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Volumetric, acoustic, and conductometric studies of ionic surfactants in aqueous ammonium acetate-ethylene glycol deep eutectic solvent

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ABSTRACT

This study investigates the molecular interactions between cationic surfactants cetyltrimethylammonium bromide (CTAB) and dodecyltrimethylammonium bromide (DTAB) in aqueous deep eutectic solvent (DES) solution over the temperature range of 293.15–313.15 K. Key parameters, including density, sound velocity, and electrical conductivity, was experimentally measured to derive a range of volumetric, acoustic, and conductometric properties that provide insights into the molecular behavior of these solutions. Apparent molar volume (ϕ_v), indicative of solute–solvent interactions; isentropic compressibility (K_S), reflecting medium elasticity; and apparent molar compressibility (ϕ_K), which elucidates solute-induced compressibility changes, were determined from the experimental data. Additionally, specific acoustic impedance (Z), represents the medium's resistance to sound propagation; relative association (RA), indicative of solute–solvent interaction strength; intermolecular free length (L_f), corresponding to the average distance between molecules; and the sound velocity number (U), which relates to the structural compactness of the solution, were also calculated. Collectively, these parameters offer a comprehensive understanding of the molecular interactions, solvation dynamics, and structural organization in the surfactant systems in the presence of DESs, enhancing our knowledge of their behavior under varying conditions.

1. Introduction

Utilization of green chemistry principles in chemical laboratories and industries is a field of great concern nowadays. Specifically, the use of volatile toxic solvents is discouraged, and the pursuit of alternative green, biodegradable, and non-toxic solvents is a major field of research [1,2]. The issues are thought to be resolved by DESs, which are also suggested as an alternative to traditional ionic liquids (ILs) [3,4]. Mostly, DESs are synthesized by binary or ternary mixing of compounds with the presence of at least one hydrogen bond donor (HBD) and

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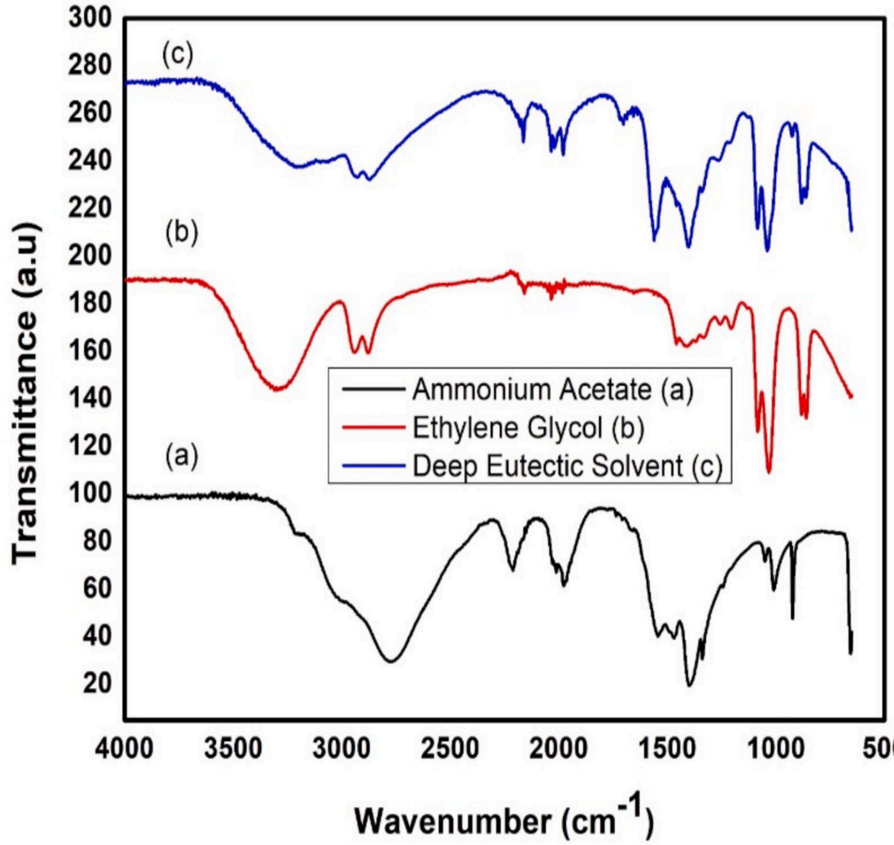

Fig. 1. FTIR Spectra of (a) ammonium acetate, (b) ethylene glycol, and (c) DES.

hydrogen bond acceptor (HBA) [5]. They are characterized by their relatively low melting points, non-volatility, non-flammable and dipolar nature, high solubility, and biodegradability [6].

Surfactants exhibit a propensity to make micelles and micro-emulsions and are of great purpose in colloidal science and technology [7]. Due to their amphiphilic nature, they reduce the surface tension of water [8] and they are also very good wetting agents, consequently effective in lowering the interfacial tension present between two liquids [9]. Furthermore, surfactant molecules are the most multifaceted elements that are typically found in emulsifiers, foaming agents, corrosion inhibitors, detergents, and cosmetics [10–13]. The aggregation behavior of surfactants is vitally important in biology, materials chemistry, chemical processes, and the petroleum industry [14–16]. Micelle formation and micellization process is generally attributed to van der Waals, hydrophobic, and electrostatic interactions [17].

