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Solvation thermodynamics of Allyl and Butyl -Methyl Imidazolium Ionic Liquids in Aqueous and Alcoholic-Aqueous Solvents

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Abstract

Conductivity, density, refractive index and ultra-violet of 1-Allyl-3-methylimidazolium chloride (AMImCl)and 1-butyl-3-methylimidazolium hexaflourophosphate (BMImPF6) ionic liquids (ILs)At 298.15 K, Mixed solvents have been tested with different mole fractions of alcohols, containing aqueous and alcoholic-aqueous (methanol, ethanol, and glycerol). The conductivity and surface tension and refractive index and ultra-violet measurements were used to assess the critical micelle concentration (CMC) of (AMImCl) and (BMImPF6). The CMC was found to increase as the alcohol mole fraction increased in all solvents used. The results indicate that the CMC of (AMImCl) and (BMImPF6) methanol, ethanol, and glycerol, in that order. Micellization was discovered to be a naturally occurring process. The molal volume of the two surfactants was calculated and discussed based on the density information. The polarizability and molal refraction of AMImCl and BMImPF6 were also measured and discussed using the refractive index results. For all calculations, a computer programmer was used.

Keywords: CMC; AMImCl; BMImPF6; Molal Volume; Refractive index..

Introduction

Ionic liquids (ILs) are new organic salts consist of a large organic cation and an inorganic polyatomic anion, that exist in the liquid state at relatively low temperatures. In the last few years, ILs has drawn the attention of the scientific community, and many studies that involve different aspects of ILs have been published in the scientific literature. From the scientific and industrial points of view, a fundamental understanding of the physico-chemical properties of ILs is needed before their application to several processes. For instance, knowledge of some basic properties can be useful for fluid property estimation, thermodynamic property calculations, and phase equilibrium[1,2]. ILs have unique properties that can include 'low melting point, negligible vapor pressure, good electrochemical and thermal stability, and tunable structures', and so forth.

From this point, the field of ILs expanded rapidly, both in terms of the different ions used and in the range of applications being investigated. The applications include those on a research lab-scale and also an industrial scale; the commercial use of ILs has been under development since the late 1990s[3].The low melting point of ILs drives interest in their use as pharmaceutical salts, where the cation or anion is an active pharmaceutical ingredient[4–6]. The low melting point removes the concern of a salt crystallizing into an alternative polymorph (crystal structure) from that which has been trialed and patented, as the formation of polymorphs has significant medical and legal implications. Having the drug in a liquid form may also make it easier to be administered top attaints.

The ionic nature of ILs also means that they provide quite unique solvation environments compared to conventional molecular solvents, and this is exploited in a variety of different synthetic reactions, materials processing/extraction, and gas separation. There is also extensive interest in their use for biomass processing. ILs are being investigated for both the dissolution of a variety of different biomaterials and for their processing into higher value products [6,7]. For biotechnological applications, the ability of ILs to dissolve and stabilize enzymes and proteins, DNA, and RNA is also extremely valuable. Unique solubilizing properties, coupled with good electrochemical stability, also underlie the use of ILs for rare-earth processing and recycling[8].

ILs are promising for two techniques–as anionic extracting for the separation of rare-earth salts, and as

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the medium for the subsequent electrodepositing of the pure rare-earth metal. Excellent electrochemical stability is arguably one of the most important characteristics of some ILs, as evidenced by their extensive use in electrochemical devices, for electrowinning, water splitting, and so on. In addition, ILs found application in a wide range of other synthetic reactions – organic, inorganic, biological, and so on[9].In the field of energetic materials[10], the huge structural variability of ILs is a great advantage, as are their low vapor pressure, wide liquid range, and good thermal stability.

Most properties are identical to those of a basic electrolyte at low concentrations.

The surface tension, which drops rapidly as the concentration of ILs rises, is one notable exception. All of the properties (interfacial and bulk) shift suddenly at a certain concentration, which is consistent with the fact that surface active ions or molecules in solution associate to form larger units at and above this concentration. Micelles (self-assembled structures) are the name for these related units, and the first aggregates formed are usually spherical.

This association phenomenon occurs at a critical micelle concentration. occurs (CMC). The Critical Micelle Concentration indicates the usually narrow range of concentrations separating the limits, at below which most of the surfactant is in the monomeric state and above which virtually all additional ILs enters the micellar state[11]. The variation of the CMC with chemical and physical parameters provides good insights into the nature of the ILs self-association. Conductivity, solubility, viscosity, light scattering, and surface tension measurement are some of the physical methods used to determine CMC measurement of ion activity, Gel filtration spectrophotometrically and counter ion magnetic resonance[12–16]. Many researchers have used conductivity measurements to investigate ionic liquid micellization[17-22] and surfactants[23–32]. The density measurements had been used to calculate the molal volume of some ionic liquids[33] and other substances in different solutions[33–44]. The refractive index measurements had been used to study the solvation of some substances in different solutions[43–47].

The aim of this research is to look into solvation AMImCl and BMImPF6 at 298.15 K, using density, surface tension, refractive index and conductivity and ultra-violet measurements in aqueous and alcoholic-aqueous solvents. The study aims to use the surface tension and, refractive index and conductivity and ultra-violet measurements to estimate the CMC and the thermodynamic parameters of AMImCl and BMImPF6. The molal volumes, the molal refraction and the polarizability estimation of AMImCl and BMImPF6 are also one of the study's aim from the density and refractive index and ultra-violet measurements. In addition to that, the conductivity and ultra violet measurements will be used to investigate the interaction between anionic surfactant (sodium dodecyl sulphate) and the four ionic liquids aqueous solutions, also for the interaction between cationic dye (methylene blue) and the four ionic liquids aqueous solutions at certain temperature (298.15 K). Mixed water with ethanol, methanol and glycerol were used to give wide range of dielectric constant (relative permittivity) and dipole moment solvent mixtures. This will give different effects on the solvation process of the studied ionic liquids.

