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Exploration of the soluting-out effect of carbohydrates on the micellization and surface activity of long-chain imidazolium ionic liquid in the aqueous medium

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ABSTRACT

In order to elucidate the role of polyhydroxy compounds (PHC) in modifying the micellization and interfacial behaviour of surface-active ionic liquids (SAILs), system consisting of 1-tetradecyl-3-methylimidazolium bromide ([C₁₄mim][Br]) in water and in aqueous solutions of D(+)-Xylose and D(+)-Glucose as additives at (298.15, 303.15 and 308.15) K using specific conductance, UV-visible spectroscopy, FT-IR spectroscopy, surface tension measurement was investigated. From the electrical conductivity measurements, various parameters such as critical micelle concentration (CMC), degree of ionization of the counterion on the micelles (α), the standard Gibbs energy of micellization (ΔG_m^{on}), etc. have been evaluated for different concentrations of carbohydrates at different temperatures. FT-IR spectroscopy is utilized to record the structural changes occurring in the studied systems at below CMC, at CMC, and above CMC concentrations. The various surface parameters including CMC, surface tension at CMC (γ_{cmc}), surface pressure at the interface (π_{cmc}), the maximum surface excess concentration (Γ_{max}), and the minimum area per surfactant molecule at the surface, A_{min} have also been obtained using surface tension measurements. The results obtained indicated that the CMC value of the IL in the presence of different concentrations for carbohydrates decreases in the order; D(+)-Glucose > D(+)-Xylose demonstrating that carbohydrates have a soluting-out effect and their tendency to lower the CMC value of IL increases with an increase of hydrophilicity of carbohydrates.

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1. Introduction

The self-assembling mechanism of ionic liquids has become an attractive area of research. The resulting micelles are then utilized as media for a variety of chemical analysis and synthesis [1,2]. Ionic Liquids (ILs) have developed as a new class of molten organic electrolytes poised of an asymmetric organic cation, and inorganic anion, that are not capable of forming organized crystal structure and thus exist in a liquid state in the broad range of temperatures below 100 °C [3,4]. In contrast to other molecular solvents, these ionic liquids incorporate characteristic physical properties, including high thermal stability, negligible vapour pressure, non-flammability, electrically conducting, good solvation ability for organic, inorganic and polymeric materials and wide liquid range [5,6]. As a result of many such properties, ionic liquids are found to have applications in diverse areas of chemistry, biological engineering, chemical engineering, biochemistry where they facilitate enzyme catalysed reactions [7], in protein-folding as co-solvents [8], electrolytes in dye-sensitized solar cells [9]. The concentration of solution at which the ionic liquid surfactant molecules commences to self-

* Corresponding author. *E-mail address:* manchandah@nitj.ac.in (H. Kumar). assemble resulting in the formation of self-aggregate structures well known as micelles is termed as critical micelle concentration (CMC). At the critical micelle concentration, the solutions of ionic liquid surfactants display severe changes in the physico-chemical properties such as conductivity, surface tension, UV–vis absorbance, turbidity, solute solubility etc. [10].

Carbohydrates are organic compounds that are significant structural constituents in living systems [11]. Due to their non-hazardous nature and benign to mammalian tissues, they are broadly utilized in cosmetics and pharmaceutical applications and also have nutritional value and industrial utilization [12,13]. Due to the flexible nature of carbohydrates such as having the different number of carbon atoms as well as number of –OH groups, varying in their point of attachment, open or closed ring structure, presence of ketonic or aldehydic group accounts for the variety of interactions that exist between carbohydrate-surfactant systems. The interactions between a hydrophobic and hydrophilic group in the microenvironment of the surfactant compete eventually to influence the aggregation phenomenon in aqueous solution.

lonic Liquids in the presence of additives such as carbohydrates have the capacity to amend the conformation of aqueous solutions of carbohydrates that results in changing the outlook, stability, and rheology of the solution [14–21]. The most frequently studied Ionic Liquids are the imidazolium-based Ionic Liquids; 1-Alkyl-3-methylimidazolium salts, where cation is abbreviated as $[C_n mim]^+$, n signifies the number of carbon atoms constituting the alkyl chain.

By adjusting the number of the carbon atoms on the alkyl chain length, the cationic and anionic structure of the ILs, the micellization behaviour of ILs can be regulated [22–24]. When n > 8, they exhibit surfactant-like behaviour and results in the formation of micellar aggregates in the aqueous solution and are termed as Surface Active Ionic Liquid [25–28]. Surface Active Ionic Liquids have been found to possess advantages over conventional surfactants such as they possess lower CMC values and also superior activity making the micellization process an economical one.

Though a lot of work has been carried out to study the effect of different additives such as surfactants, drugs, amino acids, polyelectrolytes etc. on the micellization behaviour of Ionic liquids using various techniques [29-39], but very rare information for the effect of carbohydrates as additive on the micellization behaviour of imidazolium-based ionic liquids is available in the literature [40,41]. In this context, we investigated the aqueous solution of the ionic liquid 1-tetradecyl-3methylimidazolium bromide ([C₁₄mim][Br]) in the presence of carbohydrates (D(+)-Xy) and D(+)-Glucose) at different concentrations as well as different temperatures. The primary objective of the work is to investigate the effects of carbohydrates (D(+)-Xy) and D(+)-Glucose) on the physicochemical characteristics, i.e. CMC, and various parameters of thermodynamics of Ionic liquid through techniques such as electrical conductivity, UV-Visible spectroscopy, and FT-IR and surface tension measurements. In order to examine the interactions between ionic liquid and carbohydrates, measurements have been carried out to determine the various thermodynamic parameters such as standard Gibbs free energy of micellization (ΔG_m°), standard entropy of micellization (ΔS_m°), standard enthalpy of micellization (ΔH_m°) at (298.15, 303.15, 308.15) K.

2. Experimental

2.1. Chemicals

The synthesis of the ionic liquid 1-tetradecyl-3-methylimidazolium bromide was carried out in the laboratory using 1-methylimidazole of purity >99% which was procured from HIMEDIA Laboratories Pvt. Ltd. and 1-bromotetradecane of purity >97% from Tokyo Chemical Industry co., Ltd. Tokyo, Japan. Ethyl acetate with stated purity of >99% bought from RFCL Limited India, Acetonitrile with purity >99.5% from LOBA Chemie Pvt. Ltd. Mumbai has been also used for the synthesis. D(+)-Xylose and D(+)-Glucose of purity >99% purchased from HIMEDIA Laboratories Pvt. Ltd. was used without any further purification. All the chemicals mentioned above as well as the synthesized ionic liquid were dried under vacuum and stored over P_2O_5 in vacuum desiccator for at least 48 h before their use. The solutions used in the experiment were prepared in the doubly distilled deionized water. The details of the chemicals used in this experiment i.e. the name of chemical, its source, CAS No., purification method as well as mass fraction purity

Table 1

Specification of chemicals.

have been listed in Table 1 and their chemical structures have been presented in Scheme 1.

