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**Azepanium based Protic Ionic Liquids: Synthesis, Thermophysical Properties
and COSMO-RS study**

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Abstract

Protic ionic liquids (ILs) with seven-membered azepanium cation were synthesized and characterized. The molecular structure of the synthesized ILs were confirmed using ^1H NMR and ^{13}C NMR spectroscopy. In one hand, sulphonic acid ($-\text{SO}_3\text{H}$) group was tethered to the azepanium moiety combined with HSPO_4 or H_2PO_4^- anion and on the other hand azepanium based alkyl sulfate ILs were synthesized by reacting azepane with corresponding dialkylsulphates. Thermo-physical properties (density, viscosity, glass transition temperature, thermal decomposition temperature) of the synthesized ILs were measured. All the studied ILs showed good thermal stability. From the viscosity and density data of alkyl sulfate ILs, the volumetric properties such as molar volume, lattice energy and standard molar entropy were calculated. COSMO-RS was used to predict hydrogen bonding energy, interaction energy, Van der Waals energy and H-bond accepting and H-bond donating nature of these pure ILs. Activity coefficient values have also predicted for these ILs with cellulose.

1. Introduction

In the last two decades, the field of ionic liquids (ILs) recorded exponential growth because of their beneficial properties such as very low vapour pressure, high thermal stability, large liquid range and wide electrochemical window, etc. ILs can be considered as organic salts consisting entirely of ions[1]. Some of these properties can be adjusted according to the application by a thoughtful selection of cations and anions. For instance, the melting point of ILs can be reduced by the selection of big, bulky and asymmetric cations. Hydrophobic ILs can be synthesized by using bis(trifluoromethylsulfonyl) imide ($[\text{Tf}_2\text{N}]^+$) and hexafluorophosphate ($[\text{PF}_6]^-$) anions, whereas hydrophilic and low viscous ILs can be synthesized by introducing dicyanamide ($[\text{N}(\text{CN})_2]^-$) anion. Because of this unique nature, ILs are also known as designer solvents. In general, ILs are synthesized using the common cationic cores such as 1-alkyl-3-methylimidazolium[2], 1-alkyl pyridinium, 1-alkyl-1-methyl pyrrolidinium and 1-alkyl-1-methyl piperidinium etc [2-4], which are either five or six-membered aromatic/ nonaromatic ring systems. There are only a few reports regarding the synthesis of ILs bearing cations with more than six-membered rings [4-7]. In 2011, Belhocine *et al.* reported the first synthesis of ILs containing seven-membered (azepanium) cyclic cation[5], followed by this, a few more reports regarding the application of azepanium ILs were appeared [8-10]. However, to the best of our knowledge, there are no reports regarding the synthesis and applications of functionalized azepanium ILs containing acidic ($-\text{SO}_3\text{H}$) functional groups and alkyl sulfate anions, which may be helpful for specific applications such as biomass valorization.

Functionalized ILs can be defined as ILs with a functional group tethered to cation/ anion or on both[11]. They have a unique set of properties as compared to classical ILs. For instance, the solubility of inorganic salts in classical ILs with weakly coordinating anions is very low. This is certainly a disadvantage for applications requiring high concentration of metal salts (e.g.electrodeposition of metals). The introduction of nitrile or carboxylic acid functionalities on ILs has been reported to dramatically enhance metal salts solubility in ILs [3, 12, 13].

In this work, the synthesis and characterization of proticazepanium ILs containing $-\text{SO}_3\text{H}$ functional group with anions such as hydrogen sulfate and dihydrogen phosphate were performed. Azepanium ILs containing alkyl sulfate anions were also reported. In addition, the physicochemical properties such as density, viscosity, thermal decomposition temperature, heat capacity and glass transition temperature the ILs were studied. Density and viscosity of ILs (which are liquids at room temperature) were measured. COSMO-RS was used to evaluate the potential of these ILs in cellulose dissolution. Biomass components such as cellulose, hemicelluloses, and lignin are inter linked through hydrogen and covalent bonding network. ILshave been proved to be highly efficient for the selective dissolution of biomass components. In general, anionic component of the ILs disrupting the strong inter and intra molecular hydrogen bonding network among the biomass components [14]. Nevertheless, a few reports suggest that the cationic part of ILs may also interact in a less extent with biomass. Based on this, ILs having an anionic component with high hydrogen bond basicity would be good choice for biomass dissolution. Hydrogen bond basicity can also referred as the hydrogen bond accepting nature of anion. It should be noted that ILs involving in biomass studies like dissolving cellulose [15], carbohydrate [16] and protein [17] and so on contains Cl^- , Br^- and H_2PO_4^- as anionic moieties.

2. Experimental

Hexamethyleneimine (98%), 1,4-Butanesultone ($\geq 98\%$), Dimethyl sulphate(98 %), Diethyl sulphate (98%) Sulphuric acid (100%) were purchased from Merck and used without any further purification. Hydrochloric acid (37 %) was obtained from R&M Chemicals, and 85wt % phosphoric acid (85 wt %) was purchased from Sigma Aldrich.

An Anton Paar viscometer (model SVM 3001, Austria) was used to measure the viscosity and density simultaneously. The density of the synthesized ILs was measured via ASTM D4052 and the viscosity was measured via ASTM D2270. The viscosity and density was measured in a temperature range of 283.15K to 373.15K. The thermogravimetric analysis was performed using Perkin Elmer (Pyris V-3.81, USA) with a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The specific heat capacity (C_p) and glass transition temperature (T_g) were measured using Differential Scanning Calorimetry (DSC), Perkin-Elmer (model Pyris1, USA). The measurements were performed with a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ under helium flow. The carbon, hydrogen, nitrogen and sulfur percentages in ILs were analyzed according to the approved method ASTM D-5291 by employing Leco-CHNS-932 analyzer from USA. Saphire method was used for calculating the specific heat capacity and the details can be found elsewhere [18].

