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Green synthesis and characterization of tetrabutylammonium bromide-based deep eutectic solvent

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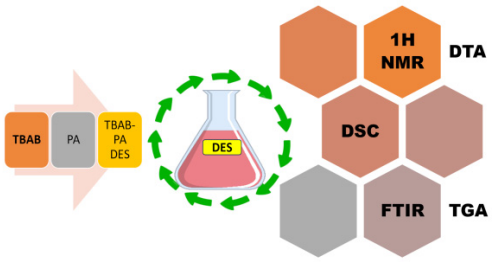
ABSTRACT

For decades "volatile organic solvents" (VOSs) and ionic liquids (ILs) have been used as promising solvents due to their interrelated and tunable properties. However, they have certain drawbacks as they are overpriced, detrimental, toxic, and poorly biodegradable. To subjugate these pitfalls of VOSs and ILs, the solvents known as "Deep Eutectic Solvents (DES)" are fabricated. The synthesis methods of DESs are green and environmentally benign. DESs are economical, nontoxic, biocompatible, and do not require any purification after synthesis. These solvents are the conjugation of hydrogen bond donors (HBD) and hydrogen bond acceptors (HBA) via hydrogen bonds. In our work, we have synthesized deep eutectic solvent combining tetrabutylammonium bromide (TBAB) as a hydrogen bond acceptor (HBA) and picric acid (PA) as a hydrogen bond donor (HBD) in their 1:1 molar composition. The preliminary study involved a feasibility test carried off by a solid-liquid phase diagram. The resulting DES was characterized by using ^{1}H NMR & FTIR, and its thermal properties were studied using TGA, DTA, and DSC. In the near future, we will compute several physical properties and computational simulation studies of this newly synthesized TBAB-PA-based DES, and its various applications are in the making in our laboratory.

Key words: *Green solvent, Tetra butyl ammonium bromide, Solid-liquid phase diagram, TGA, DSC*

Graphical abstract



Introduction

Each year more than millions of tons of organic solvents are produced for industrial purposes (De Simone, 2002), but most of these do not conform to the requirements of 'green chemistry' (Anastas *et al*., 1998). Due to certain complications such as global warming, climate change, and high energy expenditure, awareness has been created to search for "green & justifiable solvents" for various applications. Numerous volatile solvents and ionic liquids have been in use for several decades in the industry (Edokpolo *et al.*, 2014). These solvents have potential due to their complementary and tunable properties (Kareem *et al*., 2010 and Zhang *et al*., 2005) as they have low pressure, high thermal and chemical stability, and some exhibit a variety of applications. Despite this, these solvents are still not common in industrial practice (Blanchard *et al.*, 1999 and Bernot

et al., 2005) due to their many disadvantages like toxicity, detrimental, high cost, and poorly biodegradable (Mjalli *et al.*, 2017). To counter these effects, many "greener" or more sustainable solvents have been proposed and developed over the past few decades, such as deep eutectic solvents (DESs) also known as the family of designer solvents (Esperanca *et al.*, 2010 and X. Li *et al.*, 2008). These solvents are cheap, environmentally friendly, non-hazardous, less toxic, and easy to synthesize. DES synthesis shows 100% atom economy as a theoretical measure of the quantity of starting material converted into the desired product, which indicates a reaction's greenness (Crawford *et al.*, 2016). There are several research papers in which they have synthesized novel DESs with many unique combinations of HBA and HBD such as quaternary-salt of ammonium and phosphonium and HBD like amides, amino acids sugars, carboxylic acids, glycol, and carbohydrates. The very first DES prepared was a mixture of choline chloride and urea at a molar composition of 1:2 (Abbott *et al.*, 2003). Materials with low lattice energy are used to make DESs of low melting points (Yi Ting, 2019).

DESs cannot be considered as ILs for many reasons, such as a) DESs are not entirely composed of ionic species and b) DESs can also be obtained from non-ionic species. However, DESs are attractive since they exhibit similar physio-chemical properties to traditional imidazolium-based ILs and can thus advantageously replace them in numerous applications (Hou *et al.*, 2008) recognized them as possible replacements for ILs. The two components of a DES are categorized as a salt and a hydrogen bond donor (HBD). Salts like ChCl (Abbott *et al.*, 2009) methyl triphenyl phosphonium bromide (Kareem *et al.*, 2010 and 2012a), and tetra butyl phosphonium bromide (Kareem *et al.*, 2012b), while urea, thiourea, 1-methyl urea, 1,3- dimethyl urea, 1,1-dimethyl urea, acetamide, benzamide (Abbott *et al.*, 2003a) ethylene glycol, glycerol, 2,2,2-trifluoroacetamide (Kareem *et al.*, 2010) and d-fructose (Hayyan *et al.*, 2012) are the commonly used HBDs. Choline chloride $[(CH_3)_3NCH_2CH_2OH] + Cl^-$ is one of the first cited salts to be used as a starting material for DES synthesis (Abbott *et al.*, 2003a).