2.2. Synthesis and characterization of ionic liquid 1-tetradecyl-3methylimidazolium bromide ($[C_{14}mim][Br]$)

The synthesis of the Ionic liquid 1-tetradecyl-3-methylimidazolium bromide was carried out in the laboratory using the procedure described in the literature [42]. The synthesis process was accomplished through a direct reaction between 1-methylimidazole with an excess amount of 1-bromotetradecane taken in a 500 ml round bottom flask, both the chemicals dissolved using acetonitrile as the solvent. The reaction mixture was then refluxed at a constant temperature of 78–80 $^\circ \mathrm{C}$ for almost 48 h. The ongoing reaction was continuously monitored using thin-layer chromatography (TLC). After the success of the reaction, two-phase mixture was obtained that consisted of a layer of ionic liquid and acetonitrile that was expelled by decanting. [C14mimBr] synthesis was terminated by washing the end product with ethyl acetate and hexane at least three to four times and then the residual solvent was removed by rota evaporator. The product was dried over vacuum for 2 days before use. As a final point, the synthesized ionic liquid was characterized by using the ¹H NMR and FT-IR spectroscopy depicted in Figs. S1 and S2 provided in the supplementary data.

2.3. Methods

The stock solutions of ionic liquid and carbohydrates were prepared afresh by using the weighing Balance (Sartorius CPA 225 D having a precision of ± 0.00001 g). Freshly prepared deionized water doubly distilled over KMnO₄ having specific conductance of <5 μ S·cm⁻¹ has been used throughout for all the measurements.

2.3.1. Conductivity measurements

The conductivity measurements of ionic liquid 1-tetradecyl-3methylimidazolium bromide in water and in aqueous solutions of carbohydrates D(+)-Xylose and D(+)-Glucose having concentrations (0.05, 0.25, 0.50) M was performed at different temperatures (298.15, 303.15, 308.15) K. Electrical conductivities of the prepared solutions were determined using digital conductivity meter (Systronics 308) having a dip type cell. The calibration of conductivity meter was accomplished taking the standard solution of KCl ([KCl] = 0.1000 M, κ = 12.97 mS·cm⁻¹) [43]. For taking each measurement, freshly prepared, double distilled deionized water having specific conductance of <5 μ S·cm⁻¹ have been utilized for the preparation of solutions. The temperature for the experiment was maintained constant by using a high precision refrigerated circulated water thermostat procured from Macro Scientific Works Pvt. Ltd., Delhi with the temperature range of 0–100 °C having an accuracy of ± 0.1 K. The sample solutions were made homogeneous by making use of the magnetic stirrer. The solutions were prepared in units of M (mole dm⁻³). After attainment of constant temperature, the concentration of carbohydrates in solution was varied by sequentially adding 200 µL aliquots of concentrated ionic

Chemicals	Source	CAS no	Purification method	Mass fraction purity ^a
1-methylimadazole	HIMEDIA Laboratories Pvt. Ltd	616-47-7	Used as such	>99%
1-bromotetradecane	TCI Co. Ltd., Tokyo, Japan	112-71-0	Used as such	>97%
Ethyl acetate	RFCL Limited India	141-78-6	Used as such	>99%
Acetonitrile	LOBA Chemie Pvt. Ltd. Mumbai	75-05-8	Used as such	>99.5%
D(+)-Xylose	HIMEDIA Laboratories Pvt. Ltd	58-86-6	Used as such	>99%
D(+)-Glucose	HIMEDIA Laboratories Pvt. Ltd	50-99-7	Used as such	>99%
1-Tetradecyl-3-methylimidazolium bromide	Synthesized in the laboratory	471907-87-6	Vacuum drying	>99% ^b
[C ₁₄ mim][Br]				

^a As declared by the supplier.

^b As per NMR analysis.



Scheme 1. Chemical structures of investigated ionic liquid [C14mim][Br] and carbohydrates D(+)-Xylose and D(+)-Glucose.

liquid solution (having concentration 15–20 times the CMC) by means of 10–100 μ L micropipette. At least three readings were noted for each concentration which resulted in reproducibility less than \pm 0.5.

2.3.2. UV absorption spectra

For the estimation of the CMC of ionic liquid, probe less UV–Vis spectroscopy has been employed by which CMC is determined from the plot of absorbance at fixed wavelength vs concentration of sample [44]. The UV absorption spectra were recorded using Carry 631 UV–Vis spectrophotometer (Agilent Technologies) by the use of quartz cuvette that has a path length of 1 cm employed for the complete system involving ionic liquid 1-tetradecyl-3-methylimidazolium bromide ([C_{14} mim] [Br]) in the absence and in the presence of aqueous solution of carbohydrates D(+)-Xylose and D(+)-Glucose at different concentrations i.e. at 0.05, 0.25 and 0.50 M at room temperature. The absorption spectra for the whole system were recorded in the range of 200–800 nm. As can be seen from the graphs obtained represented in Figs. 3 and 4, the concentration at the point of intersection of two straight lines in the plot of absorbance versus concentration of [C_{14} mim][Br] gives the value of CMC

2.3.3. FT-IR spectroscopic studies

Fourier Transform –Infrared (FTIR) measurements were carried out with the Shimadzu spectrometer 8400S and the accessible wavenumber region for the FT-IR spectra recorded for the present work was in the range 4000 cm⁻¹ to 400 cm⁻¹. The FT-IR spectra were recorded for the three concentrations of carbohydrates (D(+)-Xylose and D(+)-Glucose) i.e., 0.05, 0.25, 0.50 M in the aqueous solutions of Ionic liquid at 298.15 K to gain insight about the interactions existing among the ionic liquid and carbohydrates. For all the experimental procedures, freshly made deionized doubly distilled (distilled using KMnO₄) water has been utilized.

2.3.4. Surface tension measurements

Surface tension measurements of the investigated aqueous solutions of ionic liquid in the absence and in the presence of different carbohydrates have been carried out using Surface Tensiometer DCAT 15 purchased from DataPhysics instruments, Germany having an accuracy of $\pm 0.01 \text{ mNm}^{-1}$. Wilhelmy plate PT 11 and the dosing unit LDU 25 are also provided along with the DCAT 33 software for the automated determination of CMC value. All the measurements were performed at 298.15 K, and the temperature was maintained using liquid temperature control unit TV 70 together with high precision refrigerated circulated water thermostat. The Wilhelmy plate was carefully cleaned by firstly washing it with acetone and then dried by heating it red hot on a flame to eradicate the adsorbed solutes before taking each measurement. To calibrate the instrument as well to check the cleanliness of glassware, the measurement for pure water at 298.15 K is carried out. At least three readings were taken for each measurement and then the average value is reported.

