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Physicochemical properties of ammonium acetate / propionic acid as a novel deep eutectic solvent and its binary mixtures with water in (298.15–353.15) K range

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HIGHLIGHTS

- Novel deep eutectic solvent (AA/PA DES) is prepared and characterized.
- Physicochemical properties of the AA/ PA DES and its binary solutions with water (cosolvent) are reported.
- Experimental data of density, sound velocity and viscosity are used to calculate excess properties.
- Excess properties are explained in terms of interactions operating within the system.
- Electrochemical potential window of AA/PA DES is investigated and found to have good window for using cyclic voltammetry.

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G R A P H I C A L A B S T R A C T



ABSTRACT

Emergence of deep eutectic solvents as potential replacements for volatile organic solvents has attracted interest of the scientific community in diverse fields of applications. Compared to ionic liquids, which exhibit similarity in many respects with this new class of green solvents, deep eutectic solvents (DESs) show low toxicity, and are easy to prepare from cheap and abundantly available starting materials. Knowledge of physicochemical properties of DESs is a prerequisite for their safe applications in technological fields and to understand the nature of interactions present in these systems. Although physicochemical properties of choline chloride based DESs are widely investigated, similar information on ammonium acetate based DESs is scant.

In this work, a novel ammonium acetate/propionic acid deep eutectic solvent (AA/PA DES) is reported which is prepared by mixing ammonium acetate (AA) and propionic acid (PA) in the 1:3 mol ratio and characterized by FTIR, ¹H and ¹³C NMR, TGA and DSC techniques. The density (ρ), sound velocity (u), viscosity (η) and conductivity (κ) of the pure DES and its binary mixtures with water are investigated over the entire composition

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Received 23 August 2023; Received in revised form 13 February 2024; Accepted 9 March 2024 Available online 14 March 2024 1386-1425/© 2024 Elsevier B.V. All rights reserved. range and temperatures (298.15–353.15) K. The excess properties, V_m^E , K_s^E , $\Delta\eta$, and ΔG^{*E} are calculated and corelated using Redlich-Kister equation (RKE). Temperature dependence of conductivity and viscosity is satisfactorily described by the Vogel – Fulcher – Tamman (VFT) equation rather than Arrhenius equation. The pure DES shows a wide electrochemical potential window ranging from – 1000 mV to + 1000 mV, which coupled with its better solubilizing characteristics, could be exploited for electrochemical work.

1. Introduction

Deep eutectic solvents (DESs) are considered as green solvents due to their potential to replace volatile and harmful organic solvents in industry, natural science labs of educational and research institutions [1]. Over the past two decades DESs have emerged as a better alternative as green solvents than ionic liquids (ILs) due to their simple method of preparation from cheap and abundantly available starting materials, and low toxicity, although both categories of liquids also enjoy many common physicochemical properties and exhibit flexibility in modulating them [2-6]. Initially ionic liquids (ILs), which are salts formed by the reaction of an organic cation (e.g., pyridinium, imidazolium) with an organic or inorganic anion, were considered environment friendly "green solvents" suitable to replace volatile organic compounds for many applications [7–9]. Due to problems associated with their preparation, purification, high cost of production and toxicity, the quest for better alternatives continued. The development of DESs, which started about two decades ago, and which are analogous to ILs in many ways, has changed the focus of scientists and intensified research on this new class of green solvents [10]. DES is formed as a eutectic mixture by interacting a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) in specific mole ratio. Deep eutectic solvents (DESs), like their predecessor ionic liquids (ILs), exhibit unique physicochemical properties such as very low vapor pressure, thermal stability, nonflammability, and electrical conductivity, which distinguish them from common organic solvents [4]. An important and advantageous property associated with them is the versatility in modulation of their properties for specific applications by a suitable combination of precursors and by making binary mixtures with appropriate cosolvents [2,11]. This later aspect has widened the range of their applications in technological fields and offers a significant advantage over nonaqueous organic solvents [1–5]. Components of deep eutectic solvents are loosely bound through hydrogen bonds. They are usually viscous fluids than aqueous and nonaqueous solvents and have melting points lower than their constituents. Tunability of physicochemical properties of DESs provide them with useful miscibility and hydrophobicity characteristics for specific applications in chemical systems [12,13].

Major cause of environmental pollution is attributed to large-scale use of harmful organic solvents in industry, and in chemical and medicinal research labs for analytical purpose and process development [14]. Most of them are volatile, toxic, flammable, and therefore present serious environmental problems. For example, inhalation of vapor, ingestion or contact with skin or eyes may cause irritation, gastrointestinal disorders/irritation with nausea, vomiting, diarrhea, and effect on nervous system. Organic solvents can be carcinogens, reproductive hazard, and neurotoxins.

Efforts to replace conventional organic solvents with environment friendly solvents has materialized in the development of deep eutectic solvents (DESs) which are considered as green solvents because of benign properties such as low vapor pressure, low toxicity, biodegradability, and biocompatibility. DESs offer an excellent ecofriendly alternative to volatile organic solvents, and harsh chemicals as a safe and viable medium in a variety of chemical reactions [15,16,6]. They can also be recovered after completion of a reaction for subsequent reuse.

Dissolution of oxides in in deep eutectic solvents demonstrates their ability as a solubilizing solvent compared to conventional solvents [17]. Most drugs are insoluble or sparingly soluble in aqueous system, for such situations DESs offer an excellent alternative for solubilization. DESs

exhibit wide electrochemical potential window, good electrical conductivity, and stability [18–20].

DESs exhibit a set of environment friendly properties unmatched by conventional volatile organic solvents and therefore justify the tag of green solvent associated with them [21]. Generally, they are viscous (η > 100 cP at room temperature) solvents, good dissolving power toward polar and nonpolar compounds [2] High viscosity of DESs is attributed to presence of extended hydrogen bond network between the components [22–25]. Their physicochemical properties (viscosity, conductivity, and volumetric) are markedly influenced by a selection of HBA, HBD, their mole ratio, cosolvent and temperature [26,27].

The range of applications of DESs is broad and includes diverse fields such as metallurgy [10], extraction [28] and recycling of metals in solution, separation [3,29], electroplating/electrodeposition [30–32], batteries [33–35], biomass processing [36,37], pharmaceutical and medical research [38,39], nanomaterials [40,41], biotechnology [42] and genomics [43,44]. Information obtained from the various applications based on physicochemical properties of DESs aids to design new systems for chemical reactions and extractions [45–49].

Choline chloride is generally used as a popular hydrogen bond acceptor in research and industry for the synthesis of environment friendly DESs due to its purity, low toxicity, biodegradability, low cost and commercial availability in large quantity. It is an industrial product whose market value in 2022 was 662.1 million US dollar, which is expected to increase further in future. Choline cation, also known as vitamin B₄, is a micronutrient and dietary supplement which occurs in nature in various kinds of food and in human beings [50–53].

Toxicity profile and biodegradability of choline chloride based DESs are dependent on constituent components (HBDs and HBAs) and their structures. NADESs are prepared from natural components such as sugars, polyalcohol, amino acids, organic acids, and bases. Hence, they fully conform to green chemistry principles, suitable for pharmaceutical and biomedical applications. DESs have several advantages over conventional organic solvents which are (i) preparation method is simple (ii) starting materials are cheap and readily available (iii) recyclability after use (iv) tunability to meet specific requirement, and (v) safe disposal. In view of these beneficial properties, it is worthwhile to look for other systems based on alternate HBAs. Ammonium acetate is one such HBA which is not yet fully investigated. Literature survey reveals that choline chloride based deep eutectic solvents have been investigated extensively. In contrast there are only few examples in the literature of the preparation of ammonium acetate based deep eutectic solvents primarily for extraction and separation purposes.

The present study reports preparation of a novel ammonium acetate/ propionic acid deep eutectic solvent, its characterization with FTIR, ¹H and ¹³C NMR spectroscopy, TGA and DSC measurements [54–58]. Physicochemical properties of AA/PA DES and its binary mixture with water are investigated over the entire composition range and temperatures (298.15–353.15) K.

Experimental density, acoustic and viscosity measurements are used to calculate excess molar volumes (V_m^E), apparent molar volumes ($V_{\phi,1}$, $V_{\phi,2}$), deviations in isentropic compressibility (K_S^E), viscosity ($\Delta \eta$) and Gibbs energy of activation (ΔG^{*E}). Excess properties are fitted with RKE, and the temperature dependence of transport properties are best described by VFT equation than Arrhenius equation.

Cyclic voltammetry is a powerful tool for the study of redox processes. Aqueous media with supporting electrolytes, H_2SO_4 , KCl or KNO₃ are the first choice in electrochemical measurements. However, most

Chemicals / equipment, Source, CAS number/ Model no., Purity, and Country of Origin.