2.1.4-(azepanium-1-yl)butane-1-sulfonate

Hexamethyleneimine (12.66g, 0.128 mol) was added to cyclohexane (20mL) in a two-necked round bottom flask and stirred for 15minutes at room temperature. 1,4-butanesultone (23.15g, 0.128mol) was then added and the mixture was allowed to stir for 2 hours until the mixture became white solid. The resulting product was washed cyclohexane (3 x 20 mL) and

dried in a rotary evaporator at 50 °C to afford a white powder. The product formed was further dried in a vacuum oven at 50 °C for 24 hours. Yield: 34.1 g (95.3%). ¹H NMR (500 MHz, D₂O): δ: 13.1 (m, 4H), 1.48 (m, 8H), 2.56 (m, 2H), 2.81 (m, 4H), 2.97 (s, 1H), 3.10 (m, 2H). ¹³C NMR (125 MHz, D₂O): δ: 21.14, 22.45, 23.57, 49.89, 50.30, 54.50, 56.50.

2.2. 1-(4-sulfobutyl)azepan-1-ium hydrogen sulfate

One equivalent of 4-(azepanium-1-yl)butane-1-sulfonate (14.4 g, 0.06 mol) was placed into a two necked-round bottom flask fitted with a magnetic stirrer. Sulphuric acid (6 g, 0.06 mol) was then added drop wise at room temperature and the resulting mixture was allowed to stir for 4 hours at room temperature leading to a homogeneous solution. The resulting solution was then washed with ethyl acetate (3 x 10 mL) and dried using a rotary evaporator. The ILs obtained was further purified with activated carbon and methanol (IL 1wt%: 1wt% methanol: 0.1wt% activated carbon) at room temperature for 8 hours. The activated carbon was removed by centrifugation (15 min, 4000 rpm) and the resulting transparent solution was then dried on a rotary evaporator at 50°C for 5 hours to remove methanol followed by further drying in Schlenk line for 48 hours at 50 °C to afford the ILs. Yield: 88 % (18.7 g). ¹H NMR (500 MHz, D₂O): δ: 1.42 (m, 4H), 1.64 (m, 8H), 2.69 (m, 2H), 2.93 (m, 4H), 3.19 (m, 2H), 3.48 (s, 1H). ¹³C NMR (125 MHz, D₂O): δ: 21.23, 22.58, 23.21, 49.94, 54.57, 56.52.

2.3. 1-(4-Sulfo-butyl)-azepaniumdihydrogen phosphate

1-(3-Sulfo-propyl)-azepaniumdihydrogen phosphate was prepared through the same procedure previously described for 1-(4-Sulfobutyl)-azepanium hydrogen sulfate using zwitterion (14.4 g, 0.06 mol) and H₂PO₄ (85%, 6.9 g, 0.06 mol). Yield: 18.5 (88%). ¹H NMR (500

MHz, D₂O): δ : 13.1(m, 4H), 1.48 (m, 8H), 2.56 (m, 2H), 2.81 (m, 4H), 2.97 (s, 1H), 3.10(m, 2H).

¹³C NMR (125 MHz, D₂O): δ : 21.14, 22.45, 23.57, 49.89, 50.30, 54.50, 56.50.

2.4.1-Methyl-azepanium methyl sulfate

Dimethyl sulfate (6.3 g, 0.05 mol) was introduced into a two-necked flask fitted with a reflux condenser and a magnetic stirrer and placed in an ice bath. Hexamethylenamine (4.97 g, 0.05 mol) was added dropwise. After 2 hours of stirring, the resulting solution was brought to room temperature and stirred for another 48 hours to ensure completion of the reaction. The washing and drying steps were then performed as described for 1-(3-sulfo-propyl)-azepanium hydrogen sulfate to afford 1-Methyl-azepanium methyl sulfate. Yield-10.3 g(92%). ¹H NMR(500 MHz, D₂O): δ : 1.58(m, 4H), 1.70 (m, 4H), 3.15(m, 4H), 2.78(s, 3H), 3.80(s, 3H), 4.12 (s, 1H). ¹³C NMR (125 MHz, D₂O): δ : 22.1, 32.1, 41.7, 55.6, 56.1.

2.5.1-ethyl-azepanium ethylsulfate

1-ethyl-azepanium ethylsulfate was prepared by the same procedure described for 1-methyl-azepanium methyl sulfate from hexamethylenamine (4.97 g, 0.05 mol) and diethylsulfate (7.9 g, 0.05 mol). ILs was washed cyclohexane (3 x 10 mL) and the residual solvent was removed using a rotary evaporator and the IL was further dried in a Schlenk line at 50 °C for 24 hours. Yield: 12.3 g(96%). ¹H NMR(500 MHz, D₂O): δ : 1.38 (t, 3H), 1.56(t, 3H), 1.60(m, 4H), 1.70(m, 4H), 3.22 (m, 4H), 3.29(m, 2H), 3.58(m, 2H), 4.1(s, 1H). ¹³C NMR (125 MHz, D₂O): δ : 9.1, 12.5, 21.7, 30.2, 44.1, 53.5, 60.7.

2.6.COSMO-RS - Methodology

Thermodynamic properties and phase behavior of the pure fluids and/or mixtures effectively predicted by COSMO-RS model [19-22]. Statistical thermodynamics in combination with