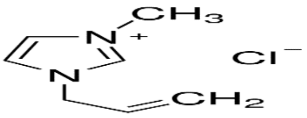
1. Experimental

1.1. Chemicals and Solutions

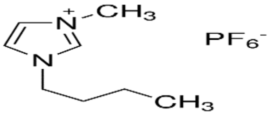
Chemicals used were all of highest available purity as shown in Table1.

2.2.Apparatus

The chemical structure of ILs under study, 1-Allyl-3-methylimidazolium chloride (AMImCl) and 1-Butyl-3-methylimidazolium hexaflourophosphate (BMImPF6) are shown in (Structure 1). Bidistilled water with conductivity of 0.05 to 0.5 $S.cm^{-1}$ was used to prepare (0.1 $mol.L^{-1}$) solution of the AMImCl and BMImPF6 surfactants.



1-Allyl-3-methylimidazolium chloride (AMImCl)



1-Butyl-3-methylimidazolium hexaflourophosphate (BMImPF6)

2.3. Apparatus and Methodology

A Jenway Conductivity Bridge was used to make the conductivity measurements. The K_{cell}, cell constant was determined various potassium chloride standard solutions were used. to calibrate the conductivity bridge[48].The conductivity was calculated as a function of the concentrations of AMImCl and BMImPF6 surfactants. To prevent dilution errors when making different AMImCl and BMImPF6. The concentration of the sample solution was progressively increased with the addition of surfactant solutions increased by adding $0.1molL^{-1}$ of the previously prepared surfactant solution to the initial sample size is 20 mL pure water in a double jacket glass cell, i.e. followed by the addition of the surfactant. Using an ultrathermostate of sort, within 0.1 K of a desired temperature, the temperature of the solution in the double jacket glass cell was kept constant (MLW 3230, Germany). After each addition, the solution was stirred to ensure uniform mixing, and the conductivity was measured.

The conductivity test has a 0.025 S.cm^{-1} uncertainty. The precise conductance was calculated twice, with the average of the results used for estimates as well as debate Surface tension measurements were taken with a wireless tensiometer K9. were made (ring method). The refractive index was measured for surfactants solution in both water and ethanol mole fraction solvent by putting one drop of the solution understudy into sample tray by using Digital Refractometer (DR101-60- A. KRÜSS Optronic GmbH – Germany). The ultra-violet measurements were carried out using Jasco V-630 UV-Visible double beam Spectroscopy. The UV absorbance of the four ionic liquids in dye aqueous solutions was measured as a function of concentration at 298.15 K. The temperature of the solution was kept constant within ±0.1 K of a desired temperature (298.15 K) using an ultrathermostate of type (MLW 3230, Germany). A different concentration from ionic liquids solutions (0.0005 to 0.02 mol/L) were prepared in fixed concentration of dye aqueous solution (3 x10^{-5} mol/L).

3. Results and Discussion

3.1. CMC determination

As stated in the experimental section, the conductivity of AMImCl and BMImPF6 ILs at 298.15 K, different mole fractions of alcohols were tested in aqueous and alcoholic-aqueous mixed solvents (methanol, ethanol, and glycerol). Relationship of measured conductivity, surface tension, refractive index and ultra-violet versus the two ILs concentrations was used to CMC Estimation of AMImCl and BMImPF6 in various solutions, as shown in Figures 1-6. Table 2 summarizes the CMC values of AMImCl and BMImPF6 with various mole fractions of alcohols.

Table1: The reg. CAS number, the purity, the supplier, and methods of the purification of the chemical compounds used.

Compound	**Reg. CAS Number**	**suppliers**	**%Purity before purification**	**Purification method**
AMImCl	65-10-3	Alfa Aesar	(98.0%)	The compounds were used without further purification
BMImPF6	174-65-5		(98.0%)	
Ethanol	232-11-1	Sigma Aldrich	(97.8%)	
Methanol	211-12-7		(97.7%)	
Glycerol	89-15-3		(97.2%)	

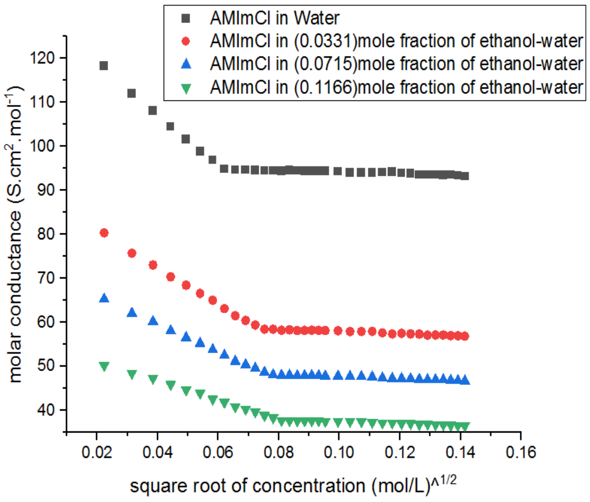


Figure 1: CMC from conductivity measurements for AMImCl in Ethanol-Water mixed solvents with different Ethanol mole fractions at 298.15 K