3. Results and discussion

3.1. Micellization and interfacial studies

3.1.1. Conductivity measurements

The experimental electrical conductivity profiles of Ionic liquid [C₁₄mim][Br] in the absence and presence of different concentrations of carbohydrates i.e. D(+)-Xylose and D(+)-Glucose (0, 0.05, 0.25) and 0.50 M) have been presented into Fig. 1 (in the absence and in the presence of D(+)-Xylose) and Fig. 2 (in the presence of D(+)-Glucose) at different temperatures i.e., 298.15 K, 303.15 K, 308.15 K. In the plots for electrical conductivity versus concentration of ionic liquid in the absence and presence of different carbohydrates, two distinguishing straight lines referring to pre and post-micellar regions have been obtained which are in agreement with the Onsager theory of electrolyte and their x-intersection has been allocated the value of CMC. As can be observed, with the increase in the concentration of ionic liquid, the conductivity value is first increasing in the pre-micellar region due to the increase in the number of free ions (C_{14} mim⁺ and Br⁻ ions). After the breakpoint i.e. in the post-micellar region, the conductivity value still increases however with the smaller slope for which the reason lies in the fact that the micelles are less mobile in comparison to free ions and also a significant loss of ionic charge occurs from the some of the counter ions getting bind to the micellar surface. Tables 2 and 3 lists the values of conductivity measurements at different concentrations and temperatures for the system studied. As can be seen from the Tables, the specific conductivity values of the [C14mim][Br] ionic liquid solution decreases more in the presence of D(+)-Glucose than D (+)-Xylose which is in the same sequence as of their soluting-out strength or even hydrophilicity of the respective carbohydrates. The explanation for the fall in specific conductivity in the presence of carbohydrates is the reduction in the surface charge density of the head group of IL $[C_{14}mim]^+$ on interaction with the hydroxyl groups of the carbohydrates. Such kind of interactions is increased by increasing the number



Fig. 1. Plots of specific conductance versus concentrations of ionic liquid [C₁₄mim][Br] in water and D(+)-Xylose at different temperatures 298.15, 303.15 and 308.15 K and concentrations 0.05 M, 0.25 M, 0.50 M.



Fig. 2. Plots of specific conductance versus concentrations of ionic liquid [C₁₄mim][Br] and D(+)-Glucose at different temperatures 298.15, 303.15 and 308.15 K and concentrations 0.05 M, 0.25 M, 0.50 M.

Conductivity values for $[C_{14}mim][Br]$ in the absence and in the presence of D(+)-Xylose at different molar concentrations and temperatures (T = 298.15 K, 303.15 K, and 308.15 K).

[C ₁₄ mim] [Br]/mM	к/µS cm	к/µ\$ cm ⁻¹										
	0 M D(+))-Xylose		0.05 M D	(+)-Xylose		0.25 M D	(+)-Xylose		0.50 M D	(+)-Xylose	
	T/K											
	298.15	303.15	308.15	298.15	303.15	308.15	298.15	303.15	308.15	298.15	303.15	308.15
0.26316	26.72	29.30	37.20	25.34	33.90	36.73	27.10	35.28	40.53	28.69	37.68	41.18
0.51948	44.20	50.55	57.45	42.10	51.95	56.99	47.47	57.85	66.98	48.73	57.30	74.90
0.76923	54.40	67.82	81.19	57.70	69.28	77.50	71.17	81.18	94.02	66.57	76.87	99.18
1.01266	74.00	84.17	101.5	72.78	86.40	96.30	90.31	103.78	122.4	87.30	96.52	123.3
1.25000	92.37	104.9	119.4	87.40	104.6	117.4	111.2	125.1	145.7	103.4	112.3	146.9
1.48148	110.4	126.1	141.0	101.7	121.2	135.6	129.2	144.5	168.7	120.7	129.1	171.5
1.70732	127.8	142.6	158.8	114.7	136.3	154.9	150.5	165.9	194.9	138.4	147.9	194.3
1.92771	145.0	162.7	174.7	129.8	153.2	171.7	168.5	183.6	214.9	152.7	162.8	215.6
2.14286	161.5	181.9	194.9	143.4	164.5	188.5	180.7	200.5	234.0	162.3	177.0	228.6
2.35294	177.1	202.1	212.4	156.3	179.4	204.2	189.5	210.9	246.7	170.1	190.4	238.0
2.55814	192.8	219.8	231.5	169.9	192.5	222.7	195.9	218.8	254.2	175.1	198.2	245.1
2.75862	207.2	235.1	249.9	176.7	208.2	236.2	199.9	224.6	261.0	180.9	203.1	252.7
2.95455	214.2	245.1	265.9	182.6	212.1	244.1	205.6	230.2	267.9	185.9	207.5	259.4
3.14607	218.5	251.3	277.6	186.7	216.9	246.9	210.7	235.6	274.7	190.2	212.7	265.6
3.33333	223.7	256.0	286.5	189.6	222.3	253.3	215.4	240.4	281.2	194.3	215.4	272.0
3.51648	228.8	261.4	292.8	193.5	224.3	258.2	219.0	245.6	287.4	198.5	219.7	278.2
3.69565	231.6	265.3	298.8	196.9	228.4	263.5	224.6	250.4	293.3	203.3	223.9	283.6
3.87097	236.9	270.7	303.5	200.3	230.4	268.2	228.6	254.2	298.7	207.6	227.5	290.3
4.04255	241.0	275.2	307.6	203.7	233.3	272.2	232.9	260.0	304.6	211.1	231.1	295.9
4.21053	243.8	278.9	312.5	206.7	237.6	277.6	237.2	264.4	309.8	215.4	236.2	301.4
4.37500	248.3	282.5	317.8	209.9	240.6	281.0	242.1	268.6	315.5	218.7	240.6	306.2
4.53608	253.5	286.5	320.4	212.8	244.4	284.5	244.9	272.8	320.3	222.4	243.7	311.1
4.69388	255.8	291.4	325.8	215.6	247.7	288.4	249.5	278.5	325.1	225.1	247.9	315.2
4.84849	259.0	296.3	329.6	218.6	251.2	292.2	253.3	280.7	332.2	227.6	251.5	320.3
5.00000	262.2	299.9	331.8	221.3	257.0	295.6	257.8	285.9	335.3	231.1	254.5	323.9
5.14852	264.8	303.7	336.6	224.0	259.5	300.3	260.5	289.3	340.6	233.6	259.7	328.1
5.29412	265.9	306.9	338.9	226.7	264.2	302.7	263.9	292.8	345.8	236.2	262.1	331.1

Standard uncertainties (u) are u (M) = $\pm 2 * 10^{-5}$ mol L⁻¹, u (κ) = ± 0.002 mS cm⁻¹ and u (T) = ± 0.1 K.

ble 3
nductivity values for $[C_{14}mim][Br]$ in the presence of $D(+)$ -Glucose at different molar concentrations and temperatures (T = 298.15 K, 303.15 K and 308.15 K).