Chemical/	Source	CAS no./	Purity	Country of
Instrument Name		Model no.		Origin
Ammonium Acetate	Sigma	631-61-8	\geq	United
	Aldrich		98.00	States
			%	
Propionic acid	Daejung	79–09-4	\geq	South Korea
			99.98	
			%	
Silica Gel	Daejung	7631-86-9		South Korea
Potassium Chloride	Sigma	7447-40-7	99 %	United
	Aldrich			States
Karl Fischer titrator	Mettler	V10S		United
	Toledo			States
FTIR Spectrometer	Bruker	ALPHA II		United
	Optics			States
NMR spectrometer	Bruker	300 MHz		United
	Optics	NMR		States
Potentiostat	Gamry	600		United
				States
Analytical Balance	Shimadzu	AUW220D		Japan
Hot plate	KML	1500A		Korea
TGA/DSC thermal	TA	Q600 SDT		United
analyser	Instruments			States
Density and sound	Anton Paar	DSA -5000		Australia
velocity meter				
Viscosity Module	Anton Paar	Lovis 2000		Australia
Seven Compact	Mettler	S230		United
	Toledo			States
Temperature-	Sci Finetech	FTCOB-501		Korea
controlled oil bath				

organic compounds, particularly majority of drugs, are insoluble in water. Therefore, organic solvents, acetonitrile (AcN), dimethyl formamide (DMF) and tetrahydrofuran (THF), which are volatile, toxic, and hazardous [14,59,60], are used with tetra alkylammonium salts as supporting electrolytes [61].

In present work it is shown that AA/PA DES has wide potential window which can be exploited for electrochemical work.

Costs per kg of ammonium acetate (Merck/Sigma Aldrich) and propionic acid (Dae-Jung Chemicals) are US \$ 96.64 and 12.33 respectively. Mixing ammonium acetate and propionic acid in 1:3 mol ratio by weight produces 264 mL (280.4 g) of DES. Therefore, the cost of preparation per kg of DES comes to US \$ 36.34. It is lower than the cost of other solvents in use, for example, Merck Sigma-Aldrich cost per kg of acetone, methanol, ethanol, acetonitrile, DMF and DMSO are respectively US dollars 116.81, 53.10, 63.78, 215.73, 224.24, and 250.91. (Table S7, supporting information).

Preparation of AA/PA DES in bulk is even cheaper. Market prices per metric ton of ammonium acetate and propionic acid in January 2024 were 1070.903 and 801.947 US dollars respectively i.e., 1.071 and 0.802 USD per kg. Therefore, calculated per kg cost of AA/PA DES would be 0.929 USD /kg or 929 USD per metric ton. For comparison, the market prices per metric ton in USD of ethanol, methanol, DMF, DMSO, Acetonitrile and acetone are respectively USD 786, 520, 1510, 2671, 1361 and 1015. (Table S7, supporting information).



Fig. 1. Temperature dependence of densities, ρ /Kg. $m^{\cdot3}$, of pure AA/PA DES and the binary mixture of AA/PA DES – water as a function of temperature, and mole fraction (x_1 = ■: 0.0; •: 0.1; ▲:0.2; •: 0.3; •: 0.4; <: 0.5; •: 0.6; • 0.7; \star : 0.8;: 0.9; •: 1.00) of AA/PA DES. Solid lines are the best fit representation of Eq. (1).

Table 3

(Parameters a_p , b_p and c_p of the 2nd order polynomial fit of Eq. (1) to the experimental density data of AA/PA DES-water binary mixtures as a function of temperature, T, and mole fraction x_1 of AA/PA DES.

x ₁	a _p /kgm ⁻³	b _p /kgm ⁻³ K ⁻¹	c _p /Kgm ⁻³ K ⁻²
0.00	826.820 ± 26.31	1.44 ± 0.16	$-2.92\times 10^{\text{-3}}\pm 2.49\times 10^{\text{-4}}$
0.10	1219.31 ± 41.94	-0.45 ± 0.26	$-5.11\times10^{\text{-4}}\pm3.96\times10^{\text{-4}}$
0.20	1266.63 ± 22.93	-0.72 ± 0.14	$-8.27\times10^{\text{-5}}\pm2.17\times10^{\text{-4}}$
0.30	1146.91 ± 23.57	0.03 ± 0.15	$-1.24 \times 10^{4} \pm 2.23 \times 10^{4}$
0.40	1140.82 ± 26.3	0.08 ± 0.16	$-1.31\times 10^{\text{-3}}\pm 2.48\times 10^{\text{-4}}$
0.50	1128.12 ± 20.88	0.18 ± 0.13	$-1.48\times10^{\text{-3}}\pm1.97\times10^{\text{-4}}$
0.60	1208.48 ± 16.32	-0.28 ± 0.10	$-8.10\times10^{\text{-4}}\pm1.54\times10^{\text{-4}}$
0.70	1289.82 ± 10.22	-0.75 ± 0.06	$-1.14\times 10^{\text{-4}}\pm 9.65\times 10^{\text{-5}}$
0.80	1352.94 ± 16.91	-1.11 ± 0.10	$4.24 \times 10^{\text{-4}} \pm 1.60 \times 10^{\text{-4}}$
0.90	1332.00 ± 2.420	-0.96 ± 0.01	$1.90 imes 10^{-4} \pm 2.29 imes 10^{-5}$
1.00	1310.67 ± 1.400	-0.83 ± 0.01	$5.32 \times 10^{\text{-6}} \pm 1.32 \times 10^{\text{-5}}$

Table 2

Experimental Densities, $\rho/kg.m^{-1}$	³ , of AA/PA DES-water mixtures as a function	on of temperature, T, and mole fraction	n ($x_1 = 0.0-1.0$) of AA/PA DES.
------------------------------------------	----------------------------------------------------------	-----------------------------------------	-------------------------------------

\mathbf{x}_1	$\rho / kg m^{-3}$											
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K	328.15K	333.15K	338.15K	343.15K	348.15K	353.15K
0.00	997.090	995.700	994.090	992.270	990.270	988.100	985.760	983.270	980.620	977.480	975.060	972.440
0.10	1040.45	1037.18	1033.29	1029.75	1025.87	1022.06	1017.89	1013.40	1009.42	1006.03	1001.89	998.39
0.20	1043.38	1039.84	1035.71	1032.15	1028.34	1024.24	1020.34	1016.31	1012.18	1008.53	1004.81	1000.98
0.30	1045.30	1042.11	1038.65	1034.56	1030.81	1027.01	1023.38	1019.22	1014.94	1011.03	1007.22	1002.87
0.40	1048.23	1044.58	1040.83	1036.96	1033.27	1029.89	1026.13	1022.14	1018.00	1013.53	1009.63	1005.61
0.50	1050.21	1046.74	1042.86	1039.03	1035.28	1031.78	1027.95	1023.80	1019.75	1015.29	1011.16	1007.05
0.60	1053.90	1050.00	1046.18	1042.38	1038.29	1034.50	1030.46	1026.17	1021.95	1018.04	1014.09	1009.53
0.70	1056.59	1052.85	1048.50	1044.48	1040.29	1036.22	1032.13	1028.03	1023.92	1019.80	1015.65	1011.49
0.80	1059.28	1055.05	1050.82	1046.58	1042.30	1037.94	1033.79	1029.90	1025.90	1021.55	1017.22	1013.45
0.90	1061.22	1056.96	1052.72	1048.46	1044.23	1040.03	1035.83	1031.63	1027.44	1023.30	1019.12	1014.90
1.00	1062.25	1058.06	1053.90	1049.74	1045.59	1041.43	1037.28	1033.14	1028.98	1024.82	1020.66	1016.48

x ₁	$V_m^E \times \times 10$	$/ /m^3.mol^{-1}$										
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K	328.15K	333.15K	338.15K	343.15K	348.15K	353.15K
0.00	0	0	0	0	0	0	0	0	0	0	0.00	0.00
0.10	-5.30	-5.09	-4.77	-4.56	-4.31	-4.09	-3.82	-3.49	-3.31	-3.35	-3.08	-3.00
0.20	-3.86	-3.67	-3.33	-3.18	-2.99	-2.73	-2.56	-2.37	-2.17	-2.18	-2.07	-1.95
0.30	-2.41	-2.39	-2.32	-2.05	-1.93	-1.81	-1.76	-1.56	-1.33	-1.30	-1.20	-0.94
0.40	-1.52	-1.43	-1.32	-1.18	-1.13	-1.22	-1.18	-1.06	-0.91	-0.68	-0.59	-0.48
0.50	-0.53	-0.58	-0.48	-0.41	-0.39	-0.50	-0.48	-0.32	-0.23	0.00	0.14	0.27
0.60	-0.55	-0.49	-0.46	-0.47	-0.34	-0.38	-0.31	-0.11	0.03	-0.02	0.00	0.32
0.70	-0.41	-0.49	-0.26	-0.21	-0.07	-0.01	0.06	0.12	0.18	0.22	0.31	0.40
0.80	-0.54	-0.42	-0.29	-0.16	-0.01	0.18	0.25	0.16	0.12	0.28	0.45	0.26
0.90	-0.48	-0.38	-0.29	-0.19	-0.10	-0.04	0.03	0.09	0.14	0.15	0.20	0.26
1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00





Fig. 2. Excess molar volume $V_m^E \times 10^7/\text{m}^3$.mol⁻¹ for AA/PA DES-water binary mixtures with mole fraction, x_1 , in the temperature range (T= \blacksquare : 298.15; \bullet : 303.15; \bigstar :308.15; \checkmark : 313.15; \blacklozenge :318.15; \bigstar : 323.15; \triangleright :328.15; \cdot :333.15; \star : 338.15; 343.15; \bullet : 348.15;+: 353.15) K. Solid lines are the best fit representation of Eq. (3).