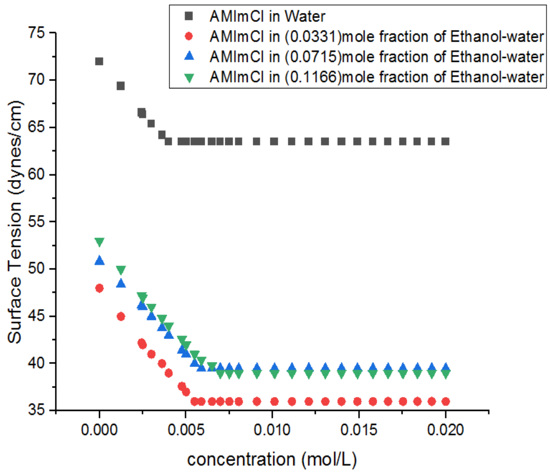


Figure 2: CMC from surface tension measurements for AMImCl in ethanol-Water mixed solvents with different Ethanol mole fractions at 298.15 K

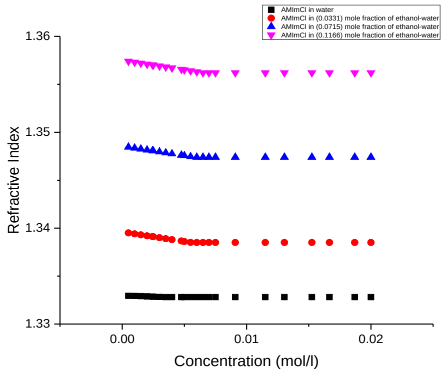


Figure 3: CMC from refractive index measurements for AMImCl in ethanol-Water mixed solvents with different Ethanol mole fractions at 298.15 K

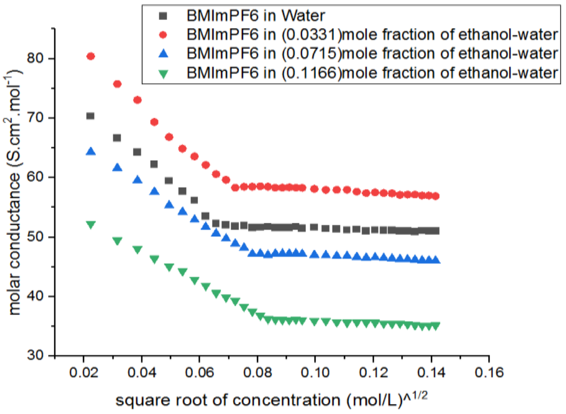


Figure 4: CMC from conductivity measurements for BMImPF6 in ethanol-Water mixed solvents with different Ethanol mole fractions at 298.15 K

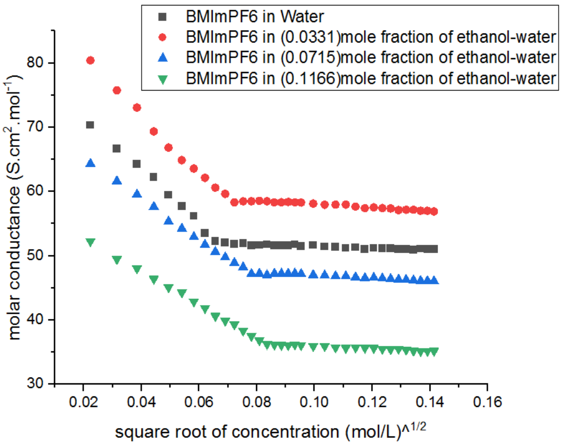


Figure 5: CMC from surface tension measurements for BMImPF6 in ethanol-Water mixed solvents with different Ethanol mole fractions at 298.15 K**.**

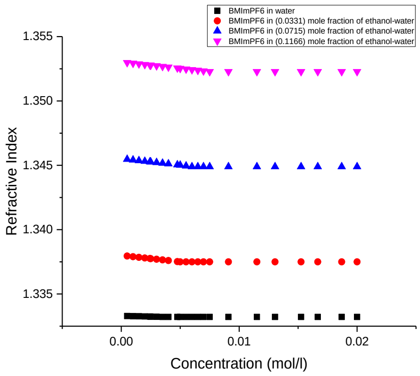


Figure 6: CMC from refractive index measurements for BMImPF6 in ethanol-Water mixed solvents with different Ethanol mole fractions at 298.15 K

The CMC values obtained for AMImCl and BMImPF6 using different techniques (Conductivity, Surface Tension and Refractive Index) are close together, indicating good agreement between these techniques and correct value of CMC (Figure 7 as example).

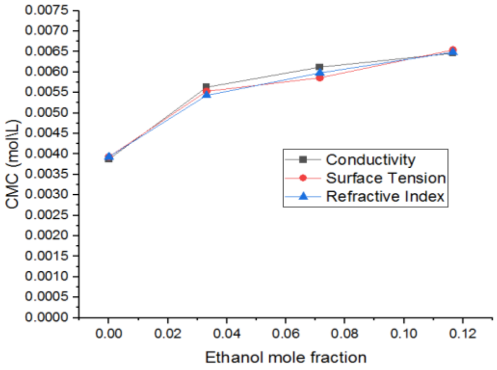


Figure 7: CMC from conductivity, Surface tension and refractive index measurements for AMImCl in Ethanol-Water mixed solvents with different Ethanol mole fractions at 298.15 K

In both solvents tested, the CMC of AMImCl and BMImPF6 increased as the alcohol mole fraction increased. Both ILs' CMC also increased in the following order: glycerol-water > ethanol-water > methanol-water. This may be related to the higher viscosity of the liquids in the same order. The higher the viscosity, the lower the solvation of AMImCl and BMImPF6, the higher the micellization, the higher the CMC values are found.