[C ₁₄ mim] [Br]/mM	$\kappa/\mu S \ cm^{-1}$	κ/μs cm ·										
	0.05 M D(+	-)-Glucose		0.25 M D(+	0.25 M D(+)-Glucose			0.50 M D(+)-Glucose				
	T/K											
	298.15	303.15	308.15	298.15	303.15	308.15	298.15	303.15	308.15			
0.26316	10.15	29.56	34.26	16.15	30.10	41.39	27.15	32.64	38.21			
0.51948	30.70	49.71	58.46	41.14	47.59	66.82	48.22	53.02	61.47			
0.76923	52.86	72.31	83.76	61.68	71.58	89.05	67.82	75.77	84.94			
1.01266	72.24	83.34	113.1	81.68	93.38	113.9	90.09	94.25	108.7			
1.25000	93.20	106.86	133.3	103.8	117.0	138.6	107.7	112.8	130.6			
1.48148	110.6	125.7	159.3	124.9	138.9	161.7	126.1	132.6	152.1			
1.70732	130.2	144.0	182.8	146.1	156.0	184.4	144.5	151.5	172.9			
1.92771	147.1	166.2	201.9	159.6	173.5	204.3	154.8	167.5	191.5			
2.14286	163.1	186.6	222.9	166.6	190.5	221.0	161.5	179.0	205.0			
2.35294	175.3	200.2	238.5	172.9	199.0	231.5	167.5	186.0	213.3			
2.55814	182.6	215.6	253.9	178.6	205.7	239.6	172.5	191.4	220.1			
2.75862	188.0	222.8	261.3	184.2	211.9	246.0	177.6	197.1	226.5			
2.95455	192.9	229.3	267.3	188.8	217.8	252.1	182.2	202.1	232.6			
3.14607	197.4	234.6	273.2	193.7	222.6	258.4	186.8	206.9	237.7			
3.33333	201.9	240.3	278.8	199.8	227.5	264.1	191.3	211.5	243.4			
3.51648	206.1	245.5	284.2	207.4	232.0	269.6	195.9	215.9	248.0			
3.69565	210.0	250.4	289.6	212.4	236.8	275.5	198.9	220.1	253.2			
3.87097	213.9	255.0	294.4	215.2	241.6	280.6	203.1	224.2	257.8			
4.04255	217.6	259.5	298.8	218.9	246.0	285.0	207.2	228.2	262.7			
4.21053	221.6	263.9	304.4	223.6	249.8	289.1	211.1	232.2	266.9			
4.37500	224.8	266.1	308.9	227.4	253.8	293.7	214.2	235.1	270.5			
4.53608	230.6	270.5	314.4	230.8	257.1	298.5	217.9	238.6	274.8			
4.69388	233.6	274.2	318.7	232.2	260.8	302.4	221.6	241.1	278.3			
4.84849	237.2	277.9	324.2	235.3	264.3	306.6	225.4	245.1	283.5			
5.00000	240.2	280.4	329.1	239.4	268.1	310.7	228.7	248.3	286.2			
5.14852	243.2	284.2	334.5	242.4	272.4	314.4	231.3	250.2	290.4			
5.29412	247.5	287.9	339.5	245.0	275.7	319.0	234.6	253.2	293.7			

Standard uncertainties (u) are u (M) = $\pm 2 * 10^{-4}$ mol L⁻¹, u (κ) = ± 0.0003 mS cm⁻¹ and u (T) = ± 0.1 K.

of carbohydrate -OH contacts and thus further reducing the conductivity which accounts for the more decrease in conductivity value of D(+)-Glucose as compared to D(+)-Xylose.

3.1.2. CMC and degree of counter-ion dissociation

The value of the degree of counter-ion dissociation (α) denotes the average number of counter ions that are bound to the micellar surface and can be evaluated from the ratio of the post (S₂) to pre (S₁) CMC slope values.

$\alpha=S_2/S_1$

The slope value variation helps to evaluate α of the system studied [45,46]. Critical micelle concentration (CMC), an important characteristic for surfactants, is the basic parameter of surface chemistry and it covers the concentration range where surfactants spontaneously form micelles [47]. The values of CMC and degree of counter-ion dissociation (α) for the investigated systems are presented in Table 4. On analysing the data, we noticed that the values of both critical micelle concentration (CMC) as well as the degree of counter-ion dissociation (α) are reduced on increasing the concentration of carbohydrates for both D(+)-Glucose as well as D(+)-Xylose while these increases with increase in temperature. The value of the CMC of ionic liquid [C14mim][Br] in the absence of carbohydrates is well in agreement with the literature [48,49].The reasons responsible for the decrease in CMC of ionic liquid $[C_{14}mim][Br]$ in the presence of D(+)-Glucose and D(+)-Xylose as additives may be (a) the electrostatic interactions among the charged head groups of ionic liquid i.e. $[C_{14}mim]^+$ and the -OH groups of carbohydrates which minimizes the repulsive interactions among the charged ionic head groups, and (b) the hydrophilic interactions between carbohydrates and water molecules which results in the distortion of the water structure in the hydration layer surrounding the ionic liquid head group and also the hydrophobic tail of ionic liquid. As the CMC values for the investigated system are decreasing, which implies that the carbohydrates decrease the availability of water molecules surrounding the ionic liquid favouring the micelle formation. Also, the decrease of CMC in case of D(+)-Glucose is more as compared to D(+)-Xylose for solute-out strength is related to number of -OH linkages which are more in D (+)-Glucose (five –OH groups) than in D(+)-Xylose (four –OH groups) and more number of -OH linkages promotes carbohydrate-water interactions, thus increasing the ionic liquid monomers accessibility which in turn facilitate the formation of micelles. On raising the temperature, micellization becomes worse which in turn results in an increase in the CMC value. Two factors are involved when the temperature is raised: (a) loss of hydration layer around ionic liquid monomers leading to decrease in CMC and (b) increase in CMC is caused due to thermal agitation at higher temperatures is enhanced which limits ionic liquid molecules to get nearer and form micelles. Thus, the second factor is dominant. The values of degree of counter-ion dissociation (α) of [C₁₄mim][Br] in the presence of carbohydrates also decreases in the same order as CMC values and the order for the ability of investigated carbohydrates to decrease α value is D(+)-Glucose > D(+)-Xylose which is again in the same order of the hydrophilicity strength of carbohydrates or their soluting out strength.