2. Materials and methods

2.1. Materials

Details of the chemicals used in the synthesis of the DES are listed in Table 1 with their CAS number, source, and purity.

2.2. Method

A mixture of ammonium acetate and propionic acid in 1:3 mol ratio was taken in a flat bottom flask fitted with a condenser at the end of which a drying tube filled with silica gel was provided. Appropriate amounts of the components weighed using analytical balance (Shimadzu AUW220D, precision, \pm 0.01 mg). For weighing, ammonium acetate was taken from the packed bottle. The contents of the flask were heated at 60–70 °C for 7 h with constant stirring using a magnetic stirrer hot plate (KML – 1500A). A homogeneous, colourless, and transparent liquid of AA/PA DES was formed which was stored in airtight bottles under ambient conditions. Water content of the prepared AA/PA DES was 0.05 % (500 ppm) determined by coulometric Karl Fischer titrator (Mettler Toledo V10S) using reagent (CombiNorm5) and methanol.

Table 5

Parameters of the RKE Eq. (3) for the Experimental $V_m^E \times 10^7 / \text{m}^3 / \text{mol}$ for AA/PA DES-water binary mixture as a function of temperature, T, and mole fraction, x₁, of AA/PA DES range (298.15 – 353.15) K with standard deviations.

T/K	$A_0 \times 10^{\text{-7}}$	$\underset{7}{\overset{A_1}{_7}}\times 10^{\text{-}}$	$A_2\times 10^{\text{-7}}$	$A_3 \times 10^{7}$	$A_4\times 10^{\text{-}7}$
298.15	$-3.11~\pm$	$\textbf{4.87} \pm$	$-13.71~\pm$	$41.29~\pm$	$-48.21\ \pm$
	0.66	2.15	7.17	5.59	12.59
303.15	$-3.09~\pm$	4.55 \pm	$-13.28~\pm$	40.67 \pm	$-44.30~\pm$
	0.63	2.07	6.93	5.40	12.17
308.15	$-2.83~\pm$	5.18 \pm	$-10.31~\pm$	$\textbf{37.03} \pm$	$-43.92~\pm$
	0.69	2.25	7.50	5.85	13.18
313.15	$-2.57~\pm$	$3.99 \pm$	$-8.20~\pm$	38.48 \pm	$-43.84~\pm$
	0.58	1.91	6.38	4.98	11.21
318.15	$-2.39~\pm$	$4.68~\pm$	$-5.43~\pm$	$35.61~\pm$	$-44.13~\pm$
	0.54	1.78	5.94	4.64	10.45
323.15	$-2.90~\pm$	$\textbf{4.88} \pm$	1.73 ± 6.13	$33.79~\pm$	$-50.08~\pm$
	0.56	1.84		4.78	10.78
328.15	$-2.74~\pm$	5.50 \pm	2.02 ± 6.00	$30.55~\pm$	$-46.35~\pm$
	0.55	1.80		4.68	10.55
333.15	$-1.98~\pm$	5.42 \pm	$-1.28~\pm$	$\textbf{27.43} \pm$	$-38.25~\pm$
	0.55	1.80	6.02	4.69	10.57
338.15	$-1.44~\pm$	$4.62 \pm$	$-1.49 \pm$	$26.81~\pm$	$-36.46 \pm$
	0.57	1.87	6.26	4.88	11.00
343.15	$-0.85~\pm$	3.78 \pm	$-3.30~\pm$	$29.74~\pm$	$-34.92 \pm$
	0.49	1.60	5.34	4.16	9.38
348.15	$-0.47~\pm$	4.17 \pm	$-3.35~\pm$	$27.71~\pm$	$-31.28~\pm$
	0.47	1.55	5.19	4.05	9.12
353.15	0.40 \pm	$3.72 \pm$	$-6.17~\pm$	$26.76~\pm$	$-28.02\ \pm$
	0.51	1.68	5.60	4.37	9.84

2.3. Characterization of AA/PA DES

2.3.1. Fourier Transform Infrared Spectroscopy

The Fourier Transform Infrared (FTIR) Spectroscopic measurements of AA/PA DES and the precursors were carried in the 4000 – 500 cm⁻¹ range on ALPHA II (Bruker Optics) FTIR Spectrometer.

2.3.2. ¹H and ¹³C Nuclear Magnetic Resonance Spectroscopy

The ¹H and ¹³C Nuclear Magnetic Resonance (NMR) spectroscopic measurements were carried on a 300 MHz NMR spectrometer (Bruker). DMSO- d_6 was used as internal reference standard.

2.3.3. Thermal Analysis (TGA and DSC)

Simultaneous Thermogravimetric (TGA) and Differential Scanning Calorimetric (DSC) measurements of the DES were carried from (298.15 – 548.15) K at heating rate of 20 K/min with TGA/DSC thermal analyser Q600 SDT (TA Instruments).

2.4. Electrochemical Measurements

The electrochemical window of neat AA/PA DES was recorded using e-corder 401 (Model ED-401) and Gamry 600 potentiostat in the -1000



Fig. 3. Apparent molar volume $V_{\varphi,1} \times 10^{5}$ / m³.mol⁻¹ for AA/PA DES-water binary mixtures with mole fraction $x_1 = 0.1$ to 1.0 of AA/PA DES in the temperature range (T= \blacksquare : 298.15; \bullet : 303.15; \bullet : 308.15; \lor : 313.15; \bullet : 318.15; \triangleleft : 323.15; \triangleright : 328.15; 333.15; \star : 338.15; 343.15; \bullet : 348.15;+: 353.15) K.

to + 1000 mV range in a three-electrode cell assembly comprising glassy carbon (dia 3 mm), silver wire (dia 1.5 mm) and platinum wire (dia 0.5 mm) as working, quasi reference and counter electrodes respectively. GC electrode was polished with fine grade alumina powder and silver wire with a slurry of alumina powder in methanol and then washed with distilled water. Argon gas was bubbled for 10 to 15 min in the AA/PA DES before recording the background.

2.5. Measurements of Physicochemical Properties

Density, sound velocity, viscosity and electrical conductivity of the DES and mixtures were measured in the (298.15 - 353.15) K range at 5 K interval. Density and sound velocity measurements were made with DSA 5000 (Anton Paar) density and sound velocity meter. Calibration of the instrument was checked as per instructions of the manufacturer. Viscosity measurements were carried with the viscosity module Lovis 2000 (Anton Par) attached to the main instrument.

Electrical conductivity measurements were done with Seven Compact S230 (Mettler Toledo) conductivity meter. Temperature of the solution during conductivity measurements was maintained within ± 1 ⁰C with temperature-controlled oil bath (Sci Finetech FTCOB-501).

3. Results and discussion

3.1. FTIR spectroscopy

Vibrational spectral data of propionic acid [62], ammonium acetate ion [63,64] both in solid and solution phases, and partially of ammonium acetate [65] have been reported previously. Loukil [66] assigned vibrational peaks of NH⁺₄. In the present work FTIR spectra of the AA/PA DES and the precursors are measured and reported in in Fig. S1 and Table S1. Vibrational frequencies of AA and PA in Table S1 (columns 1 and 2) are those recorded in this study and matched with earlier studies. Vibrational peaks of AA/PA DES are shown in column 3 and assigned considering assignment for AA and PA. A comparison of the three spectra shows generally peaks have broadened in the DES showing the effect of hydrogen bonding. Some of the peaks observed in the spectra of AA or PA are absent in the DES spectrum. Also, there are peaks which show shifting to lower frequencies.

3.2. NMR

¹H and ¹³C NMR spectra of DES shown in Fig. S2 (a) and (b) respectively are recorded and Fig. S2(c) shows its proposed structure. DMSO- d_6 was used as an internal reference. The observed ¹H NMR spectrum consists of two singlets at 1.82 (3H, CH₃) and 9.21 (1H, OH), a



Fig. 4. Temperature dependence of sound velocity, $\mu / m. s^{-1}$, of AA/PA DES and binary mixture of AA/PA DES – water as a function of temperature, T, and mole fraction ($x_1 = \blacksquare: 0.0; \bullet: 0.1; \bigstar: 0.2; \forall: 0.3; \diamondsuit: 0.4; \blacktriangleleft: 0.5; \succ: 0.6;: 0.7; \star: 0.8;: 0.9; \bullet: 1.00)$ of AA/PA.

Table 6

Experimental Sound velocity, $\mu/m. s^{-1}$, of pure AA/PA DES and binary mixture of AA/PA DES – water as a function of temperature, *T*, and mole fraction (x₁) of AA/PA DES.