The micelle's degree of ionization (α) as well as the sum binding of counter ions, β= (1- α) of (AMImCl) and (BMImPF6) in comparison to the mole fraction of alcohol was suggested as in the following equation:

$\alpha = S_2/S_1$ ……………… (1)

S_2/S_1 is the ratio of the slopes of the post and pre micelle areas, and was determined as, ($\beta = 1 - \alpha$). The slopes were calculated using linear conductivity versus IL concentration plots. The values of α are recorded in Table 3. The thermodynamic parameters of micellization were obtained using the following equation.

$\Delta G_{mic} = (2 - \alpha)\ RT \ln [CMC]$ ……………… (2)

Where (ΔG_{mic}) is the standard free energy change, α is the micelle's degree of ionization, R is the gas constant and T is the absolute temperature, the results were presented in Table 3.

From Table 3, the values of ΔG_{mic}, were found to be negative in all situations, indicating the spontaneity of the micellization process and indicating that the concentration of alcohols increases the spontaneity of the process.

Table 2: CMC values for AMImCl and BMImPF6 in water and in alcohol-water mixed solvents at 298.15 K

Solvent	**Alcohol Mole fraction**	**CMC (mol/L) of AMImCl**			**CMC (mol/L) of BMImPF6**		
		Conductivity	**Surface Tension**	**Refractive Index**	**Conductivity**	**Surface Tension**	**Refractive Index**
Ethanol-water	0.0000	0.00387	0.00393	0.00393	0.00404	0.00402	0.00402
	0.0331	0.00563	0.00553	0.00553	0.00522	0.00507	0.00507
	0.0715	0.00612	0.00586	0.00586	0.00598	0.00614	0.00614
	0.1166	0.00646	0.00654	0.00654	0.00741	0.00754	0.00754
Methanol-water	0.0000	0.00387	0.00393	0.00393	0.00404	0.00402	0.00402
	0.0470	0.00528	0.00502	0.00502	0.00478	0.00473	0.00473
	0.0999	0.00565	0.00556	0.00556	0.00541	0.00552	0.00552
	0.1598	0.00609	0.00587	0.00587	0.00655	0.00653	0.00653
Glycerol-water	0.0000	0.00387	0.00393	0.00393	0.00404	0.00402	0.00402
	0.0267	0.00565	0.00556	0.00556	0.00609	0.00616	0.00616
	0.0582	0.00609	0.00615	0.00615	0.00655	0.00694	0.00694
	0.0958	0.00697	0.00693	0.00693	0.00807	0.00805	0.00805

Standard uncertainties (u); u (CMC) = 0.00005 mol L^{-1}

Table 3: The degree of ionization (α), and the free energy of micellization of AMImCl and BMImPF6 as a property of the mole fraction of alcohol at 298.15 K

Solvent mixtures	**Solvent mole fraction**	**AMImCl**		**BMImPF6**	
		α	**ΔG_{mic} (kJ/mol)**	**α**	**ΔGmic (kJ/mol)**
Ethanol – Water	0.0000	0.99734	-14.270	0.98695	-14.540
	0.0331	0.99327	-13.360	0.99571	-13.740
	0.0715	0.99016	-13.180	0.98642	-13.510
	0.1166	0.97451	-13.250	0.98111	-13.010
Methanol – Water	0.0000	0.99734	-14.270	0.98695	-14.540
	0.0470	0.98054	-13.700	0.99921	-13.920
	0.0999	0.98823	-13.420	0.98524	-13.790
	0.1598	0.99552	-13.130	0.97179	-13.460
Glycerol – Water	0.0000	0.99734	-14.270	0.98695	-14.540
	0.0267	0.99623	-13.310	0.99281	-13.380
	0.0582	0.98159	-13.310	0.97981	-13.360
	0.0958	0.96860	-13.120	0.95021	-13.170

Standard uncertainties (u); u (α) = 0.0004, u(ΔGmic) =0.003 kJ/mol

The values of α and β were determined from the conductivity data only. In conductivity curves the slope of the graph after CMC is seem to be small, so that, α is small value and β is high value. This depends on the change in the measured conductivity which may be dependent on the electrolytic nature of ionic liquid.

The Walden product ($\Lambda^{\circ}\eta^{\circ}$) which are informative from the point of view of ion–solvent interaction49, has constant value due to the molal conductance of an ion at infinite dilution depends only upon its speed and hence, the product of ion conductance by the viscosity of the medium should be independent of the solvent nature. Hence, the Walden product ($\Lambda^{\circ}\eta^{\circ}$) is expected to be constant for a given electrolyte in a series of solvent mixtures in which the ion solvent interactions are uniform.

The Walden product (Λ°η°) values were calculated for AMImCl and BMImPF6 in at 298.15 K, the mole fractions of alcohols. Similar mole fractions of alcohols were measured in aqueous and alcoholic-aqueous mixed solvents (ethanol, methanol, and glycerol) with different mole fractions of alcohols (ethanol, methanol, and glycerol), and the findings are described in Tables 4&5. The fluidity ratio (Rx) which is the ratio between the values of the Walden product of the two surfactants in alcohol-water solvent to that of water can be calculated.

The Walden product (Λ°η°) of AMImCl and BMImPF6 solutions was found to increase in the presence of alcohol. This is due to the fact that mixed alcohol-water has a higher viscosity than pure water. As the mole fraction of alcohol (ethanol, methanol, and glycerol) increases, the value of the limiting molal conductance decreases. This means that the viscosity of the solvent, not the limiting molal conductance, is the most important factor in changing the Walden substance.

3.2. Molal volumes

At 298.15 K, the density of various molal concentrations of (AMImCl) and (BMImPF6) surfactants in aqueous and alcoholic-aqueous mixed solvents (methanol, ethanol, and glycerol) with various mole fractions of alcohols was measured. The apparent molal volume, Vφ of AMImCl, and BMImPF6 were determined using the following equations50 based on the molal concentration and density values.