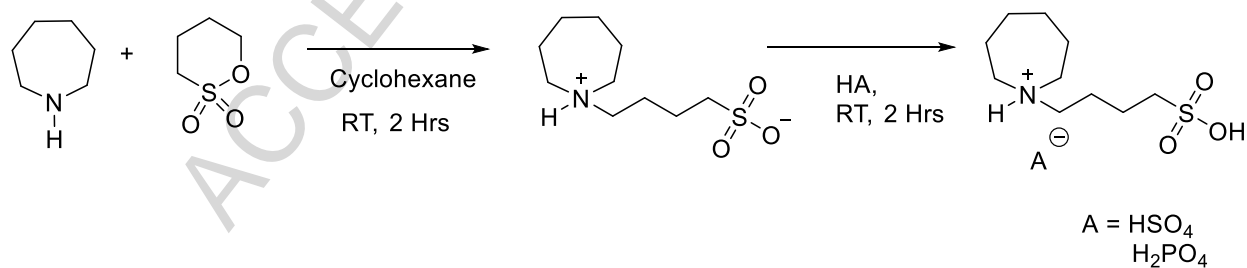
quantum chemistry (based on the dielectric continuum model) are used in COSMO-RS to compute the chemical potential of the interacting segments. Presuming the molecules are surrounded by virtual conductor environment, the interactions are completely performed on the conductor interface, considering the back polarization and electrostatic screening of the solute molecule. Hence, a discrete surface is provided around the solute molecule, which is characterized by its geometry and screening charge density (σ). It iteratively corresponds to a minimum energetic state at the conductor. Obtaining screening charge density of the segments, σ' is important since the COSMO-RS treats the surface around the solute molecule as segments. This information is available in COSMO files. The hydrogen bonding energy, E_{HB} , and the electrostatic misfit energy, E_{misfit} , are the most relevant in the molecular interaction approach. They are expressed as a function of the polarization charges of the two interacting segments. Based on the type of atoms involved, the Van der Waals energy is also considered. The complete theory of these energies can be found in the original work published by Klamt[20, 23]. Since COSMO-RS does not depend on the discrete surface geometry, it uses the 3D density distribution on the surface of each solute molecule X_i , which is converted into a distribution function called the σ -profile, $p^X(\sigma)$. The relative amount of surface segment with polarity σ is described by this distribution function. Normalized σ -profile of the system, $p_s(\sigma)$ is obtained by combining the molecular σ -profiles with the pure or mixture solvents (S) σ -profiles results in the mole fraction weighted sum of σ -profiles of its compounds, $p_S(\sigma)$, that normalized by the total surface area, A_S . Chemical potential is derived based on the normalized σ -profile of the molecular interaction [23]. The chemical potential of the components in a mixture allows the estimation of several thermodynamic properties, namely activity coefficients, distribution ratios, and phase equilibria, among others [24-26]. More complex systems like ILs, exhibit different

conformational geometries corresponding to various energy states. Conformers with lower energy give better results[27]. COSMO-RS calculations were carried out at the lower energy state of the conformers of each IL anion and IL cation.

The COSMO-RS cation and anion files were generated using BP functional with a triple- ξ valence polarized with diffuse functions basis set (TZVPD) and the resolution of identity standard (RI) approximation using the TURBOMOLE 7 program package [28]. The subsequent calculations like predicting the hydrogen bonding energy, Vander Waals energy, hydrogen bond accepting moment and hydrogen bond donating moments were calculated using the COSMOtherm employing the parameter file BP_TZVPD_FINE_C30_1701.ctd [29].

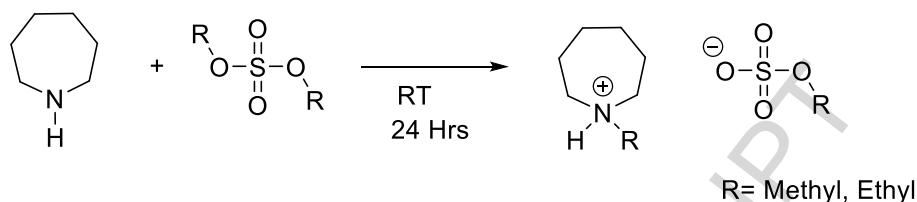
3. Results and Discussion

Two different methods were used to synthesize azepanium based protic ILs. The $-\text{SO}_3\text{H}$ functionalized protic ILs were prepared in two steps. The first step was the synthesis of the zwitterion, [1-(4-sulfobutyl)azepanium] by the reaction of azepane with 1,4-butanedisulfone. In the second step, desired anions were introduced by adding the aqueous solution of the respective mineral acids. The synthesis procedure is shown in Scheme-1.



Scheme 1. Synthesis of $-\text{SO}_3\text{H}$ functionalized azepanium ILs

The azepanium ILs with alkylsulfate anions were synthesized by the reaction of azepane with corresponding dialkylsulfates in a solvent-free condition at room temperature (Scheme 2). All the ILs were characterized using ^1H and ^{13}C NMR spectroscopy.



Scheme-2. Synthesis of azepanium based alkyl sulfate ILs

The purity of all the synthesized ILs were assessed using CHNS elemental analysis method. For a pure component, the difference between the theoretical and experimental CHNS value is only 0.4 %.

The purity of all these ionic liquids is shown in Table 1. All the synthesized ILs display purity value higher than 99 %.

Table 1 : Purity of synthesized ionic liquids using CHNS calculations

Compound name	Theoretical				Experimental				Mean Purity
	C	H	N	S	C	H	N	S	
[AzpSO ₃ H][HSO ₄]	36.02	6.95	4.2	19.23	36.08	6.98	4.18	19.27	99.68
[AzpSO ₃ H][H ₂ PO ₄]	36.03	7.26	4.2	9.62	36.07	7.29	4.18	9.65	99.67
[Azp][MeSO ₄]	42.65	8.5	6.22	14.23	42.71	8.57	6.25	14.27	99.59

[Azp][EtSO₄] 47.41 9.15 5.53 12.66 47.37 9.19 5.55 12.63 99.72

3.1 Thermal stability and glass transition temperature

All synthesized ILs displayed thermal stability higher than 523.15 K. The least stable ILs is [Azp][EtSO₄] (523.15 K) and the most stable ILs is [AzpSO₃H][H₂PO₄] (595.15 K). [AzpSO₃H][HSO₄] and [Azp][MeSO₄] ILs have thermal stability of 542.15 and 531.15 K respectively. All TGA profiles are shown in Figure 1. Considering that the thermal stability of SO₃H functionalized ILs containing 1-methylimidazolium cation with [HSO₄] anion is 561.15 K, which is only 19 °C higher than the azepanium ILs [30]. This result is consistent with previous report [31]. [AzpSO₃H][H₂PO₄] showed two stage thermal decomposition behavior. The reason for this behavior is not clear. It might be due to the evolution of SO₂ gas from the anion.

