactors provided by micelles in the RTILs.

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1. Introduction

A variety of methods are currently available for the determination of critical micelle concentration (cmc) of surfactants [1–5]. These methods are based on monitoring changes in properties of surfactant solutions such as surface tension, ionic conductivity, absorption and fluorescence as a function of concentration [1–5]. While these methods have proven to be effective in the determination of cmc values, they all suffer from some limitations including time consuming, are relatively insensitive and require relatively large amount of samples (surface tension and conductivity), intrusive (for methods based on absorption and fluorescence as they require addition of either a color dye or a fluorescence probe) [1–5]. A novel method that can sensitively and directly monitor changes in spectroscopic properties of surfactant solutions as a function of concentration is, therefore,

desirable as it is nonintrusive and universal. Method based on the near-infrared spectroscopic technique has potentials to fulfill these requirements.

Near-infrared (NIR) spectrometry has been used extensively in recent years for chemical analysis and characterization [6]. The popularity stems from the advantages of the technique including its nonintrusive, nondestructive and wide applicability. Specifically, NIR region covers the overtone and combination transitions of the C–H, O–H, N–H and C=O groups, and since all surfactants possess at least one or more of these groups, the technique can, therefore, be used for the direct (i.e., nonintrusive and nonadditive) monitoring of all surfactants [6]. Additionally, NIR absorption is known to be sensitive to intermolecular structure and interactions [6]. For example, we successfully used NIR technique to determine binding constants of inclusion complexes between various compounds with cyclodextrins in aqueous solutions as well as in room-temperature ionic liquids [7–9]. Transformation of a surfactant solution from pre-micelles to post-micelles should lead to changes in NIR absorption. NIR technique can, therefore, be used to determine cmc values of

* Corresponding author. Fax: +1-414-288-7066.

E-mail address: chieu.tran@marquette.edu (C.D. Tran).

surfactants in different media including D₂O, organic solvents, and the recently developed room-temperature ionic liquids (RTILs) that are known as the Green solvents. This feature makes the NIR method more desirable than conventional absorption and fluorescence methods as these methods rely on the use of dyes that are not only intrusive but, in general, are limited to a few solvents. Unfortunately, in spite of its potentials, to date, cmc method based on NIR has not been developed.

The information presented is indeed provocative and clearly demonstrates that NIR technique can be used to develop a universal and sensitive method for the direct determination of cmc of surfactants. Such consideration prompted us to initiate this study which aims to develop the first NIR based cmc determination method. Performance of this method will be evaluated by comparing cmc values measured using this method with those reported in literature. Subsequently, the method will be used to determine cmc values of various surfactants in RTILs.

2. Experimental

All surfactants (SDS, CTAB, polyoxyethylene-*t*-octylphenol (Triton X-100), polyoxyethylene-23 lauryl ether (Brij 35), Tween-20, *N*-dodecylsultaine (SB-12), caprylyl sulfobetaine (SB3-10) and sodium bis(*e*-ethylhexyl) sulfosuccinate or AOT) were used as received. 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIm]⁺[PF₆]⁻) RTIL is the same as those used in our previous studies [8–10]. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide [EMIm]⁺[Tf₂N]⁻ was synthesized according to previously published procedure [11]. NIR spectra were taken on the home-built spectrophotometer based on an acousto-optic tunable filter similar to that used in our previous studies [12,13].

3. Results and discussion

As described in the Introduction, NIR technique can, in principle, be used for the direct determination of cmc values of various surfactants in water. In this case, it was found, however, that compared to NIR absorption of the surfactants used in this study, the background absorption of water is so high that it is difficult to determine cmc values accurately. Accordingly, water was replaced by D₂O as it was found that the absorption of D₂O in this NIR region is much lower than that of water. Shown in Fig. 1A are spectra of D₂O solutions without and with different concentrations of CTAB. As illustrated, O–D group has a strong and broad overtone and combination absorption band in this region at about 1625 nm. Adding CTAB (from 0.0001 to 0.01 M) to D₂O led to an increase in the shoulder of bands at about 1437 and 1690 nm. This is due to the overtone and combination