\mathbf{x}_1	μ/m.s ⁻¹											
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K	328.15K	333.15K	338.15K	343.15K	348.15K	353.15K
0.00	1497.6	1510.1	1521.0	1530.0	1537.5	1543.5	1548.4	1551.8	1554.0	1554.7	1554.8	1555.6
0.10	1684.7	1678.0	1670.6	1662.9	1654.6	1646.1	1636.9	1627.4	1617.5	1607.1	1596.3	1585.3
0.20	1755.5	1745.9	1736.0	1726.0	1715.7	1705.2	1694.1	1682.7	1671.3	1659.7	1647.7	1635.5
0.30	1808.1	1796.1	1784.3	1772.2	1760.2	1748.1	1735.9	1723.5	1711.2	1698.7	1686.0	1673.3
0.40	1862.8	1849.4	1836.1	1822.9	1809.7	1796.5	1783.4	1769.9	1756.5	1743.1	1729.5	1716.0
0.50	1917.4	1902.8	1887.9	1873.6	1859.3	1844.9	1830.9	1816.4	1801.8	1787.5	1773.0	1758.6
0.60	1972.1	1956.1	1939.7	1924.3	1908.8	1893.4	1878.4	1862.8	1847.1	1831.9	1816.5	1801.3
0.70	2026.8	2009.4	1991.5	1975.0	1958.3	1941.8	1925.9	1909.3	1892.5	1876.3	1860.0	1843.9
0.80	2071.5	2052.7	2033.4	2015.7	2000.9	1980.2	1963.4	1945.7	1927.8	1910.7	1900.5	1876.6
0.90	2126.2	2106.0	2085.2	2066.3	2047.4	2028.6	2010.9	1988.3	1973.1	1955.1	1937.0	1919.2
1.00	2180.8	2159.4	2137.0	2117.0	2101.0	2077.1	2058.4	2038.6	2018.5	2000.5	1980.5	1961.9

- 10 --

Table 7

\mathbf{x}_1	$K_S \times 10^{10}$	Pa										
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K	328.15K	333.15K	338.15K	343.15K	348.15K	353.15K
0.00	4.47	4.40	4.35	4.31	4.27	4.25	4.23	4.22	4.22	4.23	4.24	4.25
0.10	3.39	3.42	3.47	3.51	3.56	3.61	3.67	3.73	3.79	3.85	3.92	3.99
0.20	3.11	3.16	3.20	3.25	3.30	3.36	3.41	3.48	3.54	3.60	3.67	3.73
0.30	2.93	2.97	3.02	3.08	3.13	3.19	3.24	3.30	3.36	3.43	3.49	3.56
0.40	2.75	2.80	2.85	2.90	2.96	3.01	3.06	3.12	3.18	3.25	3.31	3.38
0.50	2.59	2.64	2.69	2.74	2.79	2.85	2.90	2.96	3.02	3.08	3.15	3.21
0.60	2.44	2.49	2.54	2.59	2.64	2.70	2.75	2.81	2.87	2.93	2.99	3.05
0.70	2.30	2.35	2.40	2.45	2.51	2.56	2.61	2.67	2.73	2.79	2.85	2.91
0.80	2.20	2.25	2.30	2.35	2.40	2.46	2.51	2.56	2.62	2.68	2.72	2.80
0.90	2.08	2.13	2.18	2.23	2.28	2.34	2.39	2.45	2.50	2.56	2.62	2.68
1.00	1.98	2.03	2.08	2.13	2.17	2.23	2.28	2.33	2.39	2.44	2.50	2.56

 $K_S \times 10^{10}$ /Pa⁻¹, of AA/PA DES and binary mixture of AA/PA DES – water as a function of temperature, *T*, and mole fraction(x₁) of AA/PA DES.



Fig. 5. Variation of *K*_S × 10¹⁰ /*Pa*⁻¹, of pure AA/PA DES and the AA/PA DES water binary mixtures with mole fraction ($x_1 = 0.0 \ 1.0$) of AA/PA DES in the temperature range (T= \blacksquare : 298.15; ●: 303.15; ▲: 308.15; ▼: 313.15; ♦: 318.15; \blacktriangleleft : 323.15; ▶: 328.15; :333.15; ★: 338.15; 343.15; ●: 348.15; +: 353.15) K.

quartet 2.12 (2H, CH₂CH₃) and a triplet 0.98 ppm (3H, CH₂CH₃) which are explained according to numbering of protons in the proposed structure of DES. The low field singlet peak arises from the OH group protons (marked 1), while the high field singlet is due to methyl group protons from ammonium acetate (marked 4). The triplet ($J_{1,2} = 7.5$ Hz) and quartet ($J_{1,2} = 7.5$ Hz, $J_{1,3} = 15$ Hz) structures are due to methyl group protons (marked 3) and methylene group proton (marked 2) from propionic acid. The observed ¹³C NMR (75.5 MHz) spectrum Fig. S2(b) shows peaks at 176.7, 173.9, 40.5, 28.3, 22.6, 9.9 ppm. The two spectra confirm the structure as shown in Fig.S2(c) in which hydrogen bonds are formed between three hydrogen atoms of NH_4^+ group individually with proton of O–H group in each of the three propionic acid molecules [58].

3.3. Thermal Gravimetric Analysis (TGA) and Differential Scanning Coulometry (DSC)

TGA/DSC thermal analysis are useful techniques for obtaining information on thermal behaviour of compounds and properties such as melting point, decomposition and glass transition temperatures and molar heat capacity [54–57,65,67,68].

Simultaneous thermogravimetric and differential scanning calorimetric measurements of AA/PA DES are made in the (298.15 – 548.15) K range at heating rate of 20 K/min and nitrogen flow rate of 100 mL/min.

Fig. S3 show thermograms recorded for AA/PA DES. Table S2 summarizes results of thermogravimetric analytical parameters. The decomposition of the DES starts at 387 K and completes at 402 K. The DSC thermogram shows that the decomposition process is endothermic and the minimum at 353 K in the curve corresponds to temperature upto which AA/PADES is stable. The thermogram flattens beyond 394 K indicating completion of the decomposition process.

3.4. Cyclic voltammetry in AA/PA DES

In cyclic voltametric measurements aqueous systems employing H_2SO_4 , KCl or KNO₃ as electrolytes, for example, are popular for investigating redox properties of compounds. Many organic compounds, particularly majority of drugs (65%), are insoluble in water [69]. This study reports the potential of AA/PA DES, which can be prepared easily, as a potential electrolyte for electrochemical measurements.

Fig S4. shows background trace of pure AA/PA DES recorded electrolyte with finely glassy carbon electrode (GCE) from -1.0 to +1.0 V

Table 8

Experimental $K_S^E \times 10^{11}$ /Pa⁻¹, of AA/PA DES and binary mixture of AA/PA DES – water as a function of temperature, *T*, and mole fraction (x₁) of AA/PA DES.

A1	$n_{\rm S} \sim 10$ /1a												
	298.15 K	303.15 K	308.15 K	313.15 К	318.15 K	323.15 K	328.15 K	333.15 К	338.15 K	343.15 K	348.15 K	353.15 К	
0.00	0	0	0	0	0	0	0	0	0	0	0	0	
0.10	-8.36	-7.42	-6.54	-5.75	-5.01	-4.35	-3.69	-3.08	-2.53	-2.04	-1.51	-0.95	
0.20	-8.63	-7.74	-6.91	-6.17	-5.47	-4.86	-4.25	-3.69	-3.18	-2.74	-2.28	-1.76	
0.30	-7.98	-7.16	-6.43	-5.74	-5.09	-4.55	-4.02	-3.52	-3.07	-2.66	-2.26	-1.80	
0.40	-7.25	-6.54	-5.90	-5.31	-4.75	-4.31	-3.85	-3.43	-3.04	-2.67	-2.33	-1.95	
0.50	-6.36	-5.77	-5.23	-4.74	-4.25	-3.89	-3.51	-3.16	-2.83	-2.53	-2.24	-1.92	
0.60	-5.37	-4.89	-4.45	-4.07	-3.65	-3.38	-3.07	-2.78	-2.52	-2.29	-2.07	-1.80	
0.70	-4.23	-3.88	-3.54	-3.25	-2.92	-2.73	-2.50	-2.29	-2.10	-1.91	-1.75	-1.56	
0.80	-2.78	-2.53	-2.30	-2.10	-1.91	-1.73	-1.57	-1.43	-1.30	-1.16	-1.25	-0.93	
0.90	-1.44	-1.32	-1.20	-1.10	-0.93	-0.92	-0.83	-0.66	-0.69	-0.61	-0.57	-0.50	
1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	



Fig. 6. Variation of $K_5^{\text{g}} \times 10^{11}$ /Pa⁻¹, of AA/PA DES and AA/PA DES-water binary mixtures with mole fraction, \mathbf{x}_1 , in the temperature range (T=**E**: 298.15; **●**: 303.15; **▲**:308.15; **▼**: 313.15; **♦**:318.15; **<**: 323.15; **▶**:328.15;:333.15; **★**:338.15; 343.15; **●**: 348.15;+: 353.15) K.. Solid lines are the best fit representation of Eq. (3).

Parameters of the Redlich Kister Eq. (3) for the Experimental, $K_S^E \times 10^{11}$ /Pa⁻¹, for AA/PA DES-water binary system as a function of temperature, T, with mole fraction, $x_{1,}$ of AA/PA DES with standard deviation.