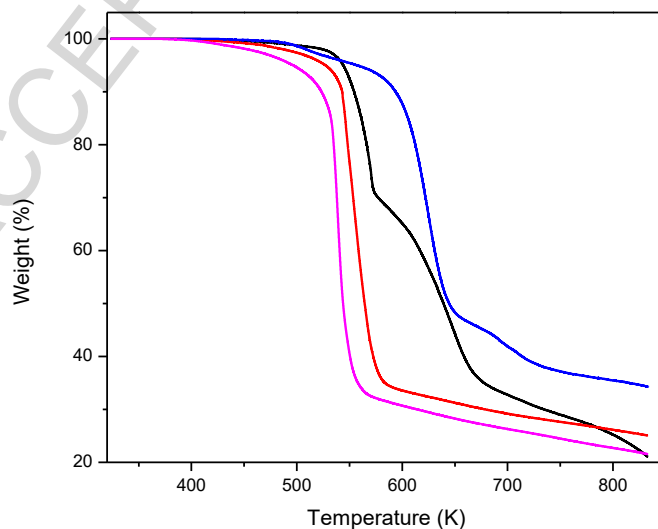


Figure 1. TGA profile of the synthesized ILs ([Azp][EtSO₄]; —, [Azp][MeSO₄]; —, —, [AzpSO₃H][HSO₄]; —, [AzpSO₃H][H₂PO₄])

All synthesized ILs showed glass transition temperature (T_g) and results are shown in Table 2 and Figure 4 (supporting information). The ILs showed no crystallization behavior during the heating and cooling cycle and no melting points were obtained. [Azp][EtSO₄] showed the lowest T_g (-83°C), while [Azp SO₃H][H₂PO₄] showed the highest T_g value (-14 °C). There is no significant difference between the T_g values between [Azp][EtSO₄] and [Azp][MeSO₄] (-72 °). However, the T_g value of [Azp SO₃H][HSO₄] (-48 °C) is significantly lower than [Azp SO₃H][H₂PO₄]. [Azp SO₃H][HSO₄] has a comparable T_g value with their imidazolium analogue (-34 °C) [30].

Table 2. Glass transition (T_g) and Thermal decomposition (T_d) of azepanium ILs

ILs	T_g (°C)	T_d (°C)
[AzpSO ₃ H][H ₂ PO ₄]	-14	322
[Azp SO ₃ H][HSO ₄]	-48	269
[Azp][MeSO ₄]	-72	258
[Azp][EtSO ₄]	-83	253

3.2 Heat Capacity

The heat capacity (C_p) of all the ILs were measured in a temperature range of 303.5 K to 353.5 K and the results are given in Figure 2. The C_p of [Azp][MeSO₄] increased from 336 J·mol⁻¹·K to 363 J·mol⁻¹·K when the temperature increased from 303.5 K to 353.5 K. Similar trend was observed in the case of [Azp][EtSO₄]. Azepanium ILs with [HSO₄] and [H₂PO₄] anions showed higher heat capacity as compared to their alkyl sulfate analogue. For instance, the C_p of [AzpSO₃H][HSO₄] is 492 J·mol⁻¹·K at 303.5 K while C_p of [AzpSO₃H][H₂PO₄] is 629 J·mol⁻¹·K at similar conditions. The fitting parameter along with the standard deviation and regression coefficient is shown in Table 3.

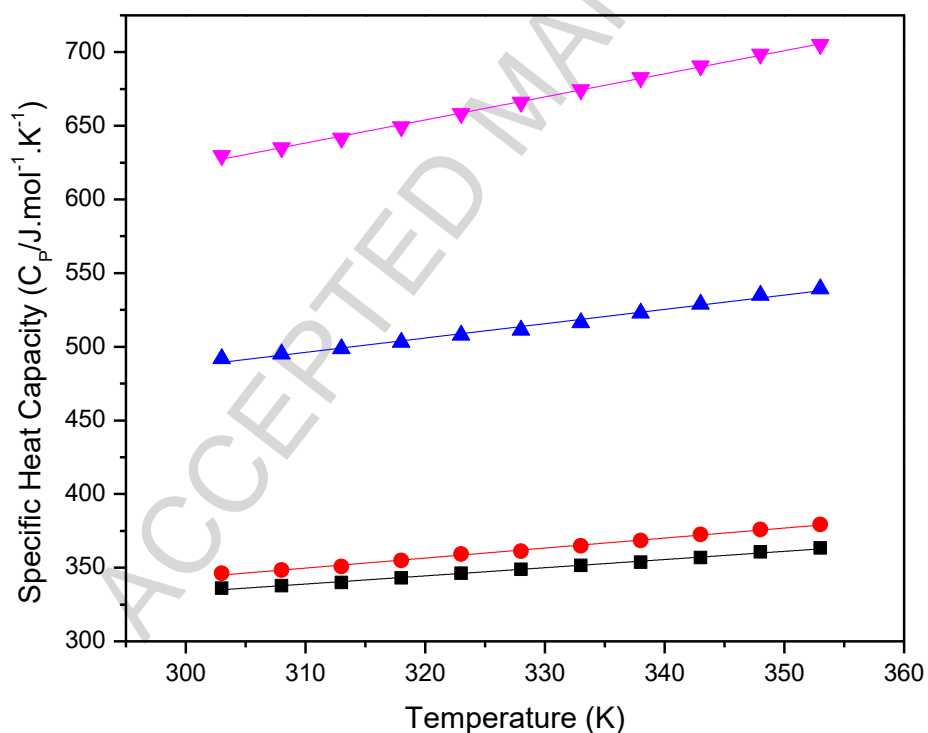


Figure 2. Heat Capacity of the ILs(●, [Azp][EtSO₄]; ■, [Azp][MeSO₄]; ▲, [AzpSO₃H][HSO₄]; ▼, [AzpSO₃H][H₂PO₄])

Table 3. Fitting parameter (A and B) values with R^2 and standard deviation (SD)^a for Specific Heat Capacity ^b of the measured ILs

	[Azp][MeSO ₄]	[Azp][EtSO ₄]	[AzpSO ₃ H][HSO ₄]	[AzpSO ₃ H][H ₂ PO ₄]
Specific Heat Capacity				
SD	5.839×10 ⁻⁶	6.762×10 ⁻⁶	1.5206	1.0702
R ²	0.996	0.996	0.99	0.998
A ₀	166.9	139.1	194.8	152.6
A ₁	0.554	0.679	0.972	1.566