band of the C–H groups of the surfactant. Clearer observation can be seen in Fig. 1B where background absorption of D₂O was subtracted from those of CTAB solutions. As illustrated, C–H groups have a pronounced bands at about 1437 and 1690 nm and the intensities of these bands are, as expected, increased concomitant with the increase in the concentration of CTAB. However, the absorbance of these bands is not linearly related to the surfactant concentration for the entire concentration range from 0.0001 to 0.01 M. Rather, as shown in Figs. 1C and 1D, the relationship for each band can be best fit with two straight lines (linear equations and r^2 values for two straight lines for each band are shown in the graphs). The fact that two straight lines for the 1690 nm band (Fig. 1C) intersect at the concentration of 1.1 ± 0.1 mM seems to indicate that at this concentration there are major changes in properties of the surfactant solution and these changes affect NIR absorption of the C–H groups. In this case, the changes correspond to micellization process, and 1.1 ± 0.1 mM corresponds to cmc of CTAB. In fact, the cmc value of 1.1×10^{-3} M determined by this NIR method is in good agreement with the value of 1.35 mM reported in literature for CTAB in D₂O [3]. The fact that the cmc value of 1.1 ± 0.1 mM determined at 1690 nm (Fig. 1C) agrees well with the value of 1.05 ± 0.18 mM determined at the other C–H band at 1437 nm (Fig. 1D) lends further credence to this NIR method.

Figs. 2A, 2B and 2C show spectra of SDS solutions with different concentrations (from 0.001 to 0.03 M) with background absorption of D₂O subtracted and plot of absorbance of the C–H bands at 1745 and 1780 nm as a function of concentration, respectively. The cmc value was found to be 6.6 and 6.3 mM from the absorbance versus concentration plot at 1745 and 1780 nm, respectively. These values agree fairly well with the literature value of 7.6 mM [3]. cmc values of other surfactants including Brij-35, Triton X-100, Tween-20, SB-12, SB3-10 and OBG determined by this method were listed in Table 1 together with those reported in literature. As expected, values determined by this NIR method agree well with those determined by other existing methods [2,3].

The method is also effective in the determination of cmc value of surfactant in apolar solvent (i.e., reversed micelles). Shown in Fig. 3A are spectra of solutions of different concentrations of AOT (from 1.87×10^{-5} to 0.005 M) in CCl₄. As illustrated, increasing AOT concentration leads to an increase in the absorption of several bands at 1745 and 1948 nm and a cluster of bands at around 2322 nm. Plot of changes in the absorbance at 2322 nm as a function of AOT concentration lead to two straight lines (Fig. 3B) which intersect at the cmc value of 0.00069 ± 0.00012 M. This value is in very good agreement with value of 0.0006 M reported in literature [4].

It was reported recently that some surfactants aggregate in RTILs such as [BMIm]⁺[PF₆]⁻ and [EMIm]⁺[Tf₂N]⁻ [14,15]. These results are of particular importance because RTILs are considered a “Green” recyclable alternative to volatile organic solvents and such surfactants aggregation in-