In the last many years, modification of surfactant properties to further enhance their potential for industrial purposes has emerged as a new research field for scientists. Generally, this is done by amending the physical properties of surfactant solutions by mixing them with organic or inorganic electrolytes [18–20]. Thermodynamic and interfacial studies of surfactant-DES systems are prone to hydrophilic, hydrophobic, and electrostatic interactions [21,22]. Molecular interactions occurring in surfactant-DES systems can further assist their utilization in biological and pharmaceutical applications [23]. Hence, research on the effect of DESs on the micellar properties of surfactants is of great scientific importance. Various researchers have used different methods to see the effect of DES on the physical properties of surfactants [24–27]. To the best of our knowledge, the effect of DES on the thermoacoustic properties of surfactants has not been studied yet. So, the density, sound velocity, and electrical conductivity values of the solution can be used to calculate and comprehend specific information about the solute/solvent, solvent/solvent interactions, the compressibility of the solution, and the impact of the solute on the creation or destruction of structures [28,29].

2. Experimental

2.1. Material

Ammonium acetate (97 %¸DAEJUNG), ethylene glycol (99.7 %, VWR Chemicals), dimethyl sulfoxide (DMSO) (99 %, VWR Chemicals), cetyltrimethylammonium bromide (CTAB) (97 %, Sigma–Aldrich) and dodecyltrimethylammonium bromide (DTAB) (97 %, Sigma–Aldrich) were used in this study.

2.2. Procedure

2.2.1. Synthesis of DESs

To synthesize DESs already published [30] protocol was followed. For synthesis, ammonium acetate, and ethylene glycol were mixed in a 1:2 mol ratio in a round bottom flask with constant heating and stirring at 60 °C for 30 mins. After that solution was kept in a desiccator to cool down and a stable solvent, without any solidification or precipitate formation, was obtained and used without any further purification.

2.2.2. Characterization of DESs

The prepared DES was subjected to Karl Fischer Titration Equipment (Mettler Toledo, V10S) to determine the moisture content present in the DES. The synthesized DES contained 0.56 % water content. FTIR spectrometer (Cary 630 FTIR) was used to record the FTIR spectra of DES and its components. The thermal properties of the DES were determined from the SDTQ 600 TA instrument TA instrument (TGA-DSC).

Table 1
Bond type, corresponding wavenumber, and vibration of synthesized DES.

Compound Name	Bond Type	Wavenumber Range (cm^{-1})	Vibration
DES	C–H	2870–2960	CH stretching
DES	OH	3200–3350	OH Stretching, weak
DES	C=O	1690–1735	Carbonyl group

2.2.3. Surfactant-DES system

For volumetric and acoustic studies of DTAB and CTAB in aqueous DESs, a 5 mM solution of DES was prepared in water which was used as a stock solution for further dilutions.

2.2.4. Density and sound velocity measurements

The density and sound velocity of neat DES, and CTAB and DTAB in aqueous DES system were measured between 293.15 K and 313.15 K with 5 K intervals, using a high-precision digital density and sound velocity meter (Anton Paar, DSA-5000).

3. Results and discussion

3.1. FTIR analysis of DES

Fig. 1 and Table 1 present the FTIR analysis of ethylene glycol, ammonium acetate, and the synthesized DES, illustrating the characteristic vibrations of functional groups in these components. The C–H stretching vibrations observed in the range of 2870–2960 cm^{-1} are attributed to the methylene (CH_2) and methyl (CH_3) groups of ethylene glycol. A broad and weak OH stretching band between 3200–3350 cm^{-1} indicates extensive hydrogen bonding between the hydroxyl groups of ethylene glycol and ammonium acetate. Additionally, the C=O stretching band around 1690–1735 cm^{-1} corresponds to the carbonyl group in the acetate anion of ammonium acetate, further highlighting the molecular interactions within the DES. These peaks provide critical insight into the hydrogen bonding and structural features that define the DES, emphasizing its robust intermolecular interactions and stability.

3.2. Thermogravimetric analysis (TGA) of DESs

Thermogravimetric analysis (TGA) results for ammonium acetate, ethylene glycol, and the synthesized deep eutectic solvent (DES) are presented in Fig. 2. The analysis reveals distinct decomposition temperatures for each component and the synthesized DES. Ammonium acetate exhibits thermal decomposition at 132 °C, followed by ethylene glycol at 151 °C, while the synthesized DES decomposes at a higher temperature of 154 °C. The elevated decomposition temperature of the synthesized DES, compared to its constituents, demonstrates its enhanced thermal stability. This suggests that the intermolecular interactions within the DES matrix, potentially involving hydrogen bonding or ionic interactions, contribute to its greater resistance to thermal degradation. Consequently, the synthesized DES is thermally more robust than ammonium acetate and ethylene glycol alone.

3.3. Density and sound velocity of surfactants in an aqueous DES system

Firstly, the density (ρ) and sound velocity (u) of neat DES as a function of temperature in the 293.15–333.15 K range was measured and the values of ρ and u are given in Table 2. Then, the ρ and u values of both surfactants in the aqueous DES system were measured as functions