^aStandard deviation values were calculated using the equation: $SD = \sqrt{\frac{(Z_{exp} - Z_{cal})^2}{n_{DAT}}}$, where

Z_{exp} and Z_{cal} are experimental and calculated data values respectively. n_{DAT} is number of experimental points

^bEquation for Specific Heat Capacity vs temperature dependence:

$$C_p / (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = A_0 + A_1 T$$

3.3 Viscosity of Ionic Liquids

[Azp SO₃H][EtSO₄] and [Azp SO₃H][MeSO₄] ILs were obtained as liquids at room temperature. AntonPaar viscometer was used to perform the viscosity measurement in a temperature range from 283.15K to 373.15K. The viscosity versus temperature data is tabulated in Figure 3, Figure 4, and Table 1 in the supporting information. The viscosity data had been fitted using Vogel-Tammann-Fulcher (VTF) equation. The resulting parameters are shown in Table 4. The parameter A is the viscosity at infinite temperature. The compositional effects are described by the parameters B and T₀.

$$\log_{10}\eta = A + \frac{B}{T-T_0} \dots \dots \dots (1)$$

Table 4:Fitting Parameters for Vogel-Tammann-Fulcher (VTF) equation and Arrhenius Equation

Vogel Tammann Fulcher (VTF) equation			
	A	B	T ₀
[Azp][MeSO ₄]	-2.0575	805.163	91.45
[Azp][EtSO ₄]	-0.8991	506.793	169.62
Arrhenius equation			
	μ ₀	E _a	
[Azp][MeSO ₄]	3.715×10 ⁻⁰⁴	435.17	
[Azp][EtSO ₄]	2.040×10 ⁻⁰⁵	640.37	

Moreover the viscosity data had been fitted using Arrhenius equation as given in equation (2),

$$\mu = \mu_0 e^{-(E_a/RT)} \dots \dots \dots (2)$$

where E_a is the activation energy, R is the universal gas constant and μ₀ is viscosity at infinite temperature. The fitting parameters for Arrhenius equation are given in Table 4. The activation energy of the [Azp][EtSO₄] is higher as compared to [Azp][MeSO₄] because of the higher chain length of the cation. The increase in the chain length causes the transfer of translational energy in the larger molecules out to the reaction coordinate into dissipative channel causing excitation of

photon in the surface. These results are in agreement with the already reported literature where the increase in the chain length increases the activation energy of the ionic liquids {Capelo, 2012 #229}.

The diethyl ILs have significantly higher viscosity than the dimethyl analog. For instance, at 283.15 K, the viscosity of [Azp][EtSO₄] is 3359 mPa.s, while the viscosity of [Azp][MeSO₄] is 146 mPa.s at similar experimental conditions. Nevertheless, at high temperature, there is no significant difference between the viscosity values of these ILs. For example, viscosity values of [Azp][EtSO₄] and [Azp][MeSO₄] are 37 mPa.s and 5 mPa.s respectively at 373.15K.

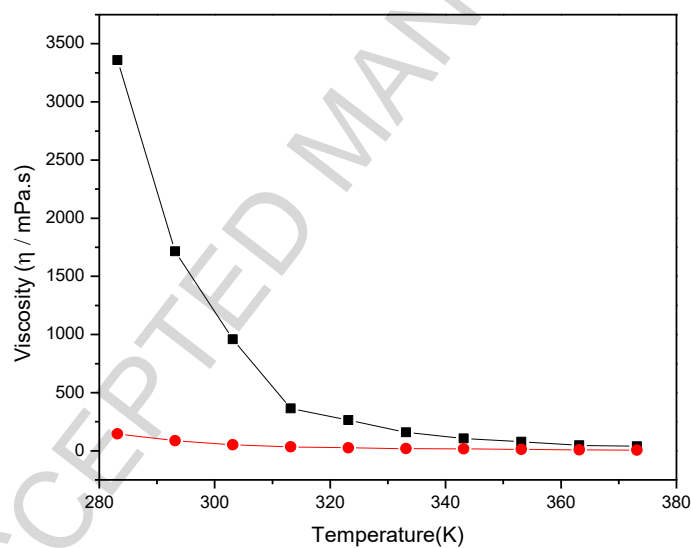


Figure3. Viscosity *versus* Temperature: ■, [Azp][EtSO₄]; ●, [Azp][MeSO₄].

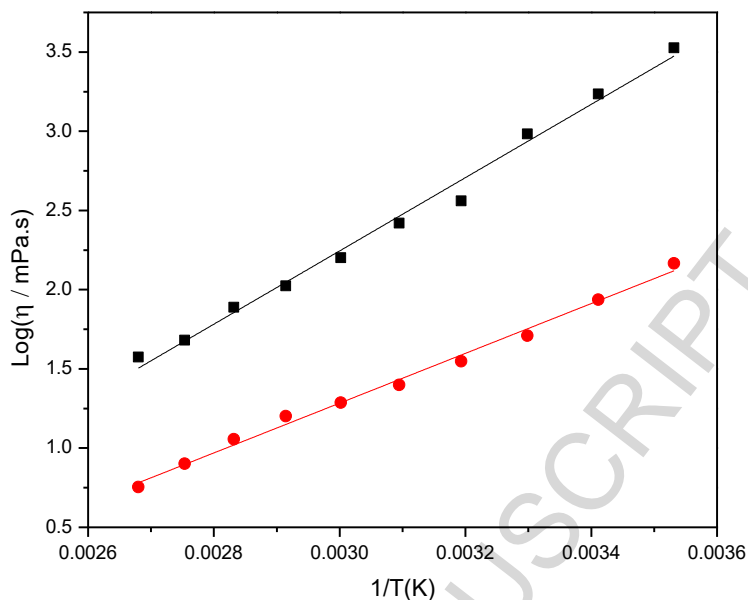


Figure 4. Plot of $\log \eta$ as a function of Temperature: ■, [Azp][EtSO₄]; ●, [Azp][MeSO₄].