Where M is the molecular weight of AMImCl, and BMImPF6, the molal concentrations of AMImCl and BMImPF6 in solution are denoted by m, and the solution and solvent densities are denoted by ρ and ρ_o, respectively. Tables 4&5 show the measured apparent molal volumes, Vφ of AMImCl and BMImPF6 in glycerol, methanol, and ethanol with different alcohol mole fractions at 298.15 K for AMImCl and BMImPF6.

The packing density (the relation between the Van der Waals volume and the partial molal volume of relatively large molecules is found to be constant 51,52. Therefore, it is possible to calculate the Van der Waals volumes (Vw) of the polymers under study by apply the following equation53.

Packing density $P=V_w/V_\varphi =0.661\pm0.017$… (4)

The electrostriction volume (Ve) which is the volume compressed by the solvent51–54, can be calculated using the following equation.

$Ve = Vw - V\varphi$ ………………… (5)

The Walden product (Λ°η°), apparent molal volume (Vφ), the Van der Waals volume (VW) and electrostriction volume (Ve) of AMImCl are presented in Tables 4&5.

In the case of methanol-water and ethanol-water solvents, the densities of AMImCl and BMImPF6 solutions decreased as the mole fraction of alcohol increased, while they increased in the case of glycerol-water solvents. In the case of methanol-water and ethanol-water, V_φ of AMImCl solutions increases with increasing the alcohol mole fraction (Figure 8 as example), but it decreases with increasing the alcohol mole fraction in the case of glycerol-water. This may be related to the density of the alcoholic solvent under investigation (glycerol has more density than methanol, water and ethanol).

Table 4: Walden product (Λ°η°), Apparent Molal Volume (V_φ), the Van der Waals Volume (V_W) and Electrostriction Volume (V_e) of AMImCl as a function of the mole fraction of alcohol at 298.15 K.

Solvent mixtures	**Mole fraction of alcohol**	**Λ°η°** **S cm^2 mol^{-1}cP**	**ρ** g cm^{-3}	***Vφ*** (cm^3/mole)	**V$_W$** (cm^3/mole)	**V$_e$** (cm^3/mole)
Ethanol - Water	0.0000	0.941	1.0398	152.551	100.840	-51.715
	0.0331	0.895	1.0198	155.552	102.820	-52.732
	0.0715	0.960	1.0140	156.439	103.410	-53.033
	0.1166	0.876	1.0083	157.316	103.990	-53.330
Methanol - Water	0.0000	0.941	1.0398	152.551	100.840	-51.715
	0.0470	0.533	1.0095	157.129	103.860	-53.267
	0.0999	0.640	1.0098	157.083	103.830	-53.251
	0.1598	0.748	1.0138	156.470	103.430	-53.043
Glycerol - Water	0.0000	0.941	1.0398	152.551	100.840	-51.715
	0.0267	0.786	1.1835	134.020	88.587	-45.433
	0.0582	0.848	1.1542	137.425	90.838	-46.587
	0.0958	0.905	1.1247	141.041	93.228	-47.813

Standard uncertainties (u); u (Λ°η°) = 0.0011 S cm^2 mol^{-1}cP, u(ρ)=0.00003 g cm^{-3}, u(V_φ)=0.05 cm^3/mole, u(V_W)=0.05 cm^3/mole , u(V_e)=0.05 cm^3/mole

Table 5: Walden product ($\Lambda^{\circ}\eta^{\circ}$), Apparent Molal Volume (V_{φ}), the Van der Waals Volume (V_W) and Electrostriction Volume (V_e) of BMImPF6 as a function of the mole fraction of alcohol at 298.15 K.

Solvent mixtures	**Mole fraction of alcohol**	**$\Lambda_o.\eta$ S cm^2 mol^{-1}cP**	**ρ** g cm^{-3}	***$V\varphi$*** (cm^3/mole)	**V_W** (cm^3/mole)	**V_e** (cm^3/mole)
Ethanol - Water	0.0000	0.523	1.0432	272.405	180.060	-92.345
	0.0331	1.185	1.0232	277.741	183.590	-94.154
	0.0715	1.292	1.0154	279.873	185.000	-94.877
	0.1166	1.264	1.0118	280.866	185.650	-95.213
Methanol - Water	0.0000	0.523	1.0432	272.405	180.060	-92.345
	0.0470	0.702	1.0113	280.997	185.740	-95.258
	0.0999	0.634	1.0098	281.410	186.010	-95.398
	0.1598	0.561	0.9936	285.996	189.040	-96.953
Glycerol - Water	0.0000	0.523	1.0432	272.405	180.060	-92.345
	0.0267	0.840	1.0923	260.152	171.960	-88.191
	0.0582	0.903	1.1578	245.433	162.230	-83.202
	0.0958	0.917	1.2368	229.756	151.870	-77.887

Standard uncertainties (u); u ($\Lambda^{\circ}\eta^{\circ}$) = 0.0011 S cm^2 mol^{-1}cP, u(ρ)=0.00003 g cm^{-3}, u(V_{φ})=0.05 cm^3/mole, u(V_W)=0.05 cm^3/mole , u(V_e)=0.05 cm^3/mole