3.1.3. Thermodynamics of micellization

CMC of ionic liquid plays a role in Gibb's free energy of micellization. Therefore, from conductivity measurements, various thermodynamic parameters of micellization have been computed along with CMC which helps to understand the thermodynamics of the process under study. The thermodynamic parameters of micellization include Standard Gibb's free energy of micellization (ΔG_m^0), Standard enthalpy of micellization (ΔF_m^0) and Standard entropy of micellization (ΔS_m^0). These three parameters have been evaluated using the following equations [2]:

$$\Delta G_m^0 = (2 - \alpha) \text{RT}(\ln X_{\text{CMC}}) \tag{1}$$

$$\Delta H_m^0 = -\mathrm{RT}^2 (2 - \alpha) [\mathrm{d}(\ln X_{\mathrm{CMC}})/\mathrm{dT}]$$
⁽²⁾

$$\Delta S_m^0 = \left(\Delta H_m^0 - \Delta G_m^0\right) / \mathrm{T} \tag{3}$$

where α is the degree of counter-ion dissociation, R is the universal gas constant, T is the temperature in Kelvin, X_{CMC} is the mole fraction of ionic liquid at CMC obtained from conductivity measurements(values shown in Table 4). Table 5 enlists the calculated values of these thermodynamic parameters of micellization for the ionic liquid [C₁₄mim][Br] in the absence and in the presence of studied carbohydrates at different concentrations as well as different temperatures. On examining the values of ΔG_m^0 evaluated at different concentrations of carbohydrates and different temperatures have become more negative in the presence of carbohydrates indicating that

Table 4

CMC and degree of counter ion dissociation α , of ionic liquid [C₁₄mim][Br] in aqueous solution, D(+)-Xylose and D(+)-Glucose at different molar concentrations and temperatures.

Carbohydrate/M		T/K	X _{CMC}	ln X _{CMC}	CMC/mM	α
	0 M	298.15	5.00E-05	-9.903	2.780	0.309
		303.15	5.17E-05	-9.870	2.873	0.315
		308.15	5.50E-05	-9.799	3.085	0.327
D(+)-Xylose	0.05 M	298.15	4.73E-05	-9.958	2.632	0.305
		303.15	4.99E-05	-9.906	2.772	0.312
		308.15	5.06E-05	-9.892	2.813	0.324
		298.15	3.88E-05	-10.156	2.158	0.303
	0.25 M	303.15	4.01E-05	-10.124	2.229	0.309
		308.15	4.04E-05	-10.117	2.245	0.321
		298.15	3.78E-05	-10.183	2.101	0.301
	0.50 M	303.15	3.96E-05	-10.139	2.196	0.308
		308.15	3.99E-05	-10.128	2.219	0.320
D(+)-Glucose	0.05 M	298.15	4.27E-05	-10.062	2.371	0.291
		303.15	4.63E-05	-9.981	2.572	0.305
		308.15	4.66E-05	-9.973	2.593	0.310
		298.15	3.57E-05	-10.241	1.983	0.287
	0.25 M	303.15	3.97E-05	-10.136	2.202	0.291
		308.15	4.03E-05	-10.119	2.241	0.299
		298.15	3.29E-05	-10.322	1.830	0.286
	0.50 M	303.15	3.88E-05	-10.158	2.154	0.287
		308.15	3.90E-05	-10.151	2.169	0.297

Standard uncertainties u are u (T) = ± 0.1 K, u (CMC) = ± 0.01 mM, u (α) = ± 0.02 .

D(+)-Glucose

0.127

0 1 2 6

0.124

0.120

0.119

0.118

0.105

0.102

0.101

0.094

0.091

0.090

0.075

0.071

0.069

Table 5

Carbohydrate/M		T/K	ΔG_m^0 kJ·mol ⁻¹	ΔH_m^0 kJ·mol ⁻¹	ΔS_m^0 kJ·mol ⁻¹ ·K ⁻¹
	0 M	298.15	-41.501	-13.501	0.094
		303.15	-41.927	-13.915	0.092
		308.15	-42.014	-14.277	0.090
D(+)-Xylose	0.05 M	298.15	-41.844	-3.220	0.130
		303.15	-42.149	-3.315	0.128
		308.15	-42.480	-3.401	0.127

-42.726

-43145

-43.527

-42.879

-43.241

-43.605

-42.639

-42.644

-43.173

-43.483

-43.668

-44.093

-43.863

 $-43\,868$

-44.279

Thermodynamic parameters of micellization of ionic liquid $[C_{14}mim][Br]$ in aqueous solution, D(+)-Xylose, and D(+)-Glucose at different molar concentrations and temperatures.

Standard uncertainties u are u (T) = ± 0.1 K, u (ΔG_0^m) = ± 0.03 kJ·mol⁻¹, u (ΔH_0^m) = ± 0.02 kJ·mol⁻¹, u (ΔS_m^0) = ± 0.02 J·mol⁻¹·K⁻¹.

298.15

303 15

308.15

298.15

303.15

308.15

298.15

303.15

308.15

298.15

303.15

308.15

298.15

303 15

308.15

the process of micellization has become more spontaneous upon increasing concentrations of carbohydrates and also with increasing temperature. Also, ΔH_m^0 i.e. the standard enthalpy of micellization, is also negative indicating that the process of micellization is exothermic in nature and the values become more negative at higher concentrations and at higher temperatures, thermal agitation is enhanced leading to increase in CMC by preventing monomers to come closer. From the values of ΔG_m^0 and ΔH_m^0 , the value of standard entropy of micellization ΔS_m^0 has been calculated using the Eq. (3), which has positive value for the process of micellization. The value of ΔS_m^0 has a major contribution towards ΔG_m^0 and gives information about the process to be entropy driven at a lower concentration of carbohydrates while enthalpic contribution becomes dominant at higher concentrations.

0.25 M

0.50 M

0.05 M

0.25 M

0.50 M

3.2. UV-vis spectroscopic studies

The simplest method for evaluating the value of CMC of ionic liquid in the absence as well as in the presence of carbohydrates is the UV-vis spectroscopy which is observed in the range of 200-800 nm. The ionic liquid i.e. [C₁₄mim][Br] is composed of imidazolium ring which is having the ability to absorb in the UV-vis region prohibits the use of any external probe [50–52]. The absorbance measurements for the system studied which comprises of (a) [C₁₄mim][Br] in the absence of carbohydrates (b) [C₁₄mim][Br] in the presence of D(+)-Xylose (c) [C₁₄mim] [Br] in the presence of D(+)-Glucose at different concentrations and 298.15 K temperature were being carried out. The graphical plots for absorbance versus concentrations have been depicted in Fig. 3 for the ionic liquid in water and in the presence of D(+)-Xylose and Fig. 4 for the ionic liquid in the presence of D(+)-Glucose at concentrations 0.05 M, 0.25 M, 0.50 M, and temperature 298.15 K. It is observable from the plots that the absorbance is first increasing with the increase in the concentration of the ionic liquid which then after the particular point is becoming almost constant and that particular point is the breakpoint which signifies the value of CMC of ionic liquid under study [46]. The values of CMC determined from this technique have been enlisted in Table 5 which shows that the values are in good agreement with that obtained using the conductivity technique. Absorbance values measured for the investigated systems have been presented in Table 6. From the data it is also observed that few absorbance values are negative. The reasonable explanation for the negative absorption is a type of emission phenomenon. The incident light and surrounding environment excited the sample to produce emission, thus forming a negative absorption (NA) or negative absorption emission (NAE) phenomenon. NAE might be due to the light exciting samples from ground states to lower molecular orbitals, or from ground states to excited states and then back to lower molecular orbitals, thus producing an emission that results in A < 0 or T% > 100%. These negative values have been observed in case of water or very negligible concentration of ionic liquid which is possible because of above mentioned explanation [53].