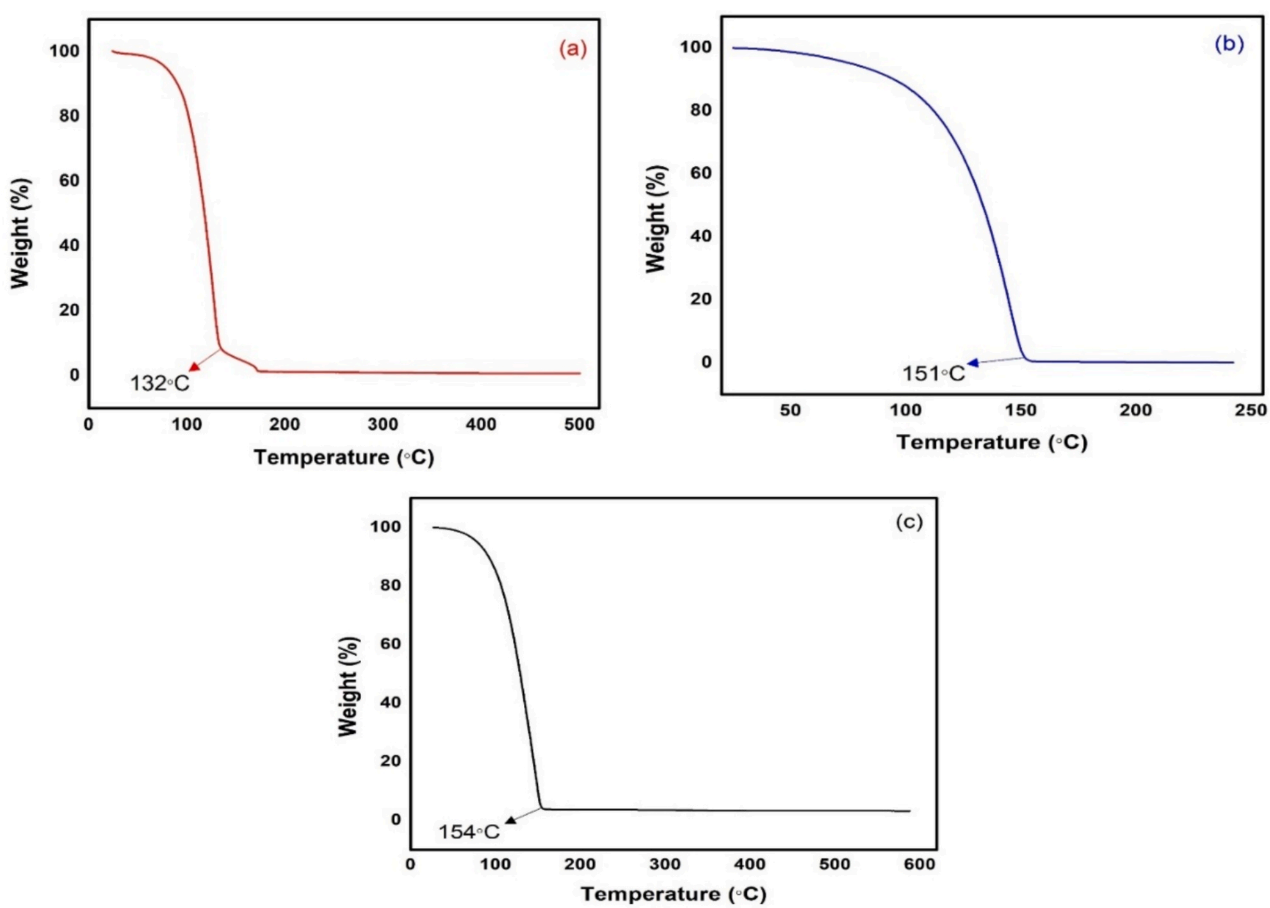

Fig. 2. Thermogravimetric curves of (a) ammonium acetate (b) ethylene glycol and (c) DES.

Table 2
Density, electrical conductivity, and sound velocity of synthesized DES.

Temperature (K)	Water content = 0.56 %		
	ρ/kg m^{-3}	σ/mS cm^{-1}	u/m s^{-1}
293.15	1139.79	2.7	1691.48
298.15	1136.696	2.9	1681.47
303.15	1133.631	4.86	1671.67
308.15	1130.567	5.54	1661.68
313.15	1127.494	6.36	1651.61
318.15	1124.419	7.32	1641.32
323.15	1121.348	8.87	1631.17
328.15	1118.256	10.24	1620.61
333.15	1115.153	12.75	1610.11

Table 3
Density values of CTAB and DTAB in aqueous DES system.

(*mol kg^{-1}*)	ρ/kg m^{-3}				
	CTAB + DES				
m/10^4	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
2.998	1001.843	1000.677	999.274	997.652	995.804
4.497	1001.843	1000.678	999.266	997.638	995.766
6.896	1001.829	1000.650	999.244	997.610	995.759
7.995	1001.810	1000.642	999.236	997.610	995.753
9.494	1001.762	1000.598	999.187	997.552	995.646
10.494	1001.764	1000.597	999.193	997.576	995.755
13.292	1001.772	1000.605	999.200	997.582	995.760
15.391	1001.771	1000.604	999.201	997.581	995.761
22.187	1001.771	1000.603	999.200	997.579	995.759
	DTAB + DES				
m/10^3	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
9.992	1001.944	1000.767	999.352	997.721	995.891
10.692	1001.971	1000.790	999.375	997.746	995.913
12.989	1002.026	1000.843	999.426	997.788	995.959
14.987	1002.071	1000.891	999.467	997.833	995.994
15.986	1002.084	1000.897	999.467	997.810	995.928
16.985	1002.102	1000.916	999.491	997.856	996.016
17.584	1002.113	1000.923	999.501	997.863	996.023

Table 4
Sound velocity values of CTAB and DTAB in aqueous DES system.

(*mol kg^{-1}*)	*u/m s^{-1}*				
	CTAB + DES				
m/10^4	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
2.998	1486.14	1500.74	1513.39	1523.97	1533.17
4.497	1486.03	1500.65	1513.28	1523.84	1532.85
6.896	1485.97	1500.58	1513.21	1523.80	1532.79
7.995	1485.98	1500.58	1513.21	1523.78	1532.78
9.494	1485.89	1500.50	1513.14	1523.71	1532.70
10.494	1485.86	1500.48	1513.11	1523.69	1532.67
13.292	1485.74	1500.43	1512.90	1523.66	1532.66
15.391	1485.78	1500.40	1512.88	1523.66	1532.67
22.187	1485.81	1500.43	1512.89	1523.65	1532.63
	DTAB + DES				
m/10^3	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
9.992	1488.03	1502.45	1514.88	1525.32	1534.10
10.692	1488.13	1502.55	1514.97	1525.41	1534.18
12.989	1488.72	1503.07	1515.45	1525.84	1534.56
14.987	1488.98	1503.34	1515.55	1526.10	1534.82
15.986	1489.08	1503.40	1515.80	1526.15	1534.90
16.985	1489.21	1503.51	1515.85	1526.20	1534.96

of temperature, ranging from 293.15 K to 313.15 K with 5 K intervals, and molality, as shown in Tables 3 and 4. The standard uncertainties for ρ and u were 0.003 kg m^{-3} and 0.5 m s^{-1}, respectively.