3.4. Density of Ionic Liquids

The effect of temperature on density values of the synthesized ILs was studied at different temperatures (293.15 K to 353.15 K) and the results are given in Figure 5 and Table 2 (supporting information). The density values showed a linear relationship with temperature as in the case of viscosity. [Azp][MeSO₄] has lower density values than its ethyl analog. The density of [Azp][MeSO₄] is 1221.7 kg m⁻³ at 293.15 K whereas, at similar experimental conditions, the density of [Azp][EtSO₄] is 1565.0 kg m⁻³.

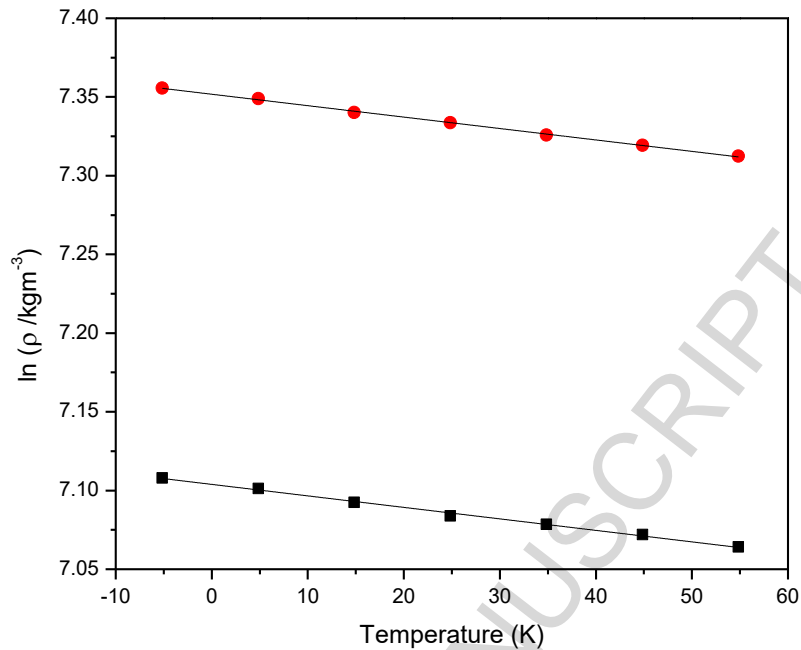


Figure 5. Density *versus* Temperature: ■, [Azp][MeSO₄] ; ●, [Azp][EtSO₄] .

Figure 5 clearly depicts that density values decrease almost linearly with increasing temperature. Furthermore, nearly constant values of the slope were observed for the density of ILs.

3.5 Estimation of Volumetric Properties. The experimental density values were linearly correlated with temperature using the equation given below.

$$\ln \left[\frac{\rho}{\text{kg.m}^{-3}} \right] = A_4 - A_5(T - 298.15)/K, \quad (3)$$

Where A_2 and A_3 are constants and its value along with the standard deviation can be found in table 5.

Table 5. Fitting parameter (A and B) values with R^2 and standard deviation (SD)^a for viscosity^b, density^c of the measured ILs

	[Azp][MeSO ₄]	[Azp][EtSO ₄]
Viscosity		
SD	3.629×10^{-2}	5.850×10^{-2}
R ²	0.9935	0.9914
A ₂	-3.4299	-4.6927
A ₃	1571.31	2312.6
Density		
SD	4.621×10^{-6}	2.362×10^{-6}
R ²	0.9962	0.9987
A ₄	7.104	7.352
A ₅	7×10^{-4}	7×10^{-4}

^aStandard deviation values were calculated using the equation $SD = \sqrt{\frac{(Z_{exp} - Z_{cal})^2}{n_{DAT}}}$, where

Z_{exp} and Z_{cal} are experimental and calculated data values respectively. n_{DAT} is number of experimental points

^bEquation for viscosity temperature dependence: $\log \eta / (mPa \cdot s) = A_2 + (A_3 / T)$

^cEquation for density temperature dependence: $\ln \rho / (kg \cdot m^{-3}) = A_4 - A_5 (T - 298.15)$

where $A_5 = \frac{\alpha}{K} = - \left(\frac{\partial \ln \rho}{\partial (T - 298.15)} \right)_p$

In addition, also A_5 was used to calculate the value of thermal expansion coefficient (α) according to the equation given below.

$$A_5 = \frac{\alpha}{K} = - \left(\frac{\partial \ln \rho}{\partial (T-298.15)} \right)_p \dots\dots\dots(4)$$

The density values also used to calculate many other important parameters such as molecular volumes, V_m , standard molar entropy (S^0) and lattice energy of the ILs according to the equations given below. All these values can be predicted with good accuracy using the quantum chemical calculations [32, 33]. The values of all these parameters can be found in Table 6.

$$V_m = \frac{M}{N_A \rho} \dots\dots\dots (5)$$

$$S^0(303.15) / J.K.mol^{-1} = 1246.5 \left(\frac{V_m}{nm^3} \right) + 29.5 \dots\dots\dots(6)$$

$$U_{POT} / kJ.mol^{-1} = 1981.2 \left(\frac{\rho}{M} \right)^{1/3} + 103.8 \dots\dots\dots (7)$$

where M is molecular weight and N_A is Avogadro's number.

Table 6. Calculated values of Volume properties of ILs at temperature 303.15K

Ionic liquid	ρ (kg.m ⁻³)	$10^4 \alpha$ (exp) K ⁻¹	V_m (nm ³)	S^0 (J.K ⁻¹ .mol ⁻¹)	U_{POT} (kJ.mol ⁻¹)
[Azp][MeSO ₄]	1213.6	7.00	0.4204	553.49	323.55
[Azp][EtSO ₄]	1554.5	7.00	0.5067	661.08	304.65

From the values of molar volume in Table 6, it can be stated that the bulkiness of the chosen anion is responsible for the increase in the molar volume. The molar volume and standard molar entropy increase with the increase in the size of cation or anion and these results are in close proximity to already reported trends [6, 34]. The value of lattice energy decreases with the bulkiness of the anion (see Table 5). The lattice energy values for ILs, [AzP][MeSO₄] and [AzP][EtSO₄], are 323.55 kJ.mol⁻¹ and 304.65 kJ.mol⁻¹ respectively and are in good agreement with previous reported data [35-38]. These ILs have significantly lower lattice energy as compared to halides salts such as NaCl which had a lattice energy of 756 kJ.mol⁻¹ and CaCl₂ (2120 kJ.mol⁻¹) [39]. This might be because of two reasons. Firstly, in alkali salts the charge on the ions is significantly higher and not delocalized and secondly, the inter ionic distance is shorter as compared to the ILs.