-4.939

-5088

-5.221

-6.859

-7.063

-7.248

-11.319

-11.604

-11.951

-15.492

-15.983

-16.433

-22271

-22.866

-21.554

3.3. FT-IR spectroscopic studies

FT-IR spectroscopic study has been carried out in order to elucidate the various interactions taking place in the process of micellization. The FT-IR spectra obtained for the system studied have been shown in Fig. 5 for [C14mim][Br] in aqueous solution, Fig. 6 (a)-(c) for $[C_{14}mim][Br]$ in the presence of D(+)-Xylose and Fig. 7(a)–(c) for $[C_{14}mim][Br]$ in the presence of D(+)-Glucose at selected concentrations (a) below CMC (b) at CMC (c) above CMC in the wavenumber range 4000-250 cm⁻¹. The important peaks in the spectra are the two major ones, one is observed at around $3200-3350 \text{ cm}^{-1}$ and the other one at around $1600-1650 \text{ cm}^{-1}$. The shift in wavenumber is observed only in $3200-3350 \text{ cm}^{-1}$ wavenumber region as can be seen from Table 7 indicating that interactions prevail in the system and this peak corresponds to -N-H str. i.e. means there occurs H-bonding which is getting affected. The other peak is observed for C==C str. i.e. around 1600–1650 cm⁻¹ which remains almost unaffected.

3.4. Surface tension measurements

The surface tension method is the versatile technique for obtaining the information concerning the processes taking place at the interface. The technique of tensiometry has been utilized to calculate the surface tension, a key parameter of colloidal science, and it emerges from interface and bulk variations in molecular energy. The surface tension measurements have been made for the currently studied system of $[C_{14}mim][Br]$ in the aqueous solution in addition to that in the presence of carbohydrates at 298.15 K. The plots shown in Fig. 8 have been drawn from the values of surface tension obtained experimentally (presented in Table 8) versus the logarithm of concentration of ionic liquid. A perusal of surface tension values from Table 8, we can observe that surface tension in the presence of carbohydrates is enhanced in comparison to the aqueous solution. From the obtained plots, it can be inferred that



Fig. 3. Plots of absorbance versus concentrations of ionic liquid [C14mim][Br] in water and D(+)-Xylose at concentrations 0.05 M, 0.25 M, 0.50 M, and temperature 298.15 K.



Fig. 4. Plots of absorbance versus concentrations of ionic liquid [C14mim][Br] in the presence of D(+)-Glucose at concentrations 0.05 M, 0.25 M, 0.50 M, and temperature 298.15 K.

Absorbance values of [C14mim][Br] solutions in the presence of	(0,0.05,0.25 and 0.50) M D(+)-Xylose and D(+)-Glucos	e in the aqueous media
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[C ₁₄ mim][Br] (mM)	0 M	D(+)-Xylose			D(+)-Glucose		
		0.05 M	0.25 M	0.50 M	0.05 M	0.25 M	0.50 M
0.0000	-0.001	-0.160	-0.253	-0.201	0.440	0.918	0.612
0.2632	-0.001	0.239	0.055	0.032	0.720	1.218	1.056
0.7692	0.003	0.699	0.734	0.494	1.304	1.997	1.751
1.2500	0.006	1.312	1.338	0.918	1.787	2.737	2.411
1.7073	0.008	1.815	2.024	1.362	2.269	3.299	3.014
2.1429	0.011	2.309	2.491	1.776	2.732	3.464	3.106
2.5581	0.013	2.387	2.582	2.112	2.780	3.464	3.090
2.9545	0.014	2.481	2.718	2.259	2.794	3.464	3.093
3.3333	0.015	2.541	2.797	2.386	2.824	3.464	3.101

Standard uncertainties u are u (T) = ± 0.1 K, u (M) = $\pm 2 * 10^{-4}$ mol L⁻¹, u(A) = $\pm 1*10^{-3}$ mol L⁻¹.

in the beginning with the increasing concentration of ionic liquid, γ value decreases till minima is reached since absorption of the ionic liquid molecules at the interface of air-solution lowers down the surface tension. This minimum corresponds to CMC value as micellization has started at this point. With more addition of ionic liquid, the value of γ increases only slowly and remains almost constant afterward. The various surface parameters such as CMC, surface tension at CMC (γ_{cmc}), surface pressure at the interface (Π_{cmc}), the maximum surface excess concentration (Γ_{max}), and the minimum area per surfactant molecule at the surface, A_{min} have been computed from surface tension



Fig. 5. FT-IR spectra of $[C_{14}mim][Br]$ in the aqueous solution at concentrations: below CMC, at CMC and above CMC.

measurements using well known Gibb's equation and have been presented in Table 8. The value of π_{cmc} represents the reduction in surface tension value to the least possible when the carbohydrates are added to the ionic liquid solution, and is calculated using the Eq. (4),

$$\pi_{\rm CMC} = \gamma_0 - \gamma_{\rm CMC} \tag{4}$$

where γ_0 is the surface tension of pure solvent and γ_{cmc} is the surface tension of the investigated system at CMC. Also, the values of other surface active parameters such as maximum surface excess concentration (Γ_{max}) have been calculated using Gibb's eq. [54] to the obtained data,

$$-2.303nRT\Gamma_{max} = \left(\frac{\partial\gamma}{\partial(\log C)}\right)$$

$$\Gamma_{max} = -\frac{1}{2.303nRT} \left(\frac{\partial\gamma}{\partial(\log C)}\right)$$
(5)

where R is the gas constant, T is the temperature, $\partial \gamma / \partial (\log C)$ is the maximum slope calculated from the surface tension plots by a linear fit of the data before the CMC point in which γ is the surface tension and C is the ionic liquid concentration, n is the number of ionic species existing in the solution after dissociation in water. Employing the value of Γ_{max} , the value of minimum surface area occupied by the single ionic liquid molecule at the interface of the solution at CMC can be obtained as [54,55],