3.4. Apparent molar volume (ϕ_v), isentropic compressibility (K_s), and compressibility (ϕ_K)

Experimentally measured ρ and u values were further used to calculate volumetric and acoustic properties. Firstly, apparent molar volume (ϕ_v) values were calculated using ρ data using the following equation [31]

$$\phi_v = \frac{M}{\rho} + \frac{[\rho_0 - \rho]}{mdd_0} \tag{1}$$

where M is the surfactant's molar mass (kg mol^{-1}), ρ_o and ρ are the densities of the pure solvent and solution, respectively, and m is the solution's molality (mol kg^{-1}), which was determined using the formula below [31].

$$m = \frac{1}{\left(\frac{\rho}{C} - \frac{M}{1000}\right)} \tag{2}$$

where C represents molar concentration (mol dm^{-3}). Plots of apparent molar volume *(*ϕ_v*)* for CTAB and DTAB vs molality are presented in Fig. 3. The computed ϕ_v values for CTAB and DTAB are reported in Table S1 of supporting information.

From the data, it is observed that in the presence of the cationic surfactants, CTAB and DTAB, the ϕ_v values for the CTAB + DES and DTAB + DES system are generally positive, except at a few pre-micellar concentrations at higher temperatures for CTAB. The ϕ_v values increase with increasing CTAB concentration but decrease with increasing DTAB concentration in the pre-micellar region.

The positive ϕ_v values observed in both surfactant-DES systems can be explained by the cosphere overlap model, which states that positive ϕ_v values arise from the overlap of hydration cospheres of two ionic or polar groups. This overlap suggests initial electrostatic interactions in the pre-micellar region, followed by ion-hydrophobic interactions between the ionic groups of the surfactant and the hydrophobic components of the DES, as well as hydrophilic-hydrophobic interactions between the hydrophilic parts of the DES and the alkyl chains of the surfactants [31]. These interactions contribute to an increase in the apparent molar volume due to the disruption of the solvent structure around the solute. The ϕ_v data can also be explained by the electrostriction effect, which occurs when a solvent (such as water) contracts around a solute (e.g., an ion or polar molecule) due to the electric field generated by the solute's charge or dipole moment. This phenomenon results from the reorientation and tighter packing of solvent molecules in response to the solute's electric field, leading to a reduction in the overall volume of the solution compared to the pure solvent [31]. In the context of the surfactant-DES system, the positive ϕ_v values indicate strong ion-ion interactions between the DES components and surfactant ions, which reduce the electrostriction volume around these ions, thereby increasing the apparent molar volume.

For the CTAB + DES system, at a concentration of 10.494 mol kg^{-1}, a decrease in ϕ_v value is observed, indicating the critical micelle concentration (CMC), which is close to the reported CMC of CTAB in water (approximately 0.001 mol kg^{-1}). At post-micellar concentrations, ϕ_v values increase in a consistent pattern. The increase in ϕ_v at pre-micellar concentrations is likely due to significant molecular interactions between the charged moieties of the DES (e.g., –C=O, –OH groups) and the cationic head group ($N^+(CH_3)_3Br^-$) of the CTAB monomer, as described above. At post-micellar concentrations, CTAB exists in micellar form, with a cluster of charges on the micellar surface. This cluster enhances attractive interactions with the charged moieties of the DES, leading to a larger magnitude of ϕ_v values compared to those at

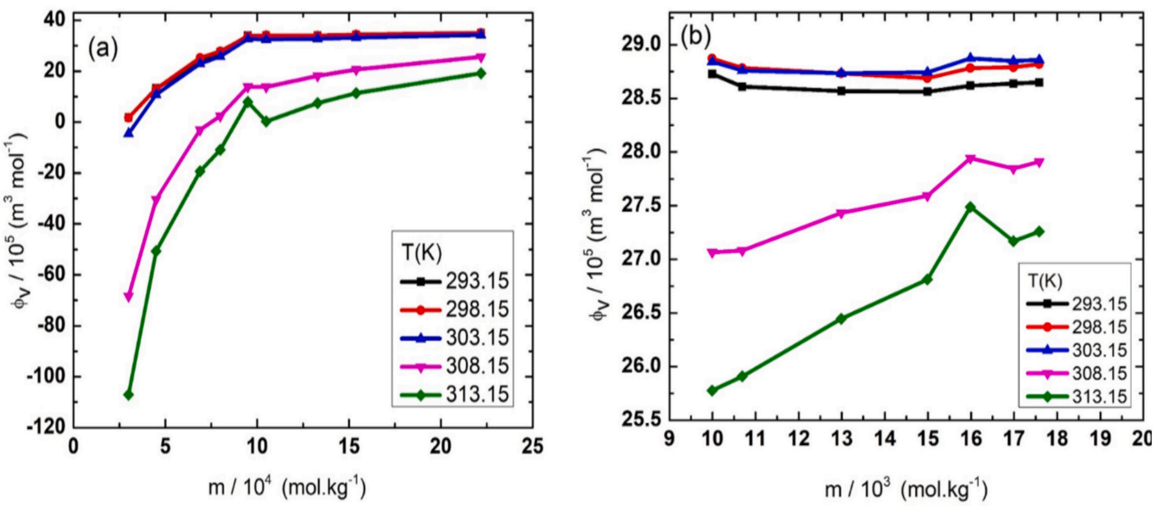

Fig. 3. Plot between m and ϕ_v of (a) CTAB + DES and (b) DTAB + DES system at various temperatures.