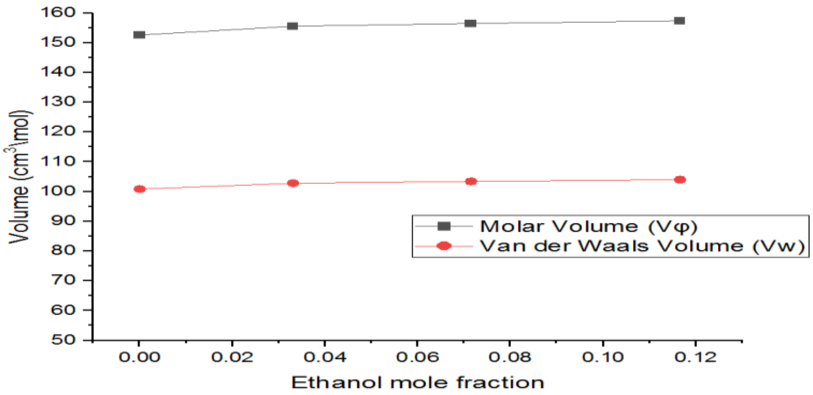


Figure 8: Change of the molal volume and the Vander Wall volume with the ethanol mole fractions for AMImCl in ethanol-Water mixed solvents at 298.15 K

3.3. Polarizability, refractive index, and molal refraction

At 298.15 K, the refractive indices of AMImCl and BMImPF6 in water, glycerol, methanol and ethanol - water with various. The mole fractions of alcohol were determined, and the findings are shown in Table 6&7. AMImCl and BMImPF6 refractive indices in methanol, glycerol, methanol, and ethanol-water solutions. As the alcoholic mole fraction increases, different alcohol mole fractions increase.

The molal refraction of the two surfactants in glycerol, ethanol, methanol-water with different alcohol mole fractions can also be determined centered on the refractive indices that have been calculated (Rm) was calculated[55] using the following equation.

$$= PA + PE = PD + PT \quad \ldots\ldots\ldots\ldots\ldots\ldots \; (6)$$

The apparent molal volume of the two surfactants in solution is given by Vφ, and n is the AMImCl solution’s refractive index. The gross molal polarization, or distortion polarization, is equal to the percentage of both the electron polarization (PE) and the atomic polarization (PA) on equation (3). The following equation was used to determine the atomic polarization (PA)[56].

$$P_A = 1.05\, n^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \; (7)$$

The optical refractive index (n) of a substance containing N molecules per unit volume can be used to measure the mean value of molecular dipole polarizability (α; dipole moment caused by electric field). The refractive index is related to the polarizability (α) of the molecules by the Lorenz-Lorenz formula [57]. As shown in the following equation

$$\frac{n^2-1}{n^2+2} = \frac{4\,\pi\,\hat{n}\,\alpha}{3} \quad \ldots\ldots \; (8)$$

Where $\hat{n} = \frac{N}{V_{\phi}}$,

(N) is the Avogadro’s number and (V_{φ}) is the apparent molal volume. From equation (8), the polarizability of AMImCl and BMImPF6 in the alcohol mole fractions of glycerol, ethanol, and methanol-water were determined. Calculated molal refraction (Rm), atomic polarization and polarizability (α) were reported, in Table 6&7.

The apparent molal volume is directly proportional to the molal refraction and polarizability. As the mole fraction of glycerol, methanol, and ethanol increases, so does the polarizability and molal refraction AMImCl and BMImPF6 in glycerol, methanol, and ethanol -water. This increase in the molal refraction and the polarizability of AMImCl and BMImPF6 with the mole fraction of glycerol, methanol and ethanol may be related to the increase in apparent molal volume of the two surfactants with glycerol, methanol, and ethanol mole fractions respectively in the apparent molal volume the two surfactants with the mole fraction of ethanol, methanol and glycerol respectively. This increase in the apparent molal volume of AMImCl and BMImPF6 with the mole fractions of ethanol, methanol, and glycerol can be due to the increase in the molal refraction and polarizability of the two surfactants with the mole fractions of ethanol, methanol, and glycerol.

The increase in the refractive index, atomic polarization and the polarizability of AMImCl as the mole fraction of ethanol increase as example was presented in Figure 9.

3.4. Ultra-Violet Visible Measurements

The UV-Visible spectra of the two ionic liquids under study, in water and in the aqueous solution of methylene blue dye (MB, fixed concentration 3x10^{-5} mole/L), have been measured experimentally at 298.15 K as described in the experimental section and presented in Tables 8&9 and Figures (10&11).

.To estimate the CMC of the two ionic liquids AMImCl and BMImPF6 in water and in the aqueous solution of dye, the relation of the measured absorbance at maximum wave length, versus the ionic liquid concentration was done Figures (12&13). The CMC values are collected in Tables 10. The effect of cationic dye, methylene blue dye (MB), on the CMC of ionic liquids under study, was discussed.

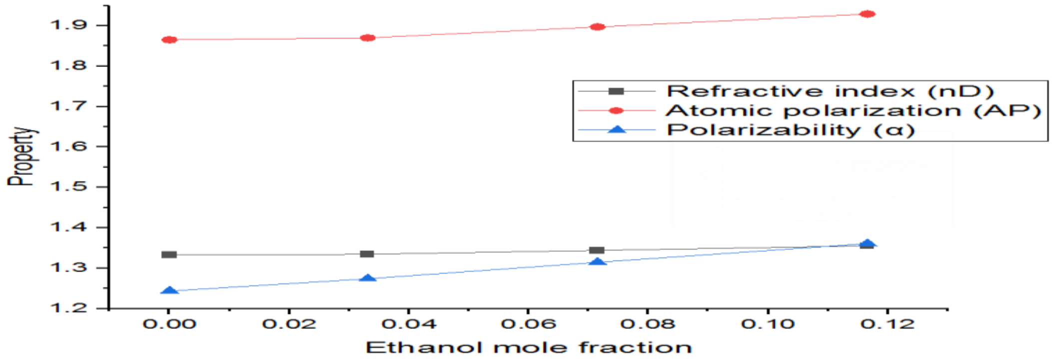


Figure 9: Change of the refractive index, atomic polarization and the polarizability with the ethanol mole fractions for AMImCl in ethanol-Water mixed solvents at 298.15 K