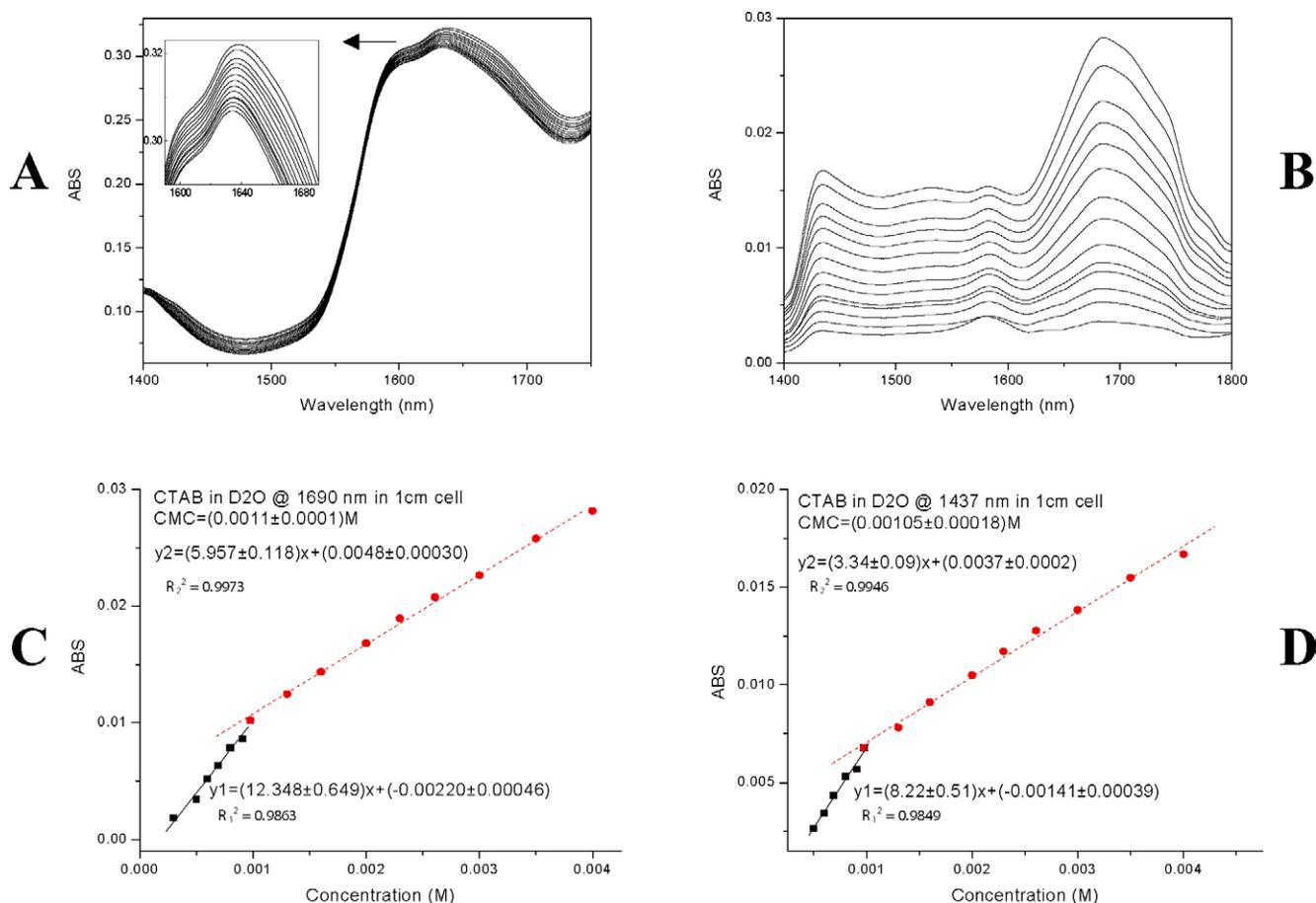


Fig. 1. (A) Near-IR spectra of D₂O solutions without and with different concentrations of CTAB (from 0.0001 to 0.01 M); insert shows plot of peaks on an expanded scale. (B) Spectra of solutions with different concentrations of CTAB with background absorption of D₂O subtracted. (C, D) Plots of absorbance at 1745 and 1780 nm, respectively, as a function of CTAB concentration.