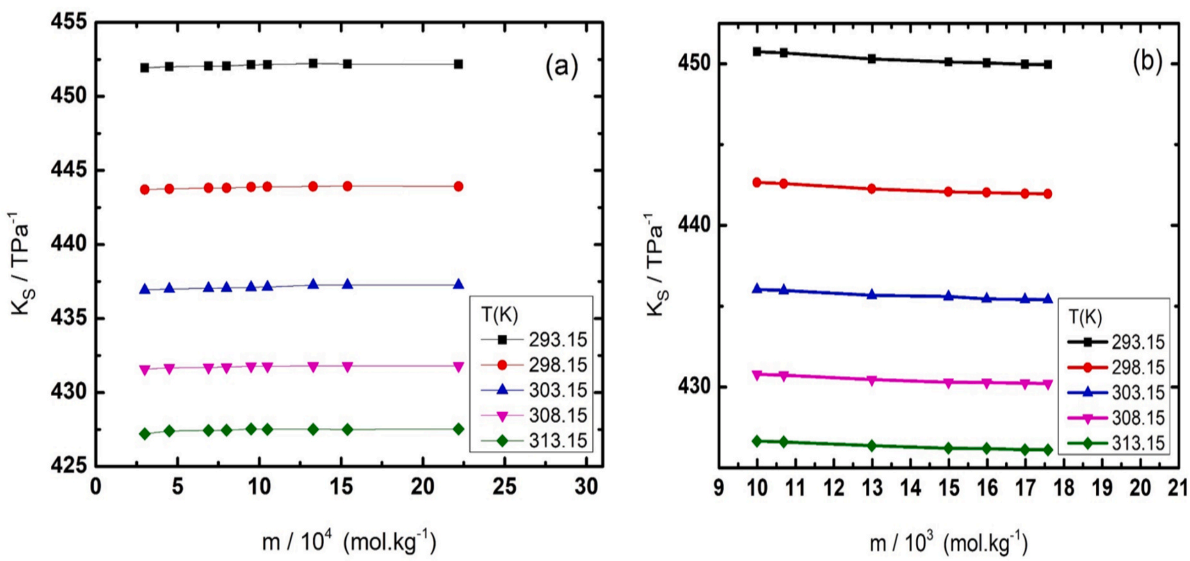

Fig. 4. Plot between m and K_S values of (a) CTAB + DES and (b) DTAB + DES system at various temperatures.

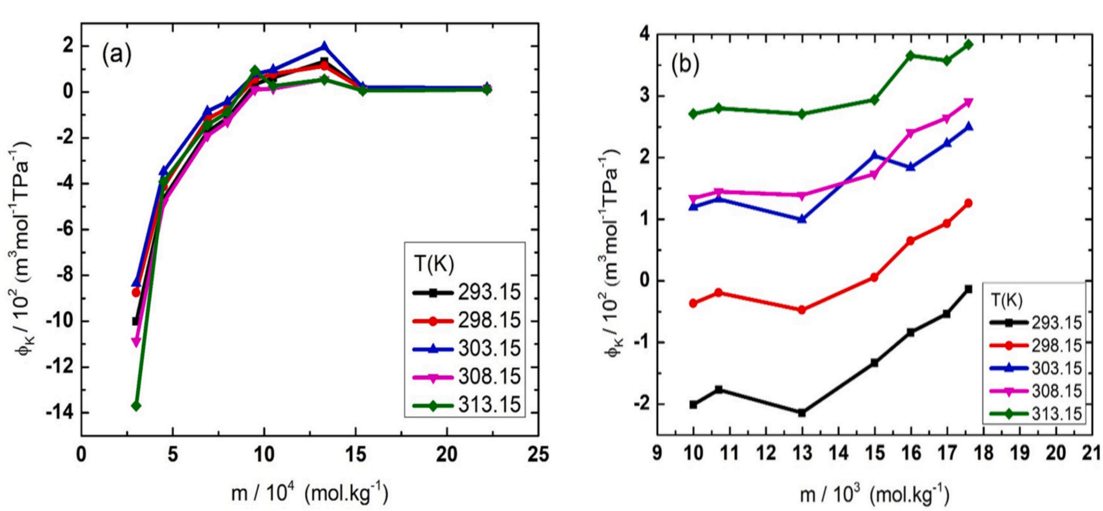

Fig. 5. Plot between m and ϕ_K of (a) CTAB + DES and (b) DTAB + DES system at various temperatures.

pre-micellar concentrations. The increased charge density on the micellar surface strengthens these interactions, resulting in a volume expansion.

In the DTAB + DES system, ϕ_v values decrease up to a concentration of 14.987 mol kg^{-1} and then increase from 15.986 mol kg^{-1} onward, which may indicate the CMC of DTAB in the presence of DES. Comparing the two cationic surfactants, the CTAB + DES system exhibits a greater magnitude of ϕ_v values than the DTAB + DES system. This difference can be attributed to stronger ion-ion, ion-hydrophobic, and hydrophobic-hydrophilic interactions between CTAB and DES molecules, likely due to CTAB's longer alkyl chain (C16) compared to DTAB's shorter chain (C12), which enhances hydrophobic interactions [32].

The following relations were used to compute isentropic compressibility (K_s) [33,34];

$$K_s = \frac{1}{u^2\rho} \tag{3}$$

$$K_0 = \frac{1}{u_0^2\rho_0} \tag{4}$$

In this case, K_0 and K_S stand for the isentropic compressibility, ρ_0 and ρ for their density, and u_0 and u for the sound velocity of the pure solvent and solution respectively. Calculated K_S values are included in the supplementary information (Table S2). Fig. 4 shows the plot of K_S values against the molality of the solution at different temperatures. It is evident from Fig. 4 that when surfactant concentration was increased, K_S values for the CTAB + DES system also increased while for the DTAB + DES system K_S decreased. This increase and decrease in K_s values for CTAB and DTAB systems indicated the presence of weak and strong solute–solvent interaction respectively [35] and aligns well with the already discussed ϕ_v data.