T/K	$A_0 \times 10^{\text{-}11}$	$\underset{11}{\overset{A_1}{\times}} \times 10^{\text{-}}$	$A_2 \times 10^{\text{-}11}$	$\underset{11}{\overset{A_3}{\times}} \times 10^{\text{-}}$	$A_4 \times 10^{\text{-}11}$
298.15	$-25.77~\pm$	15.90 \pm	$-10.73~\pm$	$43.09~\pm$	$-46.18~\pm$
	0.39	1.49	5.10	4.46	10.35
303.15	–23.37 \pm	14.08 \pm	$-9.63~\pm$	$\textbf{37.88} \pm$	$-40.00~\pm$
	0.32	1.23	4.28	3.64	8.77
308.15	$-21.16~\pm$	12.52 \pm	$-8.85~\pm$	32.71 \pm	$-33.64 \pm$
	0.26	0.99	3.52	2.86	7.26
313.15	$-19.15 \pm$	10.79 \pm	$-7.91 \pm$	29.34 \pm	$-29.29 \pm$
	0.20	0.76	2.77	2.14	5.73
318.15	$-17.14~\pm$	$9.32 \pm$	$-7.65 \pm$	$26.26~\pm$	–23.47 \pm
	0.16	0.62	2.31	1.74	4.76
323.15	$-15.73~\pm$	7.94 \pm	$-5.38~\pm$	$23.03~\pm$	–22.72 \pm
	0.13	0.52	2.03	1.43	4.19
328.15	-14.19 \pm	$6.60 \pm$	$-4.23~\pm$	$20.15~\pm$	$-19.70~\pm$
	0.12	0.48	1.91	1.3	3.97
333.15	$-12.75~\pm$	5.20 \pm	$-3.72~\pm$	18.31 \pm	$-14.71 \pm$
	0.13	0.53	2.2	1.48	4.58
338.15	$-11.52~\pm$	$4.22 \pm$	$-0.84~\pm$	15.26 \pm	$-17.04~\pm$
	0.14	0.57	2.31	1.56	4.84
343.15	$-10.29~\pm$	$3.15 \pm$	$0.06 \pm$	13.74 \pm	$-15.16\ \pm$
	0.13	0.58	2.21	1.59	4.73
348.15	$-9.09~\pm$	1.90 \pm	$-1.12~\pm$	10.15 \pm	$-9.71~\pm$
	0.12	0.58	2.14	2.02	5.09
353.15	$-7.70~\pm$	$1.25~\pm$	$-3.04~\pm$	$4.93~\pm$	$\textbf{3.44} \pm \textbf{5.93}$
	0.10	0.55	2.28	2.40	

together with that for 1M KCl for comparison. Clearly, AA/PA DES has no signal in the potential range, -1.0 to +1.0 V, which can be used as an electrochemical potential window (EPW) for electrochemical work with the DES.

3.5. Density

Experimental measurements of density of the AA/PA DES and its binary mixtures with water over the entire range of compositions and temperature (298.15 to 353.15) K are given in Table 2. Experimental data is fitted with second degree polynomial eq. (1)

$$\rho = a_p + b_\rho T + c_\rho T^2 \tag{1}$$

where a_p, b_ρ , and c_ρ are the fitting parameters.

The results of the fitting are shown in Fig. 1 and the fitting parameters are given in Table 3. Density increases with an increase in concentration of the AA/PA DES in the binary mixture, while it decreases as the temperature is increased.

Excess molar volume V_m^E values are calculated from equation (2) for the entire composition and temperature range and reported in Table 4.

$$\mathbf{V}_{m}^{E} = \frac{\mathbf{x}_{1}\mathbf{M}_{1} + \mathbf{x}_{2}\mathbf{M}_{2}}{\boldsymbol{\rho}_{mix}} - \left(\frac{\mathbf{x}_{1}\mathbf{M}_{1}}{\boldsymbol{\rho}_{1}} + \frac{\mathbf{x}_{2}\mathbf{M}_{2}}{\boldsymbol{\rho}_{2}}\right)$$
(2)

where x_1 and x_2 , ρ_1 and ρ_2 , M_1 and M_2 are mole fractions, densities and molar masses of AA/PA DES and deionized water respectively, and ρ_{mix} is the density of binary mixtures.

Excess properties, excess molar volume (V_m^E) , isentropic compressibility deviation (K_s^E) and viscosity deviation $(\Delta \eta)$ calculated from respective experimental measurements of density, speed of sound and viscosity, of binary systems are fitted with Redlich-Kister polynomial eq. (3) [70].

$$Y^{E} = x_{WATER} x_{AA/PADES} \sum_{j=0}^{k} A_{j} \left(x_{AA/PADES} - x_{WATER} \right)^{j}$$
(3)

 Y^E in the equation represents the excess property, A_j 's are coefficients to be determined and j is the degree of polynomial. The best fit results obtained by regression analysis of V_m^E with equation (2) are shown by solid lines in Fig. 2 and the coefficients obtained are collected in Table 5.

The V_m^E values of AA/PA DES and water are negative for all compositions and temperatures studied in this work except a few in the (328.15 - 353.15) K range between $x_1 = 0.7 - 0.9$ which are positive. The V_F^m values are influenced by temperature and composition of the mixture; the effect of composition is more pronounced than that of temperature. Negative values of V_m^E represent volume contraction on mixing the components because of molecular interactions. The deviation from ideal behaviour on mixing are attributed to three different types of interactions (a) physical (b) structural, and (c) chemical or specific [39,40,42]. Physical interactions are usually weak and include dipole-dipole, dipole induced dipole and dispersion interactions. Structural effects arise from interstitial accommodation of one component into the structure of the other and depend on shape and size of the components. Specific and chemical interactions are due to charge transfer and hydrogen bonding interactions between unlike molecules. Both effects (b) and (c) appear to be responsible for comparatively large negative values of V_m^E observed at higher mole fractions of water ($x_2 = 1 - x_1$). Structural effects produce a more compact structure in the system while specific interactions lead to an efficient packing of the components in the mixture. The higher negative values of V_m^E observed in water rich region indicate that water molecules are strongly involved in hydrogen bonding with AA/PA and the likely sites for bonding are C = O oxygens of carboxylic groups in propionic acids [71]. The minimum value of V_m^E -0.55 cm³/mol is found at x₁ between 0.1 and 0.2 (≈ 0.15) which lies in the water rich region. This value may be compared with glyceline + water, and ethaline + water systems where minimum value of V_m^E -0.35 cm³/mol is observed in the range of x_1 0.35–0.4 [45,72]. The comparison also reveals that the interaction of water with AA/PA DES is stronger than glyceline or ethaline systems. As concentration of AA/PA in the mixtures is increased, the hydrogen bond network within the liquid water structure and the water and DES molecules gradually break which leads to an increase in volume of the system and hence V_m^E values become less negative. These effects are also responsible for less negative values of (decreasing $|V_m^E|$) of excess molar volume as temperature is increased, and probably the reason of some positive values of V_m^E

Experimental $\eta/$	/mPa.s, of AA/PA DES and binar	y mixture of AA/PA DES – water as a function of	temperature, T , and mole fraction(x_1) of AA/PA DES.
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x ₁	η/mPa.s,												
	298.15 K	303.15 K	308.15 K	313.15 К	318.15 K	323.15 K	328.15 K	333.15 К	338.15 K	343.15 K	348.15 K	353.15 K	
0.00	0.893	0.797	0.709	0.653	0.596	0.546	0.504	0.466	0.433	0.397	0.361	0.326	
0.10	2.433	2.281	2.181	1.833	1.527	1.355	1.203	1.116	1.056	0.997	0.958	0.911	
0.20	3.746	3.509	3.016	2.616	2.139	2.006	1.708	1.586	1.519	1.563	1.525	1.478	
0.30	5.055	5.331	4.458	3.689	3.016	2.823	2.356	2.226	2.080	2.090	2.011	1.989	
0.40	7.059	6.866	5.911	4.836	3.702	3.673	3.115	2.795	2.581	2.771	2.678	2.604	
0.50	9.212	8.547	7.185	5.985	4.624	4.505	3.785	3.429	3.223	3.344	3.258	3.160	
0.60	12.16	10.47	8.75	6.863	5.518	5.35	4.467	4.125	3.914	3.895	3.876	3.709	
0.70	15.42	12.19	10.15	8.140	6.561	6.107	5.203	4.864	4.575	4.420	4.426	4.278	
0.80	18.83	14.58	11.55	9.65	7.814	7.164	6.128	5.559	5.222	5.017	4.996	5.000	
0.90	24.44	19.73	15.89	13.68	10.91	9.471	8.297	6.876	6.501	6.126	6.211	6.126	
1.00	41.33	32.9	26.7	20.52	16.25	13.78	11.76	9.94	8.893	8.306	7.851	7.250	

Table 11

Parameters of the VFT Eq. (7) for the Experimental Viscosity, $\eta/mPa.s$, of binary mixture of AA/PA DES – water as a function of temperature, T, and mole fraction, x_1 , of AA/PA DES at $\eta^0 = 1$ mPa.s.