Table 1

cmc values (in mol/L) of various surfactants in D₂O, CCl₄, [BMIm]⁺[PF₆]⁻ and [EMIm]⁺[Tf₂N]⁻ together with values reported in literature

Surfactant	Medium					
	D ₂ O [this work]	H ₂ O [1–5]	[BMIm] ⁺ [PF ₆] ⁻ [this work]	[BMIm] ⁺ [PF ₆] ⁻ [14]	[EMIm] ⁺ [Tf ₂ N] ⁻ [this work]	[EMIm] ⁺ [Tf ₂ N] ⁻ [14,15]
CTAB	0.0011 ± 0.0001	0.00135 (in D ₂ O)				
SDS	0.0066 ± 0.0021	0.0076 (in D ₂ O)				
Triton X-100	0.0010 ± 0.0002	0.0002			0.113 ± 0.019	>0.1
Brij-35	0.00011 ± 0.00002	0.0001	0.108 ± 0.009	0.115	0.060 ± 0.006	0.05
Brij-700	0.00015 ± 0.00005		0.021 ± 0.015	0.02	0.017 ± 0.002	0.01
Tween-20	0.00012 ± 0.00002	0.00008			0.070 ± 0.002	>0.05
SB-12	0.0039 ± 0.0015	0.0027				
SB3-10	0.037 ± 0.010	0.029	0.377 ± 0.09	0.466		
OBG	0.017 ± 0.003	0.024	0.108 ± 0.009	0.115		
AOT in CCl ₄	0.00069 ± 0.00012	0.00060				

creases utilization of these RTILs as it provides additional features such as microreactors for reactions between compounds soluble in nonpolar solvents and water, respectively. Accordingly, NIR method was used to determine cmc of surfactants in [BMIm]⁺[PF₆]⁻ and [EMIm]⁺[Tf₂N]⁻. Shown in Fig. 4A are NIR spectra of [BMIm]⁺[PF₆]⁻ without and with different concentrations of Brij-35. Absorption of the surfactant C–H bands at about 1441 and 1914 nm can be

clearly seen when the background absorption of the ionic liquid was subtracted, as shown in Fig. 4B. It is pleasing to see that plot of absorbance at 1441 nm band as a function of Brij-35 concentration gives a cmc value of 111 ± 37 mM which, within experimental error, is the same as the value of 108 ± 9 mM determined from the plot of the other C–H band at 1914 nm (Figs. 4C and 4D). Furthermore, the 108 ± 9 mM value determined here agrees relatively well