Eutectic temperature is the lowest temperature at which both HBA and HBD having a certain molar ratio form a homogeneous liquid. The study of the phase diagram and eutectic point detection is a significant preliminary study of any DES (Cooper *et al.*, 2004 and Liu *et al.*, 2010). For the homogeneous formation of DES, both starting materials are melted at a temperature slightly higher than their starting components. For our work, we have chosen tetra butyl ammonium bromide (TBAB) as HBA and picric acid (PA) as HBD to make this novel deep eutectic solvent. The components at a 1:1molar ratio is mixed and heated above the melting point of the individual components to form a homogeneous liquid. Characterization of prepared TBAB-PA-based DES was done by ^{1}H NMR, and FTIR techniques and thermal properties were studied by using TGA, DTA, and DSC. The synthesized TBAB -PA-based DES can be used in various applications such as the preparation of nanoparticles, as a catalyst, extraction of dye, CO_2 adsorption, metal extraction and processing of metal oxides, wastewater treatment, and more.

Experimental

Chemicals

In this present research work, we have used high-purity (> 99 %) tetrabutyl ammonium bromide (TBAB) ($C_{16}H_{36}BrN$), and picric acid (PA)($C_6H_3N_3O_7$) acquired from Amrut Lal Bhura Bhai Co. Op Pvt. Limited Mumbai, Maharashtra and K.J. Enterprises mentioned in Table 1. Since these chemicals are highly pure, no purification was required.

Materials

Hydrogen bonddonor (HBD): Picric acid (PA)
Hydrogen bondacceptor (HBA): Tetrabutylammoniumbromide (TBAB)

Table 1. Characterizations of the used Chemicals

Name	Acronym	CASreg. no	Source	Purity(as massfraction)
Tetrabutylammonium Bromide	TBAB	1643-19-2	Amrutlal Bhurabhai	≥ 0.99
Picricacid	PA	88-89-1	K.J. Enterprises	≥ 0.98

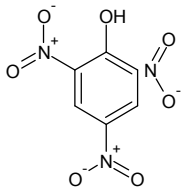


Fig. 1. Structure of PA

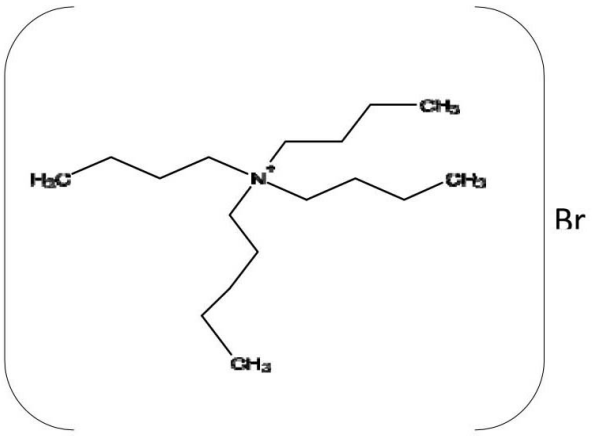


Fig. 2. Structure of TBAB

Chemistry of DES

To geta better quality of DES, one requires a better understanding of the phase diagram. As shown in Table 2, at different ratios of PA as HBD and TBAB as HBA, the melting points of each material have altered. According to the solid-liquid phase diagram (Figure 3), the TBAB-PA-based DES showed a eutectic temperatureof74.5°Cwith a 1:1 molar ratio. This can be further confirmed by the DSC study.