$$A_{min} = \frac{10^{18}}{N_A \Gamma_{max}} \tag{6}$$

where N_A is Avogadro's number. On inspection of the values from the table, we observe that the values of CMC, π_{cmc} and A_{min} have been decreased in the presence of carbohydrates as an additive while the values of γ_{cmc} and Γ_{max} increases. The higher Γ_{max} values in the presence of investigated carbohydrates indicate an increased packing of ionic liquid molecules at the air/solution interface [38] and as A_{min} is inversely proportional to Γ_{max} , which is an effective area of ionic liquid's head group, is decreased on the addition of carbohydrates. This again shows that in the presence of carbohydrates, ionic liquid molecules are less solvated due to more interaction of water molecules with the carbohydrates. As a result, the micelle formation of ionic liquid molecules is enhanced in the presence of carbohydrates resulting in lower CMC values. Also, the thermodynamic parameters such as free energy of the surface at equilibrium(G_{min}^{s}), Standard Gibbs free energy change which is required for adsorption process (ΔG_{ad}^0) have been evaluated using the previously derived surface-active parameters by making use of following equations [2,56];

$$\Delta G_{ad}^{0} = \Delta G_{m}^{0} - \frac{\pi_{CMC}}{\Gamma_{max}} \tag{7}$$

$$S_{min}^{s} = A_{min} \gamma_{CMC} N_A \tag{8}$$

(



Fig. 6. FT-IR spectra of solutions in the presence of (a) 0.05 M (b) 0.25 M (c) 0.50 M D(+)-Xylose at concentrations of [C₁₄mim][Br] below CMC, at CMC and above CMC.



Fig. 7. FT-IR spectra of solutions in the presence of (a) 0.05 M (b) 0.25 M (c) 0.50 M D(+)-Glucose at concentrations of [C14mim][Br] below CMC, at CMC and above CMC.

Wavenumber obtained from FT-IR spectra for ionic liquid [C14mim][Br] in the presence of
(0, 0.05, 0.25 and 50) M of D(+)-Xylose and $D(+)$ -Glucose at temperature 298.15 K.

Carbohydrate(M)		[C ₁₄ mim] [Br]	Wavenumber (cm ⁻¹)
	0	Below CMC	3309
		At CMC	3275
		Above CMC	3315
D(+)-Xylose	0.05	Below CMC	3323
		At CMC	3310
		Above CMC	3323
	0.25	Below CMC	3315
		At CMC	3313
		Above CMC	3323
	0.50	Below CMC	3282
		At CMC	3377
		Above CMC	3306
D(+)-Glucose	0.05	Below CMC	3329
		At CMC	3321
		Above CMC	3325
	0.25	Below CMC	3315
		At CMC	3308
		Above CMC	3327
	0.50	Below CMC	3321
		At CMC	3281
		Above CMC	3298

Their values have also been presented in Table 9. The value for ΔG_m^0 has been utilized from that obtained in conductivity measurements, rest have been already discussed. The more negative value for ΔG_{ad}^0 in comparison to ΔG_m^0 reveals that the adsorption process is the primary process taking place in comparison to micellization. Also, the negative values of ΔG_{ad}^0 indicate that for the transportation of ionic liquid monomers present at the interface to the micellization stage some work has to be carried out [57]. On the other hand, lower values of G_{min}^s suggests the realization of a highly thermodynamically stable surface due to which the surface activity is enhanced. Further, in the Table 10 we have reproted the CMC values obtained from different techniques used in this study and these values are in good agreement with each other. This suggests that result obtained using these techniques support each other.

4. Conclusions

In order to investigate the influence of carbohydrates on the micellization and surface behaviour of [C₁₄mim][Br] in aqueous solutions at different concentrations and different temperatures, four techniques comprising conductometric, UV–vis spectroscopy, IR spectroscopy and tensiometry have been employed. From the results obtained using these techniques, we conclude that micellization is more favoured in the presence of carbohydrates (solute-out effect) from the value of CMC which is lowered more in the case of D(+)-Glucose as compared to D(+)-Xylose. Therefore, the tendency of investigated carbohydrates to enhance the micellization of the ionic liquid monomers is in the order: D(+)-Glu- $\cos > D(+)$ -Xylose. The reason behind this order is attributed to the increase in the hydrophilicity of carbohydrates which is caused by more number of -OH groups resulting in more carbohydrate-water molecules interactions, due to which more ionic liquid monomers are available for micelle formation. Therefore, the solute-out strength of carbohydrates is reliant on the number of hydroxyl groups which are more in D(+)-Glucose than in D(+)-Xylose. The various thermodynamic and surface parameters evaluated using various techniques are in good agreement with each other and the values of CMC of investigated Ionic Liquid obtained using these techniques are given in Table 10. The negative values of ΔG_m^0 indicates the spontaneity of the micellization process and the exothermic nature supported by the negative values of ΔH_m^0 . Also, the micellization process is entropy-driven at lower concentrations and enthalpy driven at higher concentrations of carbohydrates suggested by the conductivity measurements. Therefore, we analysed the surface-active nature of long-chain imidazolium IL [C14mim][Br] is enhanced in the presence of carbohydrates resulting in their more superior activity in comparison to that in aqueous solutions. The main aim of our present study was to study the various interactions taking place between ionic liquid and carbohydrates in aqueous solution which in turn supported the better micellization behaviour and hence, this study supports the brilliance of the novel ways to research further for better alternatives that can be utilized in a variety of applications.

CRediT authorship contribution statement

Harsh Kumar: Conceptualization, Resources, Supervision, Writing - review & editing. Ramanjeet Kaur: Investigation, Writing - original draft.

Declaration of competing interest

Authors declare no conflict of interest.

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Fig. 8. Plots of Surface tension (γ) versus the logarithm of the concentration of ionic liquid [C_{14} mim][Br] in water, D(+)-Xylose and D(+)- Glucose at concentrations 0.05 M, 0.25 M, 0.50 M, and temperature 298.15 K.

Surface tension (γ) as a function of the concentration of [C_{14} mim][Br] in the presence of (0, 0.05, 0.25 and 0.50) M of D(+)-Xylose and D(+)-Glucose at 298.15 K in aqueous media.