3.6 COSMO-RS

Among the various advantages offered by COSMO-RS, one of them is to envision the 3D molecular surface polarity distributions in the form of histogram function called σ profile. Based on the profile, one can qualitatively analyze the interacting nature of that compound. Generally, sigma profile of the compound can be segregated into three sections namely, hydrogen bond acceptor region where $\sigma > 1 \text{ e.nm}^{-2}$, hydrogen bond donor region where $\sigma < -1 \text{ e.nm}^{-2}$ and non-polar region where $-1 < \sigma < 1 \text{ e.nm}^{-2}$. Figure 6 displays σ profile of the studied ILs.

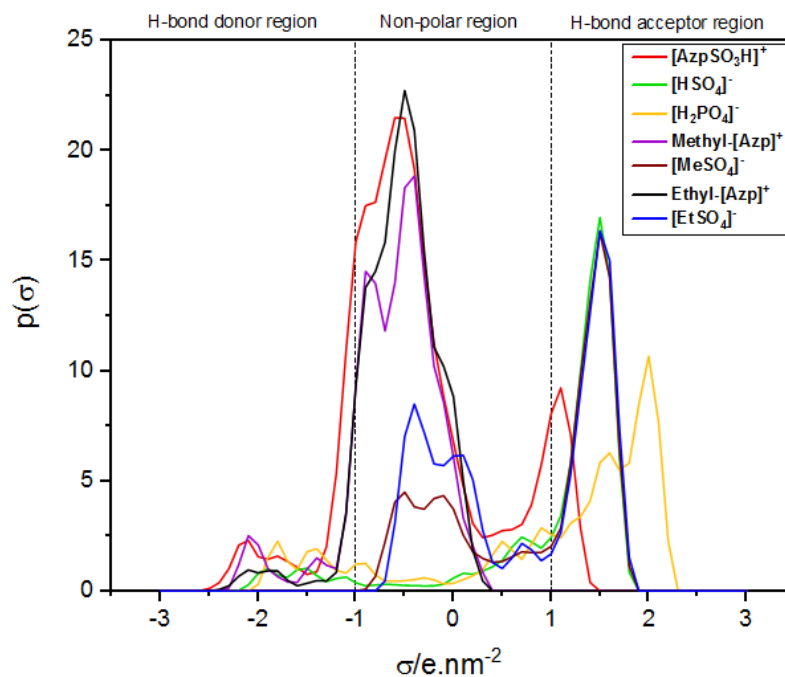


Figure 6. σ profile of the studied ILs.

The three bigger peaks in the non-polar region are from the cations ($[\text{AzpSO}_3\text{H}]^+$, $[\text{EtAzp}]^+$ and $[\text{MeAzp}]^+$) due to the presence of saturated ring structure and long alkyl chain in the case of $[\text{AzpSO}_3\text{H}]^+$. There is no peak in the hydrogen bond acceptor region for $[\text{EtAzp}]^+$ and $[\text{MeAzp}]^+$ since the sections do not bear any hydrogen acceptor groups. In the case of $[\text{AzpSO}_3\text{H}]^+$, the presence of a peak in hydrogen bond acceptor region indicates that the sulfonyl group has the potential to accept a hydrogen bond from the donors. All the three studied cations have hydrogen bond donating nature due to the presence of proton near the nitrogen of the ring. In addition to this, $[\text{AzpSO}_3\text{H}]^+$ has one more additional proton attached to the sulfonyl group. In the case of the anion, $[\text{EtSO}_4]^-$ and $[\text{MeSO}_4]^-$ (the difference is the presence of an additional methylene group in $[\text{EtSO}_4]^-$) both exhibit similar property of hydrogen bond accepting nature. In the case of $[\text{HSO}_4]^-$ and $[\text{H}_2\text{PO}_4]^-$ they have both hydrogen bonding and donating nature.

The descriptors derived from COSMO-RS contain an equivalent description of the molecules and quantitative scaling based on the solvation model – the Abraham equation [40,

41]. Detailed information about the overlapping of molecular descriptors from COSMO-RS (sigma moments) and the experimental descriptors in Abraham equation was demonstrated elsewhere [41]. Among the COSMO-RS derived descriptors of sigma moments, the hydrogen bond moments HB_acc3 and HB_don3 are corresponding to the measures of polarizability (H-bonding basicity and H-bonding acidity respectively) [41]. This parameter is of intrinsic nature and does not change with the specific solute. On the other hand, the specific interaction between solute and IL can be different due to varying molecular size, distribution, symmetry, surface charge density and more. Hence the misfit, van der Waals interaction, H-bonding energies, of the ILs should be considered in the study of their solvation behavior with different solutes. The COSMO-RS predicted values of these energies are given in Table 7.