Apparent molar compressibility (ϕ_K) was computed using the following equation [36].

$$\phi_K = \phi_v K_s + \frac{[K_s - K_0]}{m\rho_0} \tag{5}$$

The calculated ϕ_K values for CTAB and DTAB in DES system are presented in Table S3 of the supplementary information. Plots of ϕ_K versus molality are shown in Fig. 5. For the CTAB + DES system, ϕ_K values are initially negative but become less negative (approaching positive values) as the surfactant concentration increases. This trend indicates that the CTAB + DES system is initially less compressible at lower concentrations. However, as the concentration increases into the post-micellar region, ϕ_K values shift toward positive values, suggesting a more compressible CTAB + DES system. This transition from highly negative to positive ϕ_K values can be attributed to micelle formation, where the compressibility of the micellar core and the restructuring of solvent around the micelles play a significant role [36].

In the DTAB + DES system, ϕ_K values remain negative across all concentrations but become less negative with increasing molality, indicating that the DTAB + DES system becomes more compressible at higher DTAB concentrations. Unlike the CTAB + DES system, the ϕ_K values for DTAB + DES do not transition to positive, suggesting that micelle formation in this system does not sufficiently disrupt the solvent structure to yield a highly compressible state.

The strong interactions between the charged species of the DES (e.g., −C=O, –OH groups) and the cationic head groups of CTAB ($N^+(CH_3)_3Br^-$) and DTAB ($N^+(CH_3)_2(CH_2CH_3)Br^-$) disrupt the bulk aqueous structure while simultaneously organizing a portion of the solvent system around the surfactant molecules. This dual effect results in compression of the bulk solvent and a reduction in the overall system volume [32]. A comparison of the two surfactant systems reinforces the findings from the ϕ_v and K_S data, which indicate that the CTAB + DES system exhibits stronger molecular interactions than the DTAB + DES system. The stronger interactions in the CTAB + DES system are likely due to CTAB's longer alkyl chain (C16) compared to DTAB's shorter chain (C12), which enhances ion-ion, ion-hydrophobic, and hydrophobic-hydrophilic interactions, leading to greater disruption of the solvent structure and more pronounced changes in compressibility.

Further, the specific acoustic impedance (Z) is the opposition a medium provides to the propagation of sound waves. Z values of surfactant-DES systems were calculated with the following equation [37] and are given in Table 5.

$$Z = u\rho \tag{6}$$

The obtained Z values for the CTAB + DES and DTAB + DES systems increased with rising surfactant concentrations, indicating stronger interactions between the surfactant and DES. Notably, the relatively higher Z values observed for the CTAB + DES system compared to the DTAB + DES system suggest a more pronounced interaction in the case of CTAB.

Table 5
Specific acoustic impedance *(Z)* values of CTAB and DTAB in aqueous DES system.

(mol kg^{-1})	*Z × 10^4, kg m^{-1} s^{-1}*				
	CTAB + DES				
m/10^4	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
2.998	149.83	150.41	151.51	152.31	152.85
4.497	149.83	150.41	151.51	152.31	152.85
6.896	149.84	150.42	151.51	152.32	152.86
7.995	149.84	150.42	151.52	152.33	152.87
9.494	149.85	150.43	151.52	151.34	152.87
10.494	149.85	150.43	151.53	152.35	152.88
13.292	149.85	150.43	151.53	151.36	152.88
15.391	149.86	150.44	151.54	151.37	152.89
22.187	149.86	150.44	151.54	151.38	152.89
	DTAB + DES				
m/10^3	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
9.992	149.09	150.36	151.39	152.18	152.78
10.692	149.10	150.37	151.40	152.19	152.79
12.989	149.17	150.43	151.45	152.24	152.83
14.987	149.20	150.46	151.47	152.27	152.86
15.986	149.21	150.47	151.49	152.28	152.86
16.985	149.23	150.48	151.50	152.29	152.88
17.584	149.23	150.49	151.51	152.29	152.88

Table 6
Relative association *(RA)* values of CTAB and DTAB in aqueous DES system.

(mol kg^{-1})	*RA*				
	CTAB + DES				
m/10^4	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
2.998	1.0000	1.0000	1.0001	1.0003	1.0004
4.497	1.0000	1.0000	1.0001	1.0003	1.0004
6.896	1.0000	1.0000	1.0001	1.0003	1.0004
7.995	1.0000	1.0000	1.0001	1.0003	1.0004
9.494	1.0000	1.0000	1.0000	1.0002	1.0003
10.494	1.0000	1.0000	1.0000	1.0003	1.0005
13.292	1.0000	1.0000	1.0001	1.0003	1.0005
15.391	1.0000	1.0000	1.0001	1.0003	1.0005
22.187	1.0000	1.0000	1.0001	1.0003	1.0005
	DTAB + DES				
m/10^3	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
9.992	0.9997	0.9997	0.9998	1.0000	1.0003
10.692	0.9997	0.9997	0.9998	1.0001	1.0003
12.989	0.9996	0.9997	0.9997	1.0000	1.0002
14.987	0.9996	0.9997	0.9998	1.0000	1.0002
15.986	0.9996	0.9997	0.9997	1.0000	1.0001
16.985	0.9996	0.9996	0.9997	1.0000	1.0002
17.584	0.9996	0.9996	0.9997	1.0000	1.0002

Table 7
Sound velocity number *(U)* values of CTAB and DTAB in aqueous DES system.