\boldsymbol{x}_1	$\ln\!\left(\!rac{A_\eta}{\eta^0}\! ight)$	B_{η}/K	$T_{0,\eta}/\mathrm{K}$
0.00	$-8.880\ \pm$	$3.86\times10^3\pm3.42\times$	$-1.43\times10^2\pm2.07~\times$
	3.6600	10^{3}	10 ²
0.10	$-25.920\ \pm$	$3.70\times10^{4}\pm1.42\times$	$-1.08\times10^{3}\pm2.70~\times$
	50.65	10 ³	10 ³
0.20	$-3.160~\pm$	$6.92 imes10^2\pm1.15 imes$	$1.43\times10^2\pm1.49\times10^1$
	0.0300	10^{1}	
0.30	$-31.76~\pm$	$4.50\times10^{4}\pm2.75\times$	$-1.05 imes10^3\pm4.20 imes$
	100.53	10 ⁵	10^{3}
0.40	$-13.220~\pm$	$8.96\times10^3\pm1.39\times$	$-2.90 imes10^2\pm4.79 imes$
	11.36	10 ⁴	10 ²
0.50	$-2.770~\pm$	7.47 \times $10^2 \pm$ 3.90 \times	$1.49\times10^2\pm4.48\times10^1$
	1.1300	10 ²	
0.60	$-1.5900~\pm$	$4.17 imes10^2\pm1.34 imes$	${1.97\times 10^2 \pm 1.98\times 10^1}$
	0.540	10^{2}	
0.70	$-0.9500~\pm$	$3.03 imes10^2\pm7.47 imes$	$2.16\times10^2\pm1.2\times10^1$
	0.360	10 ¹	
0.80	$-0.8000~\pm$	$2.82 imes10^2\pm7.63 imes$	${\bf 2.22 \times 10^2 \pm 1.30 \times 10^1}$
	0.390	10 ¹	
0.90	$-0.5900~\pm$	$2.80 imes10^2\pm4.54 imes$	${\bf 2.24\times 10^{2}\pm 7.69\times 10^{1}}$
	0.230	10 ¹	
1.00	0.0200 ± 0.330	$2.14\times10^2\pm5.24\times$	${\bf 2.40\times 10^{2}\pm 9.37\times 10^{1}}$
		10 ¹	

observed at higher concentration and temperatures.

The Apparent molar volume $V_{\varphi,i}$ for the component "*i*" in the mixture is calculated from V_m^E values and mole fractions using eq. (4).

$$V_{\varphi,i} = V_{m,i} + \frac{V_m^E}{x_i} \tag{4}$$

 $V_{m,i}$ is the molar volume of the pure component "*i*". Results of calculation are presented in Tables S3 and S4 and the plot of $V_{\varphi,1}$ vs x_1 is shown in Fig. 3. $V_{\varphi,1}$ and $V_{\varphi,2}$ for the components are positive and increase with composition (more between $x_1 = 0.1$ –0.2, Fig. 3), which suggests that structural order in solution is enhanced [73]. Apparent molar volumes also increase with temperature.

3.6. Sound velocity

Sound velocity (u) measurements of AA/PA DES and binary solutions over the entire range of composition and temperature (298.15–353.15) K are given in Table 6, and its variation with temperature is shown in Fig. 4 together with those of neat components. Sound velocities of mixtures and neat AA/PA DES decrease with temperature, whereas acoustic behavior of water is in the opposite direction.

Isentropic compressibility (K_s) of AA/PA DES and its binary mixtures



Fig. 7. Variation of $\ln\eta/mPa.s$, of AA/PA DES and AA/PA DES-water binary mixtures with mole fraction, x_1 , of AA/PA DES in the temperature range ($x_1 = \blacksquare$: 0.0; \oplus : 0.1; \bigstar :0.2; \forall : 0.3; ϕ : 0.4; \triangleleft : 0.5; \triangleright : 0.6;: 0.7; \star : 0.8;: 0.9; \oplus : 1.00) of AA/PA DES. Solid lines are the best fit representation of Eq. (7).

with water is calculated in the temperature range studied using Laplace – Newton eq. (5) [74]. Calculate values are given in Table 7 and plotted vs x_1 in Fig 5.

$$K_s = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right) = \frac{1}{\rho \times \mu^2}$$
(5)

where ρ is the density and *u* is speed of sound of solutions.

Isentropic Compressibility of mixtures increases with dilution and temperature.

Excess isentropic compressibility (K_s^E) values given in Table 8 are calculated using eq. (6)

$$K_{S}^{E} = K_{S} - (x_{1}K_{S,1} + x_{2}K_{S,2}$$
(6)

where $K_{S,1}$ and $K_{S,2}$ are the isentropic compressibilities of pure components, and x_1 and x_2 are mole fractions of solutions of components 1 and 2 respectively. Solid lines in Fig. 6 represent the fitting of K_S^E values using Redlich-Kister polynomial eq. (3) and the derived coefficients are collected in Table 9. The isentropic compressibility deviations for binary solution are negative at all compositions and temperatures. The trend in K_S^E values is the same as observed for V_m^E i.e., they are less negative with respect to increasing temperature and composition. The minimum in the K_S^E vs x_1 plot occurs between $x_1 = 0.1-0.2$ which lies in the water rich

x ₁	$\Delta \eta / mPa.s$											
	298.15 K	303.15 K	308.15 K	313.15 К	318.15 K	323.15 K	328.15 K	333.15 K	338.15 K	343.15 K	348.15 K	353.15 K
0.00	0	0	0	0	0	0	0	0	0	0	0	0
0.10	-2.50	-1.73	-1.13	-0.81	-0.63	-0.51	-0.43	-0.30	-0.22	-0.19	-0.15	-0.11
0.20	-5.23	-3.71	-2.89	-2.01	-1.59	-1.19	-1.05	-0.77	-0.61	-0.42	-0.33	-0.23
0.30	-7.97	-5.10	-4.05	-2.92	-2.28	-1.69	-1.53	-1.08	-0.89	-0.68	-0.60	-0.41
0.40	-10.01	-6.77	-5.19	-3.76	-3.16	-2.17	-1.89	-1.46	-1.24	-0.79	-0.68	-0.49
0.50	-11.90	-8.30	-6.52	-4.60	-3.80	-2.66	-2.35	-1.77	-1.44	-1.01	-0.85	-0.63
0.60	-13.00	-9.59	-7.56	-5.71	-4.47	-3.14	-2.79	-2.03	-1.60	-1.25	-0.98	-0.77
0.70	-13.78	-11.08	-8.75	-6.42	-4.99	-3.70	-3.18	-2.23	-1.78	-1.51	-1.18	-0.89
0.80	-14.41	-11.90	-9.95	-6.90	-5.31	-3.97	-3.38	-2.49	-1.98	-1.71	-1.36	-0.86
0.90	-12.85	-9.96	-8.21	-4.86	-3.78	-2.99	-2.34	-2.12	-1.55	-1.39	-0.89	-0.43
1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00





Fig. 8. Variation of $\Delta\eta/mPa.s$, of AA/PA DES and AA/PA DES-water binary mixtures with mole fraction, x_1 , of AA/PA DES in the temperature range (T= \blacksquare : 298.15; \bullet : 303.15; \bigstar :308.15; \checkmark : 313.15; \blacklozenge :318.15; \triangleleft : 323.15; \triangleright :328.15;:333.15; \bigstar :338.15; 343.15; \ominus : 348.15;+: 353.15) K. Solid lines are the best fit representation of Eq. (3).

region

The isentropic compressibility deviation results also support the presence of dominant hydrogen bonding interactions which are reduced with increasing temperature and composition as already explained in the case of V_m^E .

3.7. Viscosity

Viscosity is an important physical property of fluids which is a measure of the internal resistance that fluid offers to flow. Experimental viscosities of AA/PA DES and its binary mixtures with water are reported in Table 10 over the entire range of compositions and temperature. The temperature dependence of transport property Y (Y = viscosity or conductivity) is satisfactorily described by the empirical Vogel–Fulcher–Tamman (VFT) eq. (7) for viscous fluids close to their glass transition temperature.

$$\ln\frac{Y}{Y^0} = \ln\frac{A_Y}{Y^0} + \frac{B_Y}{(T - T_{0,Y})}$$
(7)

where A_Y, B_Y and $T_{0,Y}$ are the adjustable parameters obtained by fitting the experimental viscosity or conductivity data [27], $Y^0 = \eta^0 =$

Table 13

Parameters of the Redlich Kister Eq. (3) for the Experimental Viscosity deviation, $\Delta\eta/mPa.s$, for AA/PA DES-water binary mixtures as a function of temperature, T, and mole fraction, x_1 , of AA/PA DES, with their standard deviations.