Table 6: At 298.15 K, the Refractive index (n_D), atomic polarization (A_P), molal refraction (R_m), and Polarizability (α) of AMImCl as a result of mole fraction of alcohol

Solvent mixtures	Mole fraction of alcohol	n_D	A_P	R_m cm^3/mol	α cm^3
Ethanol - Water	0.0000	1.3328	1.8652	31.3619	1.2435
	0.0331	1.3345	1.8700	32.1280	1.2739
	0.0715	1.3442	1.8972	33.1576	1.3147
	0.1166	1.3554	1.9290	34.3203	1.3608
Methanol - Water	0.0000	1.3328	1.8652	31.3619	1.2435
	0.0470	1.3362	1.8747	32.6024	1.2927
	0.0999	1.3446	1.8983	33.3289	1.3215
	0.1598	1.3524	1.9204	33.8761	1.3432
Glycerol - Water	0.0000	1.3328	1.8652	31.3619	1.2435
	0.0267	1.3659	1.9590	30.0124	1.1900
	0.0582	1.3711	1.9739	31.1661	1.2358
	0.0958	1.3763	1.9889	32.3863	1.2842

Standard uncertainties (u); u (n_D)=0.0001, u(A_P)=0.005, u(R_m)=0.004 cm^3/mole, u(α)=0.0005 cm^3

Table 7: At 298.15 K, the refractive index (n_D), atomic polarization (A_P), molal refraction (R_m), and Polarizability (α) of BMImPF6 are plotted as a function of the mole fraction of alcohol.

Solvent mixtures	**Mole fraction of alcohol**	**n_D**	**A_P**	**R_m cm^3/mol**	**α cm^3**
Ethanol - Water	0.0000	1.3332	1.8663	56.0630	2.2230
	0.0331	1.3352	1.8719	57.4725	2.2788
	0.0715	1.3374	1.8781	58.2580	2.3100
	0.1166	1.3392	1.8831	58.7471	2.3294
Methanol - Water	0.0000	1.3332	1.8663	56.0630	2.2230
	0.0470	1.3375	1.8784	58.5076	2.3199
	0.0999	1.3442	1.8972	59.6454	2.3650
	0.1598	1.3522	1.9199	61.8871	2.4539
Glycerol - Water	0.0000	1.3332	1.8663	56.0630	2.2230
	0.0267	1.3670	1.9621	58.4154	2.3162
	0.0582	1.3774	1.9921	56.5043	2.2405
	0.0958	1.3877	2.0220	54.1781	2.1482

Standard uncertainties (u); u (n_D)=0.0001, u(A_P)=0.005, u(R_m)=0.004 cm^3/mole, u(α)=0.0005 cm^3

Table 8. The maximum Abs values for the different concentration from AMImCl in aqueous solution of (3 x 10^{-5} mole/l) MB at 298.15 K

Concentration mole / l	**Abs**	
	AMImCl	**AMImCl + MB**
	289 nm	**657 nm**
0.0019	0.4769	0.6325
0.0024	0.5124	0.6501
0.0029	0.5465	0.6921
0.0033	0.5787	0.7364
0.0038	0.5853	0.8316
0.0043	0.5897	0.8689
0.0065	0.6049	0.8789
0.0080	0.6087	0.8843
0.0100	0.6149	0.8875

Table 9. The maximum Abs values for the different concentration from BMImPF6 in aqueous solution of (3 x 10^{-5} mole/l) MB at 298.15 K

Concentration mole / l	**Abs**	
	BMIMPF6	**BMIMPF6 + MB**
	289 nm	**657 nm**
0.0019	0.3207	0.6167
0.0024	0.3601	0.6787
0.0029	0.4044	0.7183
0.0038	0.4812	0.7967
0.0040	0.5287	0.8313
0.0055	0.5428	0.9246
0.0065	0.5513	0.9714
0.0080	0.5573	0.9784
0.0100	0.5625	0.9847

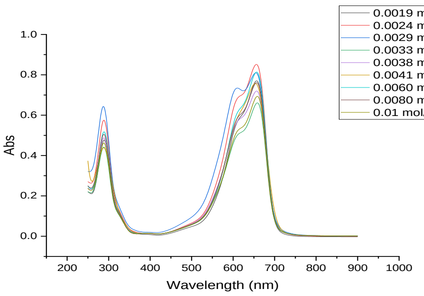


Figure 10. UV-Visible spectra for (0.0019-0.01) mole/l AMImCl in aqueous solution of 3 x 10^{-5} MB at 298.15 K.

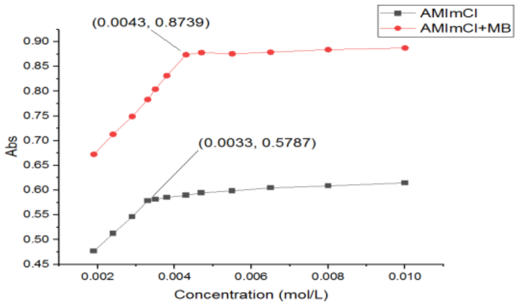


Figure 11. UV-Visible spectra for (0.0019-0.01) mole/l BMImPF6 in aqueous solution of 3 x 10^{-5} MB at 298.15 K