A heating method was used for the synthesis of TBAB-PA-based DES which is similar to that originally reported by Abbott et al. and in other previous publications (Jibril *et al.*, 2014 and Mjalli *et al.*, 2014) In this investigation, we tried different molar ratios of PA: TBAB prepared by heating the TBAB, and PA in a glass round bottom flask on a rota heating mantle fixed with a magnetic stirrer for 40 minutes. The temperature was set at 140 °C which is above the melting point of the individual components. The outcome of the experiment to synthesize TBAB-PA-based DES as homogeneous liquids is first manifestly noticed at ambient temperature. By the time all the samples were melted into homogeneous liquids, they were removed from the hot plate and cooled to room temperature. We observed that only 1:1, 2:3, and 3:2 formed a transparent liquid with high viscosity while the other PA: TBAB molar ratio products solidified. Usually, these products remain in liquid form at high temperatures but begin to crystallize as they gradually cool to room temperature. Therefore, the samples with (PA: TBAB molar ratios of 1:1, 2:3, and 3:2) were stored for the next 36 hours at ambient temperature. The other two (PA: TBAB molar ratios i.e., the 2:3 and 3:2) combinations formed a solid. Thus, the TBAB-PA-based DES of (molar ratio 1:1) forms a homogenous liquid at ambient temperature.Table3.givesthecontour of the prepared TBA-PA-based DES.

Table 2. Melting point of products with different ratios of materials

Mole% of PA	Mole % of TBAB	Temperature (°C)
0	100	103
10	90	98
20	80	98
30	70	90
40	60	87
50	50	74.5
60	40	80.5
70	30	92
80	20	105
90	10	115
100	0	122

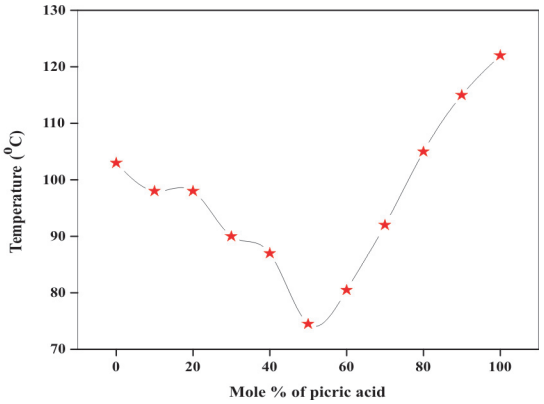


Fig. 3. Phase diagram of DES composed of PA and TBAB

Characterization Methods

For weighing and heating electronic balance with (Model No. CA-123) and Rota heating mantle with a magnetic stirrer (Model BPL-158) were used. DES was characterized using FTIR (BRUKER Model-ALPHA), and NMR measurements were performed on an ECZR Series 600 MHz NMR SPECTROMETER, TGA & DTA was performed by HITACHI

NEXTA STA300 model, and DSC was performed by HITACHI - DSC7020 model.

Results and Discussion

(a) Fourier Transform Infrared Radiation (FTIR)

The attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy was used to determine the functional groups present in the DES and to disclose the interaction between TBAB and PA. Each sample was scanned 24 times from 600 to 4000 cm^{-1}. The FTIR spectra of the TBAB-PA-based DES are shown in (Figure 4). The broad peak between 3000 and 3500 cm^{-1} reveals the presence of H-bonded alcoholic O-H groups. Picric acid shows the characteristic peaks at 1631, 1610, 1561, 1483, 1342, 1316, 1089, and 738 $cm^{-1,}$ and tetrabutyl ammonium bromide shows peaks at 2954, 2873, 1625, 1466, 1383, 1163, 1106,1063,1028,883,797,737,526 cm^{-1} which can also be observed in the DES.