T/K	A ₀	A_1	A ₂	A ₃	A ₄
298.15	$-47.70~\pm$	$-25.43~\pm$	$-12.86~\pm$	-64.86 \pm	$-65.280~\pm$
	0.34	1.32	4.81	3.54	9.80
303.15	–32.88 \pm	$-27.71~\pm$	–33.08 \pm	$-44.31~\pm$	$-26.350~\pm$
	0.26	0.98	3.24	2.86	6.77
308.15	$-25.52\ \pm$	$-21.42\ \pm$	$-31.36~\pm$	$-45.64~\pm$	$-20.44~\pm$
	0.38	1.49	4.99	4.49	10.45
313.15	$-18.40~\pm$	$-18.11~\pm$	$-26.95~\pm$	$-20.86~\pm$	$3.300~\pm$
	0.27	0.95	3.39	2.94	7.230
318.15	$-15.18~\pm$	$-12.91~\pm$	$-14.43~\pm$	$-19.01~\pm$	$-6.960~\pm$
	0.21	0.75	2.64	2.21	5.50
323.15	$-10.51~\pm$	$-9.820~\pm$	$-15.03~\pm$	$-13.30~\pm$	$-0.830~\pm$
	0.08	0.31	1.03	0.93	2.22
328.15	$-9.240~\pm$	$-8.530~\pm$	$-13.28~\pm$	$-10.21~\pm$	$2.060~\pm$
	0.12	0.43	1.59	1.37	3.40
333.15	$-7.050~\pm$	$-4.910\ \pm$	$-5.140~\pm$	$-12.15~\pm$	$-8.160\ \pm$
	0.09	0.35	1.21	1.03	2.48
338.15	$-5.730~\pm$	$-3.390~\pm$	$-3.850~\pm$	$-10.90~\pm$	-6.420 \pm
	0.07	0.29	1.01	0.86	2.12
343.15	$-3.970~\pm$	$-4.150~\pm$	$-7.600~\pm$	$-6.810~\pm$	$0.060~\pm$
	0.07	0.25	0.87	0.76	1.86
348.15	$-3.290~\pm$	$-2.800~\pm$	$-6.050~\pm$	$-6.330~\pm$	0.610 \pm
	0.10	0.40	1.54	1.28	3.36
353.15	$-2.480~\pm$	$-2.950~\pm$	$-4.780~\pm$	$-0.080~\pm$	5.550 \pm
	0.06	0.20	0.78	0.75	1.67

 $1mPa^{-1}$ or $(Y^0 = \frac{1}{\kappa^0} = 1Sm - 1$ in the case of resistivity of κ^{-1}). VFT equation describes the slowing down of system's dynamics as it approaches the critical VFT temperature $(T_{0,Y})$ which is usually 10–15 K below the calorimetric glass transition temperature of the system. A_Y represents the property Y as $T \longrightarrow \infty$, the quantity $E_a = B_Y \times R$ (where R is general gas constant) is the pseudo activation energy, and $T_{0,Y}$ is the Vogel temperature [48]. The calculated values of the fitting VFT parameters are listed in Table 11.

Arrhenius equation is considered as a simplistic description for temperature dependence of transport.

properties. However, Arrhenius model is also applied on experimental viscosity data of AA/PA DES and its binary solutions as shown in Fig. S5 and the parameters given in Table S5. Comparison of the parametric values from the two models establishes that the VFT model is satisfactory to describe temperature dependence of the system under study as shown by Fig. 7 (ln η vs T plot) and parameters reported with standard deviations in Table 11.

Viscosity deviation $\Delta \eta$ is calculated with the equation (8)

$$\Delta \eta = \eta - (\eta_1 x_1 + \eta_2 x_2) \tag{8}$$

where η is viscosity of the mixture, and η_1, η_2, x_1 and x_2 are the viscosities

ale freetier (m) of AA (DA DEC

Table 14

Experimental x/3.m	of AA/TA DES and binary inixture of AA/TA DES – water as a function of temperature, T, and more fraction(x1) of AA/TA DES.
$x_1 \kappa/S.m^{-1}$	

of AA /DA DEC

	298.15 K	303.15 K	308.15 K	313.15 К	318.15 K	323.15 K	328.15 K	333.15 К	338.15 K	343.15 K	348.15 K	353.15 K
0.1	2.69	2.76	2.85	2.96	3.12	3.31	3.55	3.85	4.12	4.44	4.71	4.91
0.2	1.03	1.14	1.17	1.28	1.40	1.58	1.70	1.84	2.00	2.33	2.55	2.87
0.3	1.02	1.28	1.34	1.40	1.48	1.57	1.68	1.78	1.93	2.10	2.33	2.80
0.4	1.03	1.04	1.07	1.12	1.19	1.28	1.39	1.53	1.68	1.90	2.24	2.64
0.5	0.82	0.84	0.86	0.90	0.95	1.03	1.09	1.17	1.26	1.39	1.58	1.81
0.6	0.70	0.73	0.78	0.84	0.92	1.02	1.12	1.24	1.37	1.50	1.69	1.90
0.7	0.54	0.57	0.62	0.63	0.67	0.71	0.78	0.87	0.99	1.13	1.33	1.43
0.8	0.40	0.43	0.47	0.52	0.57	0.65	0.74	0.85	0.99	1.15	1.39	1.49
0.9	0.25	0.29	0.35	0.39	0.42	0.55	0.58	0.66	0.76	0.91	1.10	1.43
1	0.17	0.19	0.21	0.24	0.27	0.30	0.35	0.40	0.47	0.55	0.66	0.78

Table 15

Parameters of the VFT Eq. (7) for the Experimental electrical conductivity κ /m. S⁻¹ for AA/PA DES-water binary mixtures as a function of temperature, T, and mole fraction, x₁: $x^0 = 1Sm^{-1}$

\boldsymbol{x}_1	$\ln(A\kappa imes\kappa^0)$	B_{κ}/K	$T_{0,\kappa}/\mathrm{K}$
0.10	-33.05 ± 246.24	$\begin{array}{c} 8.56\times10^{4}\pm1.32\times\\ 10^{6}\end{array}$	${-2.37\times 10^{3}\pm 2.08\times }\\{10^{4}}$
0.20	-46.27 ± 243.27	${\begin{array}{c} 1.13\times 10^{5}\pm 1.20\times \\ 10^{6}\end{array}}$	${-2.14\times 10^{3}\pm 1.31\times 10^{4}}$
0.30	-37.95 ± 398.32	$\begin{array}{l} 9.16\times10^5\pm1.94\times\\ 10^6\end{array}$	${-2.12\times 10^{3}\pm 2.60\times }\\{10^{4}}$
0.40	-58.05 ± 1120.62	$\frac{1.98\times10^5\pm7.67\times}{10^6}$	$\frac{-3.09\times 10^{3}\pm 6.65\times }{10^{4}}$
0.50	-45.93 ± 723.07	${\begin{array}{*{20}c} 1.50\times 10^{5}\pm 4.73\times \\ 10^{6}\end{array}}$	$-2.94 \times 10^{3} \pm 5.16 \times 10^{4}$
0.60	-47.33 ± 253.75	${\begin{array}{c} 1.20\times 10^{5}\pm 1.29\times \\ 10^{6}\end{array}}$	${-2.22\times 10^{3}\pm 1.36\times }\\{10^{4}}$
0.70	-55.60 ± 770.24	${\begin{array}{*{20}c} 1.73\times 10^{5}\pm 4.78\times \\ 10^{6}\end{array}}$	$\begin{array}{c}-2.78\times10^{3}\pm4.28\times\\10^{4}\end{array}$
0.80	-65.05 ± 403.88	${\begin{array}{*{20}c} 1.70\times 10^{5}\pm 2.10\times \\ 10^{6}\end{array}}$	${-2.28\times 10^{3}\pm 1.60\times }\\{10^{4}}$
0.90	-67.37 ± 357.77	${\begin{array}{c} 1.54\times 10^{5}\pm 1.62\times \\ 10^{6}\end{array}}$	${-1.95\times 10^{3}\pm 1.19\times 10^{4}}$
1.00	-67.96 ± 317.29	${\begin{array}{c} 1.71\times 10^{5}\pm 1.57\times \\ 10^{6}\end{array}}$	$-2.16 \times 10^{3} \pm 1.14 \times 10^{4}$



Fig. 10. Variation of *κ*/*Sm*⁻¹, of AA/PA DES and AA/PA DES-water binary mixtures as a function of mole fraction (x₁) in temperature range(T=■: 298.15; ●: 303.15; ▲:308.15; ▼: 313.15; ♦:318.15; ◀: 323.15;▶:328.15;:333.15; ★:338.15; 343.15;●: 348.15;+: 353.15) of AA/PA DES



Fig. 9. Variation $ln\kappa^{-1}/S^{-1}.m$, of AA/PA DES and AA/PA DES-water binary mixtures with the temperature, T, for mole fraction ($x_1 = (\blacksquare: 0.1; \oplus: 0.2; A: 0.3; \forall: 0.4; \oplus: 0.5; \blacktriangleleft: 0.6; \succ: 0.7;: 0.8; \star: 0.9;: 1.00)$ of AA/PA DES -water mixtures. Solid lines are the best fit representation of Eq. (7).

and mole fractions of pure component 1 and 2 respectively in the mixture. Calculated $\Delta\eta$ values are given in Table 12 and the Redlich – Kister polynomial plots of $\Delta\eta$ against x_1 for all temperatures studied are shown in Fig. 8.

Calculated viscosity deviations, $\Delta \eta$, are negative over the entire range of composition and temperature studied in this work. The $\Delta \eta$ has become increasingly more negative with increase in the concentration of AA/PA in the mixture. In comparison $\Delta \eta$ values are less negative and the change is smaller in magnitude as temperature increased.