0 M	0 M D(+)-Xylose						D(+)-Glucose						
		0.05 M		0.25 M		0.50 M		0.05 M		0.25 M		0.50 M	
[C ₁₄ mim] [Br] (mM)	γ (mN/m)	[C ₁₄ mim] [Br] (mM)	γ (mN/m)	[C ₁₄ mim] [Br] (mM)	γ (mN/m)	[C ₁₄ mim] [Br] (mM)	γ (mN/m)	[C ₁₄ mim] [Br] (mM)	γ (mN/m)	[C ₁₄ mim] [Br] (mM)	γ (mN/m)	[C ₁₄ mim] [Br] (mM)	γ (mN/m)
0	70.42	0	71.24	0	72.48	0	73.56	0	71.69	0	72.71	0	73.85
0.10000	60.29	0.10000	62.94	0.10000	65.54	0.10000	68.14	0.10000	65.58	0.10000	68.81	0.10000	70.19
0.34286	54.64	0.34286	56.72	0.34286	61.85	0.34286	63.64	0.34286	60.80	0.30714	64.88	0.30714	67.95
0.58571	50.99	0.58571	54.60	0.58571	58.08	0.58571	60.18	0.58571	56.12	0.51429	61.14	0.51429	63.15
0.82857	48.99	0.82857	52.42	0.82857	55.63	0.82857	57.04	0.82857	53.42	0.72143	57.08	0.72143	59.59
1.07143	46.12	1.07143	50.69	1.07143	53.14	1.07143	55.48	1.07143	51.62	0.92857	55.17	0.92857	55.93
1.31429	45.73	1.31429	47.31	1.31429	51.35	1.31429	52.73	1.31429	48.03	1.13571	52.45	1.13571	53.62
1.55714	44.22	1.55714	46.56	1.55714	50.15	1.55714	51.18	1.55714	47.35	1.34286	50.30	1.34286	52.24
1.80000	42.71	1.80000	44.05	1.80000	47.61	1.80000	49.27	1.80000	45.69	1.55000	49.03	1.55000	50.86
2.04286	40.27	2.04286	42.11	2.04286	45.20	2.04286	46.47	2.04286	43.65	1.75714	48.54	1.75714	49.44
2.28571	39.60	2.28571	40.48	2.28571	44.85	2.28571	46.44	2.28571	41.42	1.96429	47.89	1.96429	49.20
2.52857	38.37	2.52857	40.61	2.52857	44.84	2.52857	46.42	2.52857	40.92	2.17143	47.87	2.17143	49.18
2.77143	36.05	2.77143	39.32	2.77143	44.82	2.77143	46.41	2.77143	40.91	2.37857	47.85	2.37857	49.15
3.01429	36.01	3.01429	39.77	3.01429	44.82	3.01429	46.41	3.01429	40.90	2.58571	47.85	2.58571	49.15
3.25714	35.99	3.25714	39.75	3.25714	44.81	3.25714	46.4	3.25714	40.90	2.79286	47.82	2.79286	49.11
3.50000	35.98	3.50000	39.75	3.50000	44.80	3.50000	46.39	3.50000	40.89	3.00000	47.81	3.00000	49.10

Standard uncertainties u are u (T) = ± 0.1 K, u (γ) = ± 0.01 mN/m.

Table 9

Surface active parameters and thermodynamic parameters of $[C_{14}mim][Br]$ in the aqueous solution, D(+)-Xylose and D(+)-Glucose at different molar concentrations and temperature 298.15 K.

CMC (mM)	$\gamma_{cmc} (mN/m)$	$\pi_{cmc} (mN/m)$	$10^6\Gamma_{max}(mol/m^2)$	$A_{min} (nm^2)$	ΔG_m^0 (kJ mol ⁻¹)	$\Delta G_{ad}^0 (\mathrm{kJ}\mathrm{mol}^{-1})$	G_{min}^{s} (kJ mol ⁻¹)
2.78	36.05	34.37	2.27	0.73	-41.50	-56.61	15.11
2.56	39.89	31.35	2.49	0.66	-41.84	-54.40	12.56
2.17	46.03	26.45	2.53	0.65	-42.73	-53.18	10.45
2.07	47.9	25.66	2.60	0.64	-42.88	-52.74	9.858
2.38	41.13	30.56	2.69	0.62	-42.64	-54.01	11.37
1.96	48.01	24.7	2.94	0.56	-43.48	-51.87	8.387
1.81	49.31	24.54	3.18	0.52	-43.86	-51.58	7.717
	CMC (mM) 2.78 2.56 2.17 2.07 2.38 1.96 1.81	CMC (mM) γ _{cmc} (mN/m) 2.78 36.05 2.56 39.89 2.17 46.03 2.07 47.9 2.38 41.13 1.96 48.01 1.81 49.31	$\begin{array}{c c} \mbox{CMC (mM)} & \gamma_{cmc} (mN/m) & \pi_{cmc} (mN/m) \\ \hline 2.78 & 36.05 & 34.37 \\ 2.56 & 39.89 & 31.35 \\ 2.17 & 46.03 & 26.45 \\ 2.07 & 47.9 & 25.66 \\ 2.38 & 41.13 & 30.56 \\ 1.96 & 48.01 & 24.7 \\ 1.81 & 49.31 & 24.54 \\ \hline \end{array}$	$\begin{array}{c c} \mbox{CMC (mM)} & \gamma_{cmc} (mN/m) & \pi_{cmc} (mN/m) & 10^6 \Gamma_{max} (mol/m^2) \\ \hline 2.78 & 36.05 & 34.37 & 2.27 \\ 2.56 & 39.89 & 31.35 & 2.49 \\ 2.17 & 46.03 & 26.45 & 2.53 \\ 2.07 & 47.9 & 25.66 & 2.60 \\ 2.38 & 41.13 & 30.56 & 2.69 \\ 1.96 & 48.01 & 24.7 & 2.94 \\ 1.81 & 49.31 & 24.54 & 3.18 \\ \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $

Standard uncertainties u are u (T) = ± 0.1 K, u (CMC) = ± 0.01 mM, u (γ_{cmc}) = ± 0.1 mN/m, u (π_{cmc}) = ± 0.1 mN/m, u (Γ_{max}) = ± 0.01 µmol/m², u (A_{min}) = ± 0.01 nm², u (ΔG_{m}^{0}) = ± 0.03 kJ·mol⁻¹, u (ΔG_{ad}^{0}) = ± 0.02 kJ·mol⁻¹, u (ΔG_{ad}^{0}) = ± 0.03 kJ·mol⁻¹.

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Table 10

Comparison of CMC of [C₁₄mim][Br] in the absence and presence of D(+)-Xylose and D (+)-Glucose at different temperatures, obtained from conductivity measurements, UV-visible spectral studies and surface tension measurements.

Carbohydrates(M)		CMC of [C ₁₄ mim][Br] (mM)				
		Conductivity measurements			UV-Vis spectral studies	Surface tension measurements
		298.15 K	303.15 K	308.15 K	298.15 K	298.15 K
	0	2.779	2.873	3.085	2.615	2.787
D(+)-Xylose	0.05	2.632	2.772	2.812	2.558	2.556
	0.25	2.158	2.229	2.245	2.146	2.172
	0.50	2.101	2.196	2.219	2.081	2.070
D(+)-Glucose	0.05	2.371	2.572	2.593	2.259	2.385
	0.25	1.982	2.202	2.241	1.840	1.965
	0.50	1.829	2.154	2.169	1.804	1.811

Standard uncertainties u are u (T) = ± 0.1 K, u (CMC) = ± 0.01 mM.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.molliq.2020.114209.

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