$(mol\ kg^{-1})$	U, $kg\ mol^{-1}$				
	CTAB + DES				
$m/10^4$	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
2.998	0.944	0.823	0.726	0.393	0.346
4.497	0.465	0.415	0.323	0.073	−0.231
6.896	0.244	0.203	0.144	0.009	−0.207
7.995	0.219	0.175	0.124	−0.008	−0.187
9.494	0.121	0.091	0.056	−0.055	−0.212
10.494	0.090	0.070	0.031	−0.062	−0.210
13.292	0.010	0.030	−0.079	−0.064	−0.171
15.391	0.026	0.013	−0.077	−0.055	−0.143
22.187	0.027	0.018	−0.051	−0.041	−0.111
	DTAB + DES				
$m/10^3$	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
9.992	0.156	0.139	0.120	0.100	0.071
10.692	0.152	0.136	0.118	0.099	0.071
12.989	0.156	0.139	0.121	0.103	0.077
14.987	0.147	0.132	0.110	0.101	0.078
15.986	0.142	0.126	0.113	0.097	0.077
16.985	0.138	0.123	0.108	0.093	0.075
17.584	0.134	0.120	0.105	0.090	0.072

Table 8
Intermolecular free length *(L_f)* values of CTAB and DTAB in aqueous DES system.

$(mol\ kg^{-1})$	$L_f/10^{10}$, m				
	CTAB + DES				
$m/10^4$	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
2.998	58.75	58.21	57.77	57.41	57.12
4.497	58.75	58.21	57.77	57.41	57.12
6.896	58.75	58.21	57.76	57.41	57.11
7.995	58.74	58.20	57.76	57.40	57.11
9.494	58.74	58.20	57.75	57.40	57.10
10.494	58.73	58.19	57.75	57.39	57.10
13.292	58.73	58.19	57.74	57.39	57.09
15.391	58.73	58.19	57.74	57.38	57.08
	DTAB + DES				
$m/10^3$	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
9.992	58.65	58.13	57.69	57.34	57.07
10.692	58.65	58.12	57.69	57.34	57.06
12.989	58.63	58.10	57.67	57.32	57.05
14.987	58.61	58.09	57.66	57.31	57.04
15.986	58.61	58.09	57.65	57.31	57.04
16.985	58.60	58.08	57.65	57.30	57.03
17.584	58.60	58.08	57.65	57.30	57.03

Relative association (*RA*) is a parameter used to measure the extent of molecular or ionic interactions (association) in a solution relative to the interactions in the solvent alone. It was computed using the following relation [38] and given in Table 6.

$$RA = \left(\frac{\rho}{\rho_0}\right)\left(\frac{u_0}{u}\right)^{\frac{1}{3}} \tag{7}$$

The *RA* values increased for the CTAB + DES system and decreased for the DTAB + DES system, which can be attributed to the corresponding increase and decrease in ion solvation for the respective surfactants.

The sound velocity number (*U*) provides insight into the molecular interactions and structural characteristics of the medium, particularly concerning the propagation of sound waves. It was obtained by using the following [39].

Table 9
Electrical conductivity (σ) values of CTAB and DTAB in aqueous DES system.

$(mol\ m^{-3})$	$\sigma/mho\ m^{-1}$				
	CTAB + DES				
m	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
0.3	0.049	0.050	0.056	0.057	0.057
0.45	0.043	0.045	0.053	0.054	0.055
0.55	0.041	0.044	0.049	0.050	0.052
0.69	0.035	0.037	0.042	0.048	0.050
0.8	0.036	0.041	0.046	0.048	0.048
0.85	0.034	0.040	0.046	0.047	0.048
0.95	0.032	0.039	0.046	0.046	0.048
1.05	0.032	0.035	0.038	0.045	0.045
1.33	0.031	0.036	0.045	0.042	0.043
1.54	0.031	0.036	0.045	0.042	0.042
2.22	0.030	0.035	0.041	0.040	0.041
2.86	0.028	0.033	0.041	0.038	0.038
	DTAB + DES				
m	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
10	0.106	0.106	0.114	0.115	0.117
10.7	0.110	0.111	0.114	0.121	0.123
11.2	0.111	0.115	0.119	0.123	0.129
12	0.118	0.120	0.126	0.128	0.130
13	0.129	0.124	0.139	0.141	0.144
13.5	0.133	0.131	0.138	0.140	0.145
15	0.138	0.139	0.150	0.157	0.164
16	0.140	0.139	0.155	0.158	0.161
16.4	0.141	0.143	0.159	0.162	0.165

$$U = \frac{u - u_0}{u_0 m} \tag{8}$$

The *U* values presented in Table 7 indicate a decrease with increasing surfactant concentrations in both surfactant systems, suggesting a pronounced and stronger association between the surfactants and DES.

Intermolecular free length (L_f) describes the average distance between molecules that are not in direct contact, reflecting the free space available for molecular motion. It was calculated using Eq. (9) [40].

$$L_f = \frac{K}{u\rho^{1/2}} \tag{9}$$

Here K represents the temperature-dependent constant which is

$K = (93.875 + 0.375)T \times 10^{-8}$

The *Lf* values listed in Table 8 show a decreasing trend with increasing surfactant concentrations in both systems, further indicating the presence of stronger interactions in the surfactant–DES systems. These findings further support the results obtained for ϕ_v, K_S, and ϕ_K, demonstrating that the CTAB + DES system exhibits comparatively stronger interactions than the DTAB + DES system.

3.5. Conductance studies

Electrical conductivity (σ) values of CTAB and DTAB in aqueous DES system are given in Table 9 which were measured from 293.15 K to 313.15 K at 5 K intervals as a function of the surfactant concentration. The σ values for the CTAB + DES system are found to decrease with increasing CTAB concentration. But for the DTAB + DES system, σ values are increasing with increasing surfactant concentration. These σ values were further used to calculate molar conductance (Λ_m).