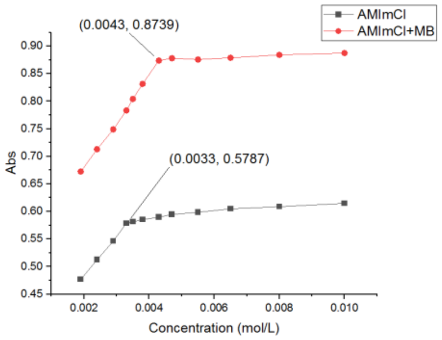


Figure 12. Absorbance versus concentration for AMImCl in aqueous solution in absence and in presence of (3 x 10^{-5} mole/l) MB at 298.15 K

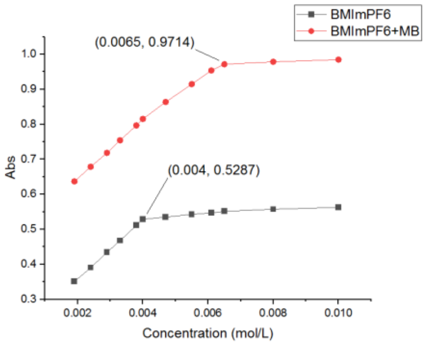


Figure 13. Absorbance versus concentration for BMImFP6 in aqueous solution in absence and in presence of (3 x 10^{-5} mole/l) MB at 298.15 K

Table 10. CMC (mol/L) values for AMImCl and BMImPF6 in 3x10^{-5} aqueous solution of methylene blue at 298.15 K using UV spectroscopy measurements

Solution	**Dye Concentration**	**CMC mol/l**	
		AMImCl	**BMImPF6**
Water	0.000	0.00334	0.00407
Methylene blue	3×10^{-5}	0.00430	0.00650

3.5. Effect of anionic surfactants on ionic liquids

The conductivity of the ionic liquid in aqueous solution of the anionic surfactant (0.1 mole/l from SDS) has been measured experimentally at 298.15 K, as described in the experimental section. To estimate the CMC of the mixed system, the relation of the conductivity versus the concentration was done as presented in Figures 14&15. The CMC values for the mixed systems were collected in Table 11.

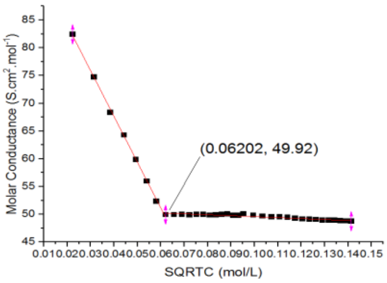


Figure 14. Molar conductance as a function of square root of concentration for AMImCl in aqueous solution of SDS at 298.15 K

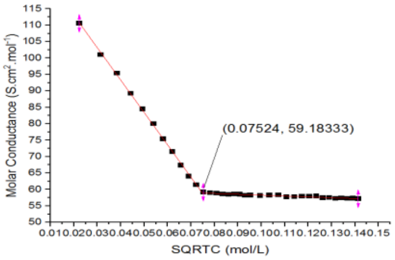


Figure 15. Molar conductance as a function of square root of concentration for BMImPF6 in aqueous solution of SDS at 298.15 K

Table 11. CMC (mol/L) values for AMImCl and BMImPF6 in Water and aqueous solution of SDS at 298.15 K using conductivity method

Solvent	**CMC (mole/l)**	
	AMImCl	**BMImPF6**
Water	0.00387	0.00404
Aqueous solution of SDS	0.00382	0.00566

3.6. Relation between the measured properties

Inspection to the data of the measured and calculated properties (CMC, molal volumes, refractive index, polarizability, atomic polarization and molal refraction), it was found that there is a relation between these different properties. It was found that as the alcohol (methanol and ethanol) mole fraction increase, the density of solution decrease, and so the molal volumes increase. As the molal volumes increase the CMC value, the refractive index, the polarizability, atomic polarization and the molal refraction were increased. In the case of glycerol, it was found that as the glycerol mole fraction increase, the density of solution increase, and so the molal volumes decrease. As the molal volumes decrease the CMC value, the refractive index, the polarizability, atomic polarization and the molal refraction were decreased.

Conclusion

The CMC of 1-Allyl-3-methylimidazolium chloride (AMImCl) and 1-Butyl-3-methylimidazolium hexaflourophosphate (BMImPF6) experimentally, In aqueous and alcoholic-aqueous mixed solvents, surfactants are used (glycerol, methanol, and ethanol) with various mole percentages of alcohols have been calculated at 298.15.K using the refractive index, surface tension, conductivity and The UV-Visible spectra measurements. The CMC of (AMImCl) and (BMImPF6) was found to increase in all solvents used, the alcohol mole fraction increased. The CMC value from conductivity, surface tension, and refractive index measurements is found to be in good agreement.

The temperature dependence of micellization constants was used to measure the thermodynamic parameters (ΔG°) of the micellization processes. It was also discovered that the CMC of (AMImCl) and (BMImPF6) increases in the following order: methanol ethanol glycerol. Micellization was discovered to be a normal process. At 298.15 K, the refractive index and density of AMImCl and BMImPF6 in aqueous and alcoholic-aqueous mixed solvents (ethanol, glycerol, and glycerol methanol) with various mole fractions of alcohols were determined experimentally. The molal volume of the two surfactants was calculated using density data. The molal refraction and polarizability of AMImCl and BMImPF6 were also calculated using the refractive index data.

The critical micelle concentration (CMC) of AMImCl, and BMImPF6 ware in methylene blue ($3*10^{-5}$) is higher than in water (Figures 12-13). Where (CMC) values appear at the highest peak in (Figures 10-11). From Table 10 it was observed that the critical micelle concentration of the two ionic liquids increased with addition of dye. Such phenomenon can be explained due to addition of counter ions (e.g., N^+ and Cl^-) for the carrying current. The use of UV-Visible Spectroscopy technique was a very good and easy way of determining the critical micelle concentration.

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