Negative viscosity deviations are usually expected in systems exhibiting weak intermolecular interactions resulting from dispersion forces between components on mixing. The trend in V_m^E and K_S^E is that they become less negative on increasing x_1 whereas the trend is opposite in case of $\Delta \eta$.

The $\Delta \eta$ values becoming more negative on increasing x_1 indicates that the intermolecular forces present in water rich region between components of the mixtures are progressively getting weaker which is in agreement with the V_m^E and K_s^E results. The minimum in the $\Delta \eta$ vs x_1 plot in Fig. 8 lies in the AA/PA rich region ($x_1 \approx 0.8$) where intermolecular forces are the weakest. It appears that viscosity deviations are influenced by a combination of interactive and noninteractive forces, structure of the liquid (entropy factor), and size and shape of the molecules.

The behaviour of the three excess properties $(V_m^E, K_S^E \text{ and } \Delta \eta)$ with respect to temperature is the same, i.e. they become less negative as temperature is increased.

Experimental $\Delta G^{*E} \times 10^3$ /J.mol⁻¹, of AA/PA DES and binary mixture of AA/PA DES – water as a function of temperature, *T*, and mole fraction, x₁, of AA/PA DES.

$\mathbf{x_1}$	$G^{*E} imes 10^3/\mathrm{J.mol}^{-1}$											
	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K	328.15 K	333.15 K	338.15 K	343.15 K	348.15 K	353.15 K
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.10	1.77	1.92	2.12	1.94	1.75	1.69	1.61	1.64	1.70	1.77	1.89	2.02
0.20	2.08	2.26	2.22	2.16	1.95	2.05	1.89	1.94	2.04	2.32	2.47	2.64
0.30	1.97	2.47	2.38	2.25	2.08	2.19	2.00	2.12	2.16	2.38	2.49	2.70
0.40	1.87	2.20	2.21	2.09	1.80	2.07	1.94	1.96	1.98	2.35	2.46	2.63
0.50	1.56	1.80	1.77	1.75	1.51	1.76	1.62	1.69	1.76	2.05	2.17	2.32
0.60	1.24	1.32	1.30	1.18	1.07	1.33	1.20	1.33	1.43	1.61	1.77	1.89
0.70	0.79	0.69	0.69	0.66	0.59	0.77	0.71	0.89	0.98	1.08	1.25	1.38
0.80	0.23	0.10	0.00	0.11	0.10	0.25	0.22	0.35	0.45	0.53	0.68	0.89
0.90	-0.21	-0.20	-0.24	-0.01	-0.03	0.01	0.06	-0.01	0.12	0.14	0.33	0.50
1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 17

Parameters of the Redlich Kister Eq. (3) for the Experimental $\Delta G^{*E} \times 10^3$ /J. mol⁻¹, for AA/PA DES-water binary system in the temperature range, T, (293.15 – 353.15) K with their standard deviations.

T/K	$A_0 \times 10^{\text{-}3}$	$A_1 \times 10^{\text{-}3}$	$A_2 \times 10^{\text{-}3}$
298.15	6.61 ± 0.53	-9.7 ± 0.79	-1.49 ± 1.61
303.15	$\textbf{7.23} \pm \textbf{0.25}$	-11.45 ± 0.34	-0.28 ± 0.84
308.15	6.94 ± 0.38	-11.48 ± 0.56	-0.54 ± 1.31
313.15	6.49 ± 0.27	-10.18 ± 0.46	$\textbf{2.29} \pm \textbf{1.05}$
318.15	5.82 ± 0.22	-9.48 ± 0.33	$\textbf{2.28} \pm \textbf{0.81}$
323.15	6.87 ± 0.18	-8.84 ± 0.28	$\textbf{0.69} \pm \textbf{0.72}$
328.15	6.32 ± 0.21	-7.99 ± 0.32	$\textbf{0.87} \pm \textbf{0.84}$
333.15	6.75 ± 0.22	-8.35 ± 0.36	$\textbf{0.34} \pm \textbf{0.87}$
338.15	6.93 ± 0.22	-7.81 ± 0.37	1.88 ± 0.98
343.15	8.11 ± 0.22	-8.42 ± 0.41	$\textbf{0.89} \pm \textbf{0.98}$
348.15	$\textbf{8.6} \pm \textbf{0.24}$	-8.06 ± 0.48	$\textbf{2.43} \pm \textbf{1.18}$
353.15	$\textbf{9.12}\pm\textbf{0.19}$	-8.04 ± 0.36	$\textbf{4.34} \pm \textbf{0.99}$



Fig. 11. Experimental, $\Delta G^{*E} \times 10^3$ /J.mol⁻¹, of AA/PA DES and binary mixture of AA/PA DES – water as a function of mole fraction,x₁,of AA/PA DES in the temperature range (T=■: 298.15; •: 303.15; **▲**: 308.15; **▼**: 313.15; **♦**: 318.15; **∢**: 313.15; **♦**: 318.15; **∢**: 323.15; **>**: 328.15;: 333.15; **★**: 338.15; 343.15; **●**: 348.15;+: 353.15) K. Solid lines are the best fit representation of Eq. (3).

The $\Delta \eta$ is fitted by the RKE eq. (3) and the values of the fitting parameters with their standard deviations are reported on Table 13 and the plots of $\Delta \eta$ vs x_1 is shown in Fig. 8.

3.8. Conductivity

Experimental conductivity of the AA/PA DES is reported in Table 14 and the conductivity data is best fit by VFT eq. (7) and fitted parameters are listed in Table 15. Conductivity of pure AA/PA is low due to anion cation interaction which results in reduced mobility of ions and hence conductivity is also reduced. However, as water content in the mixture is increased, conductivity of the solution also increases. As regards the effect of temperature, for example, values of 2.69 S m⁻¹ and 4.91 S m⁻¹ for $x_1 = 0.1$ mol fraction are observed at 298.15 and 353.15 K respectively. For all compositions, conductivity increases with temperature and dilution as shown in Fig. 10. The increase of conductivity with dilution is due to increase in concentration of charge carriers and increased mobility of ions due to reduction in viscosity. The increase in temperature also affects conductivity in the same way, i.e., reduced viscosity of solution, increased in number of charges due to break up of aggregates. Fig. S6 shows Arrhenius plot of the experimental conductivity data of AA/PA DES and its binary mixtures with water. The relevant parameters obtained are given in Table S6. Comparison of two models shows that VFT model best fit to describe the temperature dependence of system as shown in Fig. 9.

(Fig. 10)

Excess Gibbs energy of activation ΔG^{*E} of viscous flow is calculated with eq. (9)

$$\Delta G^{*E} == RT \left(\ln \left(\frac{\eta V}{\eta_2 V_2} \right) - x_1 \left(\frac{\eta_1 V_1}{\eta_2 V_2} \right)$$
(9)

where V, η are molar volume and viscosity of binary solutions, V_1, V_2 and η_1, η_2 molar volumes and viscosities of AA/PA DES and water respectively. RK polynomial equation is used to fit the calculated values of ΔG^{*E} given Table 16, RKE parameters are reported in Table 17, and the solid lines in Fig. 11 are the best fit. ΔG^{*E} values are positive in the entire range of composition and temperature. The positive values of excess Gibbs free energy of activation for viscous flow indicate that the intermolecular forces between components are specific and strong. The ΔG^{*E} value is maximum at $x_1 \approx 0.3$ which indicates that intermolecular forces are stronger in the water rich region. At higher mole fractions of AA/PA ($x_1 > 0.3$), ΔG^{*E} values have decreased indicating increased role of dispersion forces and weakening of association.

4. Conclusion

Excess properties V_m^E , K_S^E , $\Delta\eta$ and ΔG^{*E} of binary solutions of novel AA/PA DES with water are calculated from experimental data and fitted with RKE. V_m^E and K_S^E are negative and are highly influenced by the temperature and composition. With increasing dilution of the DES, V_m^E and K_S^E values become more negative indicating stronger interactions between components because of increased hydrogen bonding. ΔG^{*E}

values are positive over the entire composition range and indicate that interactions between components are stronger in water rich region, $\Delta\eta$ values are also negative for all composition but with increased dilution they have become less negative, which again shows that stronger interactions dominate at lower mole fractions. Viscosity and conductivity data are well described by VFT equation instead of Arrhenius equation. Electrochemical studies of the DES shows that it has a good wide electrochemical window, ranging from -1000 mV to +1000 mV, which can be exploited for electrochemical work as a green solvent and self-electrolyte. Stronger bonding is even more dominant at lower temperature which is weakened at higher temperatures. Conclusively, temperature of the mixture and compositions of the two components play an important role for the studied physiochemical properties.

CRediT authorship contribution statement

Iqra Saleem: Data curation, Investigation, Software, Writing – original draft, Writing – review & editing. **Aafia Sheikh:** Writing – review & editing. **Athar Yaseen Khan:** Writing – original draft, Writing – review & editing. **Safeer Ahmed:** Formal analysis. **Muhammad Abbas:** Formal analysis, Validation.

Declaration of competing 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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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