FTIR spectra confirmed the formation of the hydrogen bonds between constituents of the DES system. As the strength of the hydrogen bond depends upon the nature of HBA and HBD, it can largely affect the witnessed OH stretching vibrations. Usually, a broad hydrogen bond at wave numbers between 3650 and 3300 cm^{-1} demonstrates the existence of an OH stretching band in the condensed phase. Bands in this region of 3700-3100 cm^{-1} can be typically attributed to the various hydroxyl (OH) stretching vibrations. In the case of water, alcohols, and phenols, the OH stretching bands can be usually witnessed at 3400 cm^{-1} (Larkin, 2011 and Guo *et al.*, 2013) Figure 4. As can be seen, the O-H stretching bands of the prepared DES are at 3400cm^{-1}. Thereare no intensive hydroxyl stretching bands at wave number between 3800 and 3400 cm^{-1}. This indicates that the formed DESs have very low water content. The O-H stretching bands of the prepared DES shifted to higher wavelengths in comparison to the pure HBD component. This is probably due to a decrease in the force constant as a result of the transfer of the oxygen electron cloud toward the hydrogen bond (Larkin, 2011). Therefore, the change in the O-H peak position can be attributed to the hydrogen bond formation between the HBAs and HBD, which led to the formation of the DES mixtures. The peak at 2962 cm^{-1} shows CH_2 aliphatic group which can also be seen in PA. The stretching vibration frequency for the phenol group is between 1500-1450 cm^{-1} as it is present in HBD, here it can be seen at 1545 cm^{-1}. It also indicates the C-N amide II band. The peak at 1075 cm^{-1} show C-O carbohydrates also present in HBA. Here, in the region of 800-750cm^{-1}, there is a peak at about 737cm^{-1} that may possibly involve the OH wagging vibration. From Figure 4 we can see that the peak shown at 707 cm^{-1} in TBAB-PA-based DES is also seen in the IR spectra of TBAB showing the presence of bromine in formed DES. So, we can conclude that the peak at 707 cm^{-1} in TBA-PA-based DES is the aryl CH deformation vibration bond. The FTIR spectra provided evidence of intermolecular interactions between the starting reagents used to synthesize this novel eutectic solvent. Confirmation of the synthesis was obtained by analyzing the infrared spectrum and observing the preservation of bands characteristic of the constituent materials.

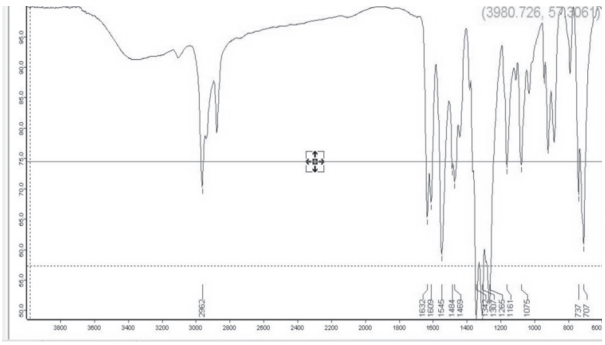


Fig. 4. FTIR spectra of TBAB-PA-based DES

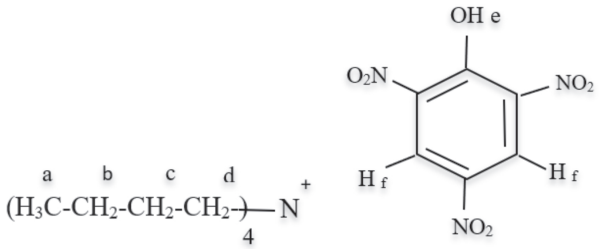
(b) Nuclear magnetic resonance (NMR)

The sample purity and chemical structure can be confirmed by using ^1H NMR. DES was characterized by using ECZR Series 600 MHz NMR SPECTROMETER 600 MHz NMR for 60 minutes using a direct 5-mm double resonance broadband probe with z-axis gradients as shown in Figure 6. The temperature was kept constant in the ambient environment. The solvent used for sample dilution was deuterium chloroform (CDCl3). Figure 7 (a) & (b) shows

Table 4. Configuration of the prepared TBAB-PA-based DES

HBD	HBA	Molar Ratio	Abbreviation
Picric acid(PA)	Tetrabutylammoniumbromide(TBAB)	1:1	TBAB-PA

related elaborated peaks of the ^{1}H NMR spectrum of this TBAB – PA-based DES. Figure 5 (i) & (ii) shows the hydrogen position in structure and also specify that the chemical shift, peaks of CH2 -N and aliphatic hydrogen of TBAB along with hydrogen present of this DES in PA: ä 0.9981-1.0105 (t, 12 H, Ha), ä 1.4322 - 1.4934 (M, 8H, Hb), ä 1.6715-1.7245 (M, 8H, Hc), ä 3.3438-3.3720 (t,8h, Hd), ä 5.7404 (S,1H, He) broad & less intense peak of phenolic -OH. Ä 9.0525 (S, 2H, H_f) shows the aromatic hydrogen of picric acid.