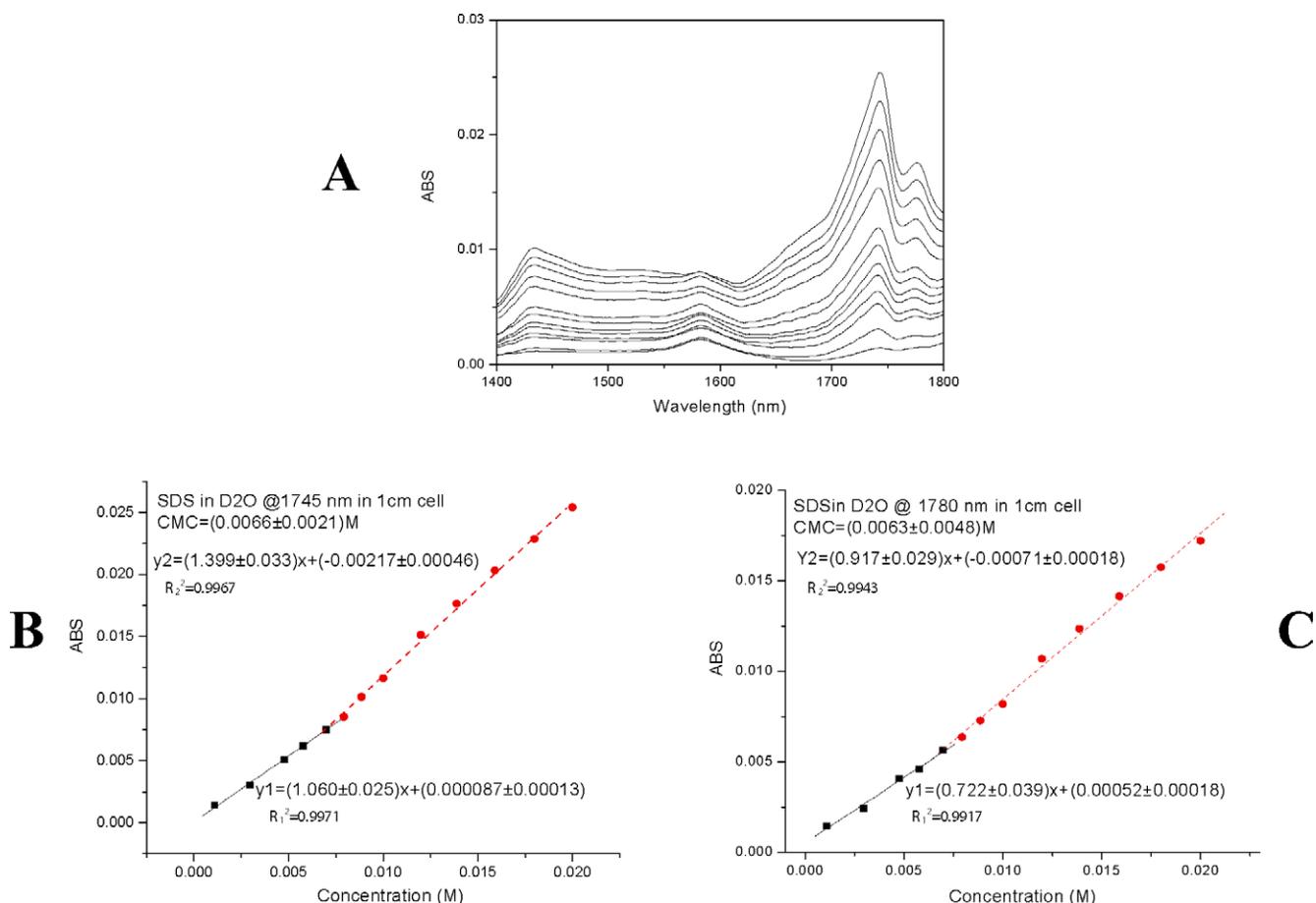


Fig. 2. (A) Spectra of D₂O solutions with different concentrations of SDS (from 0.001 to 0.03 M) with background absorption of D₂O subtracted. (B, C) Plots of absorbance at 1690 and 1437 nm, respectively, as a function of SDS concentration.