3.5.1. Molar conductance

Molar conductance (Λ_m) is a measure of the electrical conductivity of an electrolyte solution per mole of the electrolyte. It quantifies the efficiency with which a solution conducts electricity, accounting for the concentration of the electrolyte, and is particularly significant in the

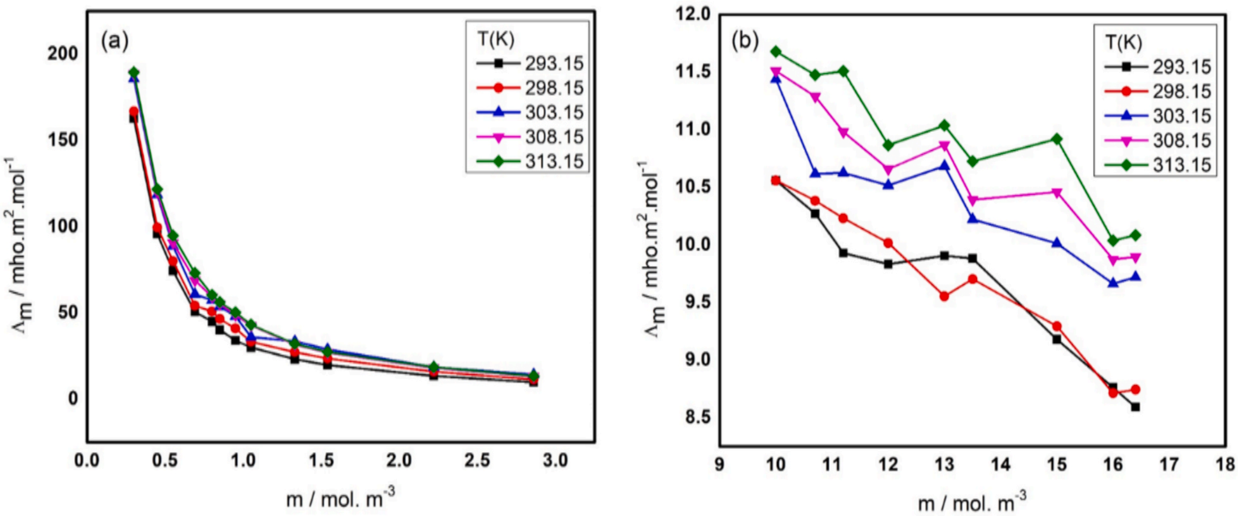

Fig. 6. The plot of Molar conductance (Λ_m) vs molarity of (a) CTAB + DES and (b) DTAB + DES system.

study of ionic solutions [41].

The Λ_m is calculated using Eq. (10) for CTAB and DTAB in aqueous DES system at various temperatures using data in Table 9. Plots of Λ_m vs molality are presented in Fig. 6 and values are given in Table S4.

$$\Lambda_m = \frac{\sigma \times 1000}{C} \tag{10}$$

σ is measured conductance and C is molar concentration. Λ_m values for CTAB and DTAB in an aqueous DES system are increased as the temperature is raised. More specifically, for CTAB + DES, the larger increase in Λ_m suggests that free ions (below or near CMC) benefit more from enhanced mobility of ionic species and reduced viscosity as temperature is increased. Besides that, high Λ_m at low concentrations indicates free ions, with a transition to micellization as concentration increases. For both surfactant–aqueous DES systems Λ_m values have decreased as the concentration of surfactant increased, which might be explained by an increase in solute-co-solute interactions [42].

4. Conclusions

In this work, ammonium acetate-ethylene glycol DES was prepared and characterized by FTIR and TGA analyses. Further physicochemical properties (density ρ, sound velocity u, and electrical conductivity σ) were measured in the temperature range 293.15–333.15 K. The study specifically focused on the interactions of two different surfactants, CTAB and DTAB with the DES in an aqueous system as a function of temperature (293.15 K–313.15 K) and surfactant concentration. The results revealed that the CTAB + DES system exhibited stronger and more attractive interactions compared to the DTAB + DES system. This observation suggests that the longer hydrophobic chain of CTAB facilitates the overall interaction strength between the surfactant and the DES, while the shorter hydrophobic chain of DTAB facilitates stronger interactions with the solvent. This difference in surfactant behavior underscores the role of surfactant structure, specifically the length of the hydrophobic tail in influencing the physicochemical properties of the surfactant-DES mixtures. These findings also highlight the significance of selecting appropriate surfactants for designing DES systems with tailored properties for specific applications, such as solubilization, stability, and reactivity, which can be modulated by altering surfactant characteristics.

Author contributions

The manuscript was written with the contributions of all authors. All authors have approved the final version of the manuscript.

CRediT authorship contribution statement

Saqib Rabbani: Writing – original draft, Formal analysis, Data curation. **Hina Abid:** Writing – review & editing, Validation, Software. **Athar Yaseen Khan:** Project administration, Methodology, Formal analysis. **Muhammad Tariq Qamar:** Writing – original draft, Resources, Project administration. **Ammar Zidan:** Writing – review & editing, Validation, Software, Methodology. **Ali Bahadur:** Writing – review & editing, Visualization, Project administration. **Shahid Iqbal:** Writing – original draft, Supervision, Conceptualization. **Muhammad Saad:** Writing – review & editing, Resources, Formal analysis, Data curation. **Sajid Mahmood:** Writing – review & editing, Software, Investigation. **Mohammed T. Alotaibi:** Writing – review & editing, Software, Resources, Funding acquisition. **Toheed Akhter:** Writing – review & editing, Software, Resources, Formal analysis.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2025.127971.

Data availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

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