(i) (ii)

Fig. 5(i) & (ii). Shows the hydrogen position in structure of TBAB and PA

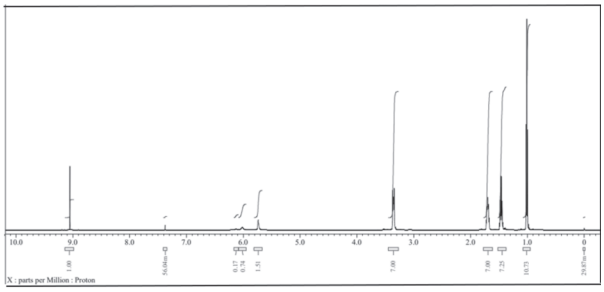
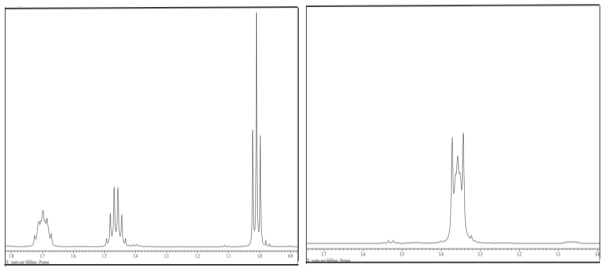


Fig. 6. Shows the ^{1}H NMR of TBAB-PA-based DES

(c) Thermal gravimetric analysis (TGA) & Differential thermal analysis (DTA)

Thermogravimetric Analysis (TGA) and Differential thermal analysis (DTA) tests were used to check the thermic strength of the prepared TBAB-PA-based DES. In TGA, the change in mass of a sample as it is heated is measured. The heating process is precisely controlled, and the mass loss or gain of the sample is plotted as a function of temperature. The thermal stability of the solvents can be influenced by many factors such as electrostatic interactions, water compositions, type of HBD, number of carbon atoms of the main chain of hydrogen bond acceptor, and the extent of hydrogen bonding. All these factors affect the thermal properties of synthesized DES. When the sample changes physically and chemically, the DTA curve would be parallel to the time or temperature axis. The differential signal peak appears when the sample has reached the temperature of change of state. DTA detects every physical or chemical change whether or not it is accompanied by a change in weight and yields a signal. In DTA, the difference in heat flow to the sample and a reference (an empty aluminum pan) is recorded as a function of temperature at a constant heating rate. Information obtained from both TGA & DTA is complementary as they can exonerate by the application of the other. Figures 8 & 9 illustrate thermo grams obtained from TGA and DTA curves of TBAB-PA-based DES.



(a) (b)

Fig. 7. (a) & (b) shows the various elaborated peaks of ^{1}H NMR of TBAB-PA-based DES

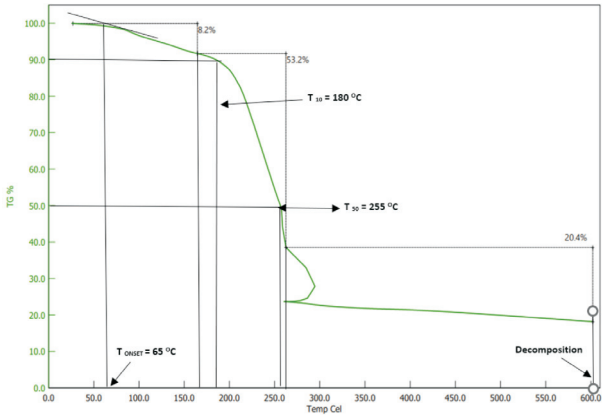


Fig. 8. Shows TGA thermo grams of TBAB-PA-based DES

12.6 mg of DES sample was placed in an aluminum hermetic pan. It was then heated under a nitrogen atmosphere having a flow rate of 10 cm^3/min from 25 °C to 600 °C at a temperature ramp of 20 °C per min. The TGA thermo grams for the DES sample showed a single major degradation step which occurred in the temperature range of 50 °C to 270 °C. The TGA thermo gram consisted of a gradual weight loss starting at about 65 °C and the sudden drop in the TGA curve at 165 °C corresponds to the