Table 7: Energies predicted from COSMO-RS of the studied cation and anion

S. No	Compound	H_int KJ/mol	H_MF KJ/mol	H_HB KJ/mol	H_vdW KJ/mol	COSMO- RS Area nm ²	Moment_HBacc	Moment_HBdon
1	[AzpSO ₃ H] ⁺	-51.22	27.27	-31.38	-47.11	2.66	0.67	10.54
2	[HSO ₄] ⁻	-61.20	6.57	-51.49	-16.28	0.98	18.40	3.25
3	[H ₂ PO ₄] ⁻	-118.00	9.45	-110.41	-17.04	1.02	35.46	4.83
4	[MeAzp] ⁺	-22.16	22.76	-13.65	-31.27	1.63	0.00	6.76
5	[MeSO ₄] ⁻	-22.07	13.00	-13.65	-21.42	1.18	18.34	0.00
6	[EtAzp] ⁺	-18.68	25.88	-9.45	-35.11	1.81	0.00	4.02
7	[EtSO ₄] ⁻	-18.83	16.31	-9.45	-25.69	1.39	19.20	0.00

Interaction energy, misfit, hydrogen bonding and van der Waals energy values predicted for all the ILs are negative. The negative values indicate that it is thermodynamically favorable to interact or dissolve a neutral molecule. Cations can be ordered as follows for interaction and

hydrogen bonding energy, $[\text{AzpSO}_3\text{H}]^+ > [\text{MeAzp}]^+ > [\text{EtAzp}]^+$. For misfit energy, and Van der Waals energy, the cations follow slightly different order as $[\text{AzpSO}_3\text{H}]^+ > [\text{EtAzp}]^+ > [\text{MeAzp}]^+$. Similarly, anions can be ordered as follows for interaction and hydrogen bonding energy $[\text{H}_2\text{PO}_4]^- > [\text{HSO}_4]^- > [\text{MeSO}_4]^- > [\text{EtSO}_4]^-$. A different trend is observed for misfit energy and Van der Waals energy ($[\text{H}_2\text{PO}_4]^- > [\text{HSO}_4]^- > [\text{EtSO}_4]^- > [\text{MeSO}_4]^-$). Based on H-bonding basicity (Moment_HBacc) the anions are arranged as follows: $[\text{H}_2\text{PO}_4]^- > [\text{EtSO}_4]^- > [\text{HSO}_4]^- \approx [\text{MeSO}_4]^-$. Since $[\text{AzpSO}_3\text{H}]^+$ cation and $[\text{H}_2\text{PO}_4]^-$ anion have strong negative energy values and both hydrogen bond donating and accepting groups, it is worth exploring this cation/anion combination for biomass dissolution studies.

In addition, to understand the potential of these ILs in biomass dissolution studies, activity coefficient at infinite dilution ($\ln \gamma^\infty$) have been predicted for these ILs with cellulose. Table 8, displays the $\ln \gamma^\infty$ values, and the IL with more negative value displays favorable interaction towards cellulose. The COSMO-RS geometry of these ILs and cellulose are given in supporting information (Figure 1, Figure 2 and Figure 3). Based on the activity coefficient values, ILs can be ordered as follows: $[\text{AzpSO}_3\text{H}][\text{H}_2\text{PO}_4] > [\text{Ethyl-Azp}][\text{EtSO}_4] > [\text{Methyl-Azp}][\text{MeSO}_4] > [\text{AzpSO}_3\text{H}][\text{HSO}_4]$. It is observed that $\ln \gamma^\infty$ trend of IL is similar to the anion H-bonding basicity trend. $[\text{AzpSO}_3\text{H}][\text{H}_2\text{PO}_4]$ has lower $\ln \gamma^\infty$ compared to other ILs. Lower $\ln \gamma^\infty$ of $[\text{AzpSO}_3\text{H}][\text{H}_2\text{PO}_4]$ could be due to higher hydrogen bond accepting moments of the anion. Based on the previous studies for cellulose dissolution studies using ILs with anions like acetate [42] and chloride [43], $[\text{H}_2\text{PO}_4]^-$ anion's hydrogen bonding pattern with cellulose is shown in Figure 7. $[\text{AzpSO}_3\text{H}][\text{HSO}_4]$ has lower $\ln \gamma^\infty$ predicted due to the difference in the geometry of ions (smaller anion size from Table 7) and lower hydrogen bond accepting moments. Based on

the above energy predictions and $\ln \gamma$ prediction, it is confirmed that $[\text{AzpSO}_3\text{H}][\text{H}_2\text{PO}_4]$ could be a potential IL in biomass dissolution studies.

Table 8. Activity coefficients of ILs for cellulose

Cation	Anion	$\ln \gamma$
AzpSO ₃ H	HSO ₄	-1.92
Methyl -Azp	MeSO ₄	-5.62
Ethyl- Azp	EtSO ₄	-6.54
AzpSO ₃ H	H ₂ PO ₄	-7.72

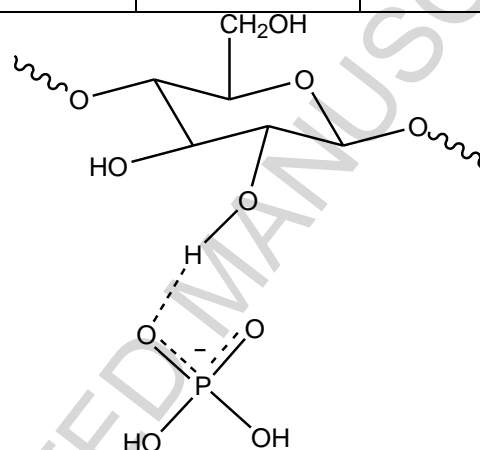


Figure 7. Hydrogen bond pattern for $[\text{H}_2\text{PO}_4]^-$ anion.

Conclusion

Protic ILs based on cyclic seven-membered azepanium cation in combination with different anions were synthesized and characterized. Sulphonyl ($-\text{SO}_3\text{H}$) group was attached to the azepanium cationic core. The thermal decomposition temperature (T_d) and glass transition temperature (T_g) was determined. All the ILs showed good thermal stability. Density and viscosity of the room temperature ILs were determined. Experimental values of density and viscosity were used to calculate volumetric properties such as molecular volumes, V_m , standard

molar entropy (S^0) and lattice energy. Based on the COSMO-RS predictions, [AzpSO₃H][H₂PO₄] IL has both hydrogen bond donor and hydrogen bond acceptor groups. It also has high heat capacity and thermal stability values among the studied ILs. This makes it a versatile solvent for multiple applications in biomass studies.

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Highlights

Synthesis and characterization of protic ionic liquids were performed

Seven membered cyclic azepanium ring was used as the cationic core

Physico-chemical properties of the new ionic liquids were evaluated

COSMO-RS study was performed to assess the potential of the ionic liquids for biomass dissolution

Volumetric properties were calculated from the viscosity and density data

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