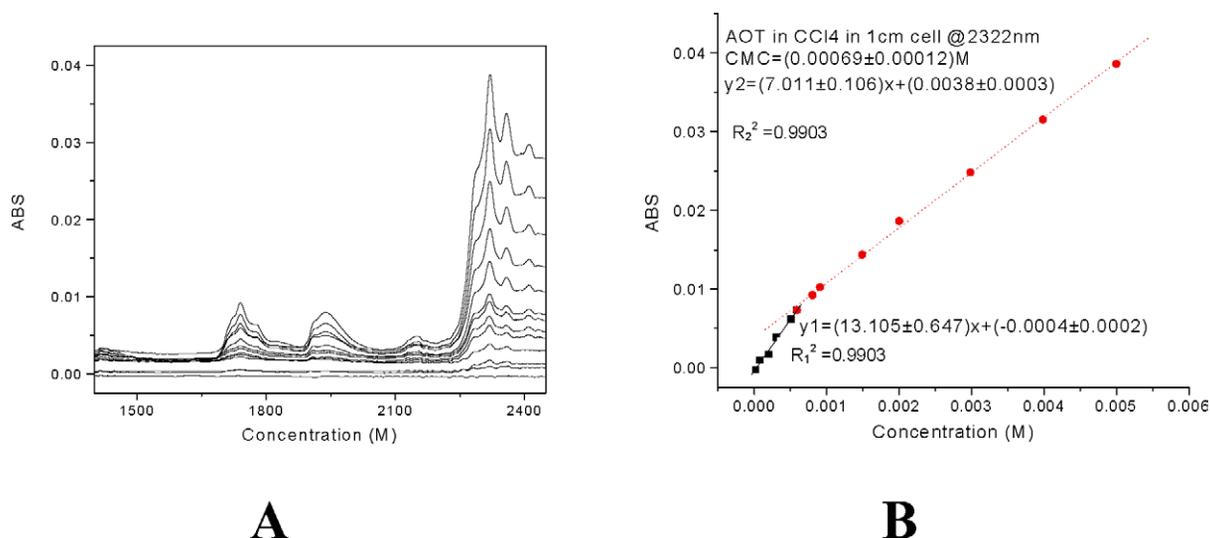


Fig. 3. (A) Spectra of CCl₄ solutions with different concentrations of AOT (from 1.87×10^{-5} to 0.005 M) with background absorption of CCl₄ subtracted. (B) Plot of absorbance at 2322 nm as a function of AOT concentration.

with the value of 115 mM reported recently [14]. cmc of Brij-35 in other RTIL, i.e., [EMIm]⁺[Tf₂N]⁻, was also determined by this NIR method to be 60 ± 6 mM (Table 1) which is in agreement with the literature value of 50 mM

[15]. Good agreement was also found for cmc values of Brij-700 in [BMIm]⁺[PF₆]⁻ and [EMIm]⁺[Tf₂N]⁻ which were determined to be 21 ± 15 and 17 ± 2 mM, respectively, with reported values of 20 and 10 mM, respectively [15].