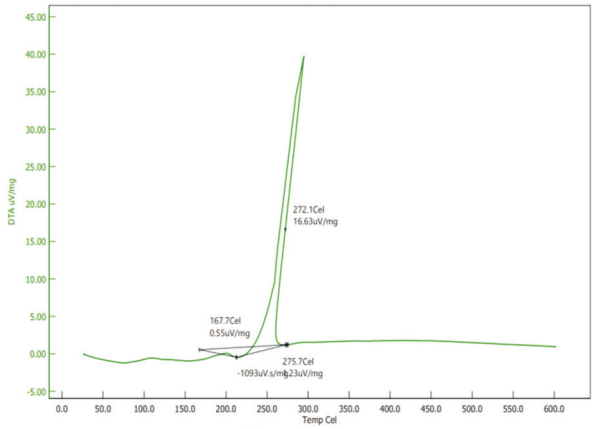


Fig. 9. Shows DTA image of TBAB-PA-based DES

thermal decomposition of DES. The onset decomposition temperature is the noticeable thermal property of DES as it determines the maximum temperature at which DES has stability in its liquid state without any decomposition, and this is the thermal stability range for the use of that solvent. The onset decomposition temperature of the synthesized DES is 65 °C, with $T_{10\%}$ is 180 °C and $T_{50\%}$ is 255 °C. Thus, the synthesized DES is stable up to 65 °C, confirming that it can be safely used as reaction medium below 65 °C. DTA curve announces that the decomposition of synthesized DES is exothermic with peak temperatures of 272.1 °C and 275.7 °C. It is essential to select DES constituents with low volatility to ensure a wide range of temperatures at which DESs maintain their liquid state and their range of applications. Its study helps to properly develop alternative solvents with a real potential to be used at an industrial scale.

(d) Differential scanning calorimetry (DSC)

Characterization of the melting point (mp) of a DES is important as it distinguishes DESs from normal eutectics; however, many reports do not provide this data. The ideal method for determining the mp of a DES is differential scanning calorimetry (DSC), as only a small amount of sample (~ 5 mg) is required. In an inert environment, the DES is put into an oxidefree hermetically sealed aluminum pan (achieved by heating Al pans to >330 °C). The melting points of the individual components of the DESs are 103 °C (TBAB) and 121.8 °C for (PA) respectively. From Figure 10 the eutectic point for TBAB - PA based DES at molar ratios of 1:1, showed at 74.5 °C respectively. Hence data obtained after constructing the phase diagram can be confirmed by using DSC. As can be seen, the melting points of the eutectic mixtures are lower than those of the pure individual components. Such decreases in melting points may be associated with the ability of HBD to seize bromide ions. The formed hydrogen bond between the HBAs and HBD shields anions from quaternary ammonium cations and reduces the electrostatic attractions between the cations and anions. As a result of this weakening of the electrostatic attractions, the lattice energy of the DESs decreases, leading to a decrease in their melting point.

Conclusion

This research showed a consecutive relation between preliminary experimental data with the spectral and thermal studies of the synthesized TBAB-PA-based DES. In this investigative work, products with a different molar ratio of PA: TBAB were synthesized using the thermal method. DES sample of 1:1 molar ratio was characterized as it formed a eutectic point at 74.5 °C, which was earlier studied with the help of a phase diagram. Its synthesis offered many advantages such as easily available raw materials, less complication in preparation, pocket-friendly, and 100 % atom economy. FTIR & ^{1}H NMR analysis and TGA, DTA & DSC analysis were utilized for spectral study and thermal study respectively. FTIR & NMR analysis indicated purity and hydrogen bonding between DES components. Thus, overall outcomes can manifest that TBAB-PA-based DES can be tuned and further studied for its thermo-physical properties. In the future, the computational simulation study of TBAB- PA-based DES will provide a new advent in redesigning numerous applications. All these advantages open alternative routes for the emergence of this newly syn-

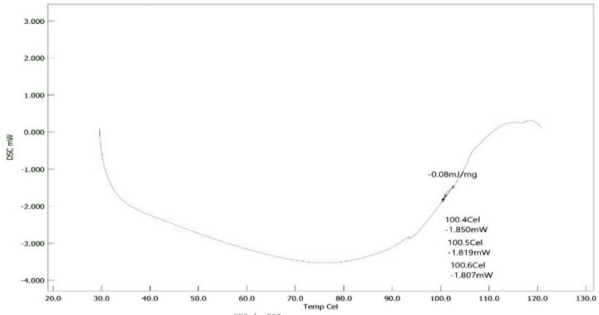


Fig. 10. Shows the image of the DSC curve of 1:1 molar ratio TBAB-PA-based DES

thesized DES in a wide range of industrial applications in nano science, extractions of dye from wastewater, and CO2 capture.

Author information

Priyanka Sharma: Conceptualization, Formal analysis, Investigation, Data curation, Writing Original draft, Visualization
Abhay Sawant: Methodology, Conceptualization, Validation, Supervision.

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Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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