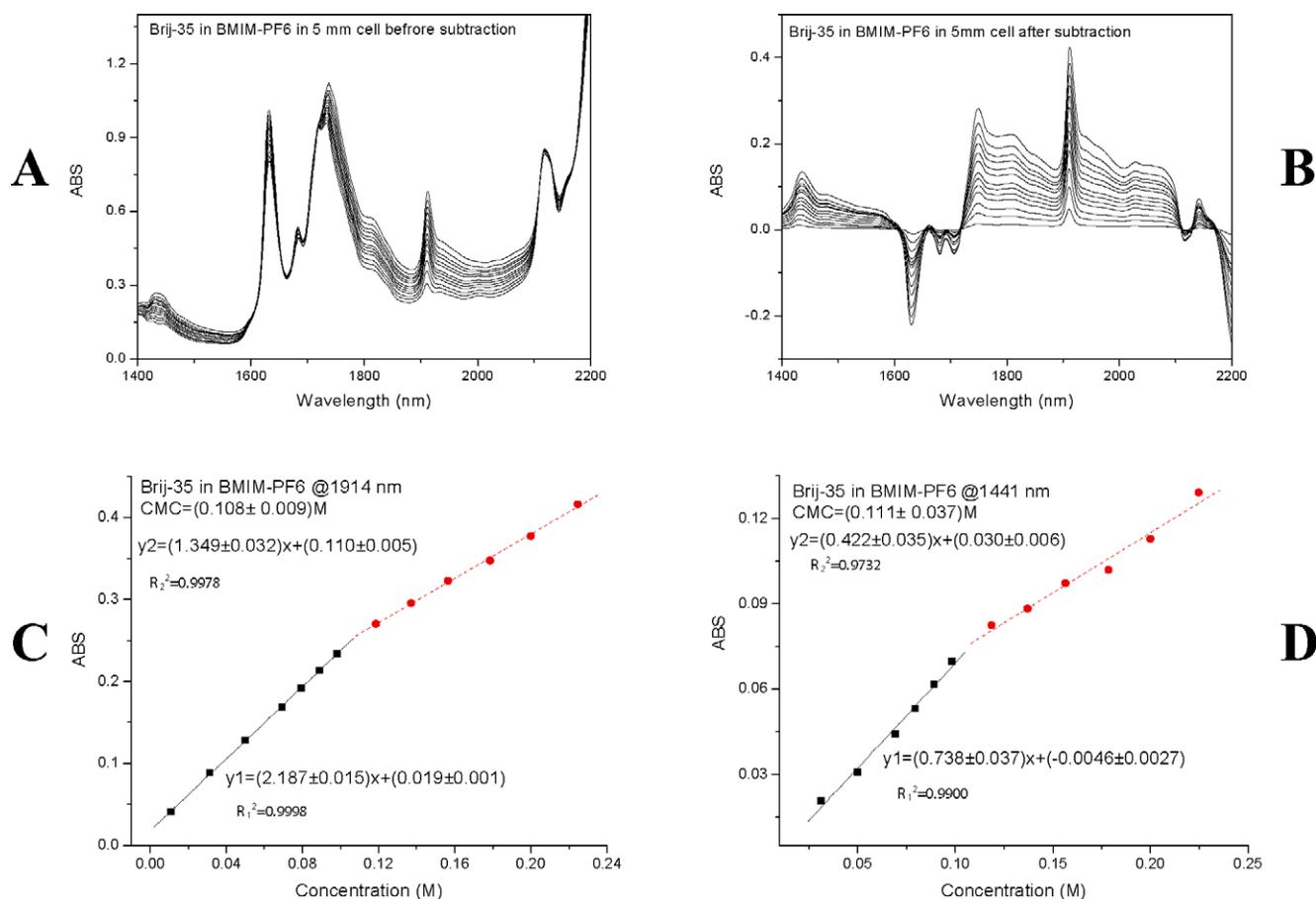


Fig. 4. (A) Spectra of $[\text{BMImM}]^+[\text{PF}_6]^-$ room-temperature ionic liquid without and with different concentrations of Brij-35. (B) Spectra of $[\text{BMImM}]^+[\text{PF}_6]^-$ solutions with different concentrations of Brij-35 with background absorption of the RTIL subtracted. (C, D) Plots of absorbance at 1910 and 1441 nm, respectively, as a function of Brij-35 concentration.

cmc value of SB3-10 in $[\text{BMIm}]^+[\text{PF}_6]^-$ determined by this method, 377 ± 90 mM, is similar to the reported value of 466 mM [15]. Using a combination of dye and fluorescent probes, it was reported that Triton X-100 aggregates in $[\text{EMIm}]^+[\text{Tf}_2\text{N}]^-$ with a cmc value to be greater than 0.1 M [15]. By use of this NIR method, we were able to determine the cmc to be 113 ± 19 mM. (Spectroscopic data and corresponding cmc determination plots for Triton X-100, Brij-35, Brij-700 and Tween-20 in $[\text{EMIm}]^+[\text{Tf}_2\text{N}]^-$ ionic liquid are shown in Figs. S1–S4 of the Supplementary material.)

In summary, we have successfully developed a new cmc determination method based on a NIR spectroscopic technique. Comparing to other cmc determination methods, this NIR method is universal, sensitive, nonintrusive and nonadditive; namely, it can be used for the direct measurements of cmc without adding any dye or fluorescent probe. cmc values of various surfactants including CTAB, SDS, Triton X-100, Brij-35, Brij-700, Tween-20, SB-12, SB3-10 determined by this method agree very well with those determined by other methods. Because water has strong absorption in the same region as the surfactants used in this study, the cmc values were determined in D_2O . cmc values in D_2O are

known to be different from those in water [16–19]. However, the differences are very small and in some cases can be considered to be insignificant within experimental error [16–19]. More importantly is the fact that the method can be used for the direct determination of cmc values of various nonionic surfactants in room-temperature ionic liquids including $[\text{BMIm}]^+[\text{PF}_6]^-$ and $[\text{EMIm}]^+[\text{Tf}_2\text{N}]^-$. The preliminary results presented here clearly demonstrate that it is possible to use the NIR technique not only to characterize aggregation of surfactants in RTILs but also to monitor kinetics and identify products of reactions in RTILs as well as in microreactors provided by micelles in the RTILs. Such possibilities are subject of our current intense investigation.

Supplementary material

Spectroscopic data and corresponding cmc determination plots for Triton X-100, Brij-35, Brij-700 and Tween-20 in $[\text{EMIm}]^+[\text{Tf}_2\text{N}]^-$ ionic liquid are shown in Figs. S1–S4. This material is available free of charge in the online version of this article.

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