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Temperature effect on the molecular interactions between two ammonium ionic liquids and dimethylsulfoxide

Varadhi Govinda ^a, Pankaj Attri ^b, P. Venkatesu ^{b,*}, P. Venkateswarlu ^a

^a Department of Chemistry, Sri Venkateswara University, Tirupati - 517 502, India

^b Department of Chemistry, University of Delhi, Delhi - 110 007, India

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ABSTRACT

To understand the molecular interactions between newly synthesized ammonium ionic liquids (ILs) and highly polar solvent dimethylsulfoxide (DMSO), precise measurements such as densities (ρ), ultrasonic sound velocities (u) and viscosities (η) have been performed over the whole composition range at temperature ranging from 298.15 to 308.15 K and at atmospheric pressure. The ILs investigated in the present study included diethyl ammonium acetate ([Et₂NH][CH₃COO], DEAA) and triethyl ammonium acetate ([Et₃NH] [CH₃COO], TEAA). Further, to gain some insight into the nature of molecular interactions in these mixed solvents, we predicted the excess molar volume (V^{E}), the deviation in isentropic compressibilities (ΔK_{s}) and deviation in viscosity ($\Delta \eta$) as a function of the concentration of IL using the measured properties of ρ , uand η , respectively. Redlich–Kister polynomial was used to correlate the results. The intermolecular interactions and structural effects were analyzed on the basis of the measured and the derived properties. A qualitative analysis of the results is discussed in terms of the ion–dipole, ion–pair interactions, and hydrogen bonding between ILs and DMSO molecules and their structural factors.

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1. Introduction

During the past decade, ionic liquids (ILs), a class of environmental friendly solvents, have been used for a wide range of industrial applications. ILs are emerging green solvents and a novel class of liquids mainly due to their special features, such as non-volatility, high polarizability/dipolarity and their ability to dissolve compounds of varying polarities. They are simple salts that are liquids below 100 °C or at room-temperature and are entirely composed of different organic ions [1–7]. They appear to be replacements for noxious volatile organic compounds (VOCs). ILs are also chemically diverse owing to the huge number of possible cation/anion combinations that can be synthesized at laboratory level [8]. ILs were initially synthesized in the early 20th century [9]. To date, there are over 250 types of ILs prepared, and some of them have been successfully applied in organic synthesis and other aspects.

Due to the ionic nature of the materials, ILs have essentially negligible vapor pressure and so can be envisioned as being useful in a variety of applications [8,10]. The development of ILs as solvents for chemical synthesis holds a great promise for green chemistry applications [10]. Their perceived status as "designer", alternative "green" solvents has contributed largely to the chemical industry, i.e., the existence of fluids

with no measurable volatility and are able to selectively dissolve different types of solute merely by exchanging one of the ions that form the IL, or even more subtly, by altering one of the organic residues within a given ion. These properties make them very attractive especially in the emerging field of green chemistry. Therefore, they have become most promising solvents.

Mixed solvents are almost ubiquitous in the chemical industry in very different fields ranging from petrochemistry to pharmaceutical industries. Thermophysical properties of mixed solvents have been particularly informative in elucidating the solute–solute and solute–solvent interactions that exist in these solutions. Although a qualitative connection between the macroscopic and microscopic features is feasible, quantitative conclusions are of interest to both academic and industrial communities. In spite of importance of properties of ILs in different solvent media, a small number of thermophysical data are available in the literature, which mainly characterize ILs [1–3,11–16]. In this context, in the present manuscript, we have explored closely three key thermophysical properties such as densities (ρ), ultrasonic sound velocities (u) and viscosities (η) for the mixed solvents of ILs and polar solvent at various temperatures.

The highly polar self-associated and aprotic solvent such as dimethylsulfoxide (DMSO) (μ =4.06 D) [17] was chosen because of its wide use in applied chemistry and participation in biological processes [18,19]. DMSO is a versatile organic liquid having a special solvent power to promote a chemical reaction when used as a reaction medium. It also exerts a solvent effect sufficient to accelerate a reaction brought about by another reagent. It is also used as a solvent

^{*} Corresponding author. Tel.: + 91 11 276666646 142; fax: + 91 11 2766 6605. *E-mail addresses*: venkatesup@hotmail.com, pvenkatesu@chemistry.du.ac.in (P. Venkatesu).

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for polymerization reactions and displacement reactions because of its high dielectric constant value (ε =46.45 at 298.15 K) [17]. The computer molecular dynamics (MD) simulations reveal that in liquid DMSO, the weak H-bonds C-H··O=S are formed [20,21].

To characterize the type and magnitude of the molecular interactions between DMSO with ILs, we present here the $V^{\rm E}$, ultrasonic studies and $\Delta \eta$ of DMSO with two ILs, diethyl ammonium acetate ([Et₂NH][CH₃COO], DEAA) and triethyl ammonium acetate ([Et₃NH] [CH₃COO], TEAA) at the temperature ranging from 298.15 to 308.15 K and at atmospheric pressure over the whole composition range. No effort appears to have been made in literature to study the molecular interactions between DMSO and these ILs in terms of $V^{\rm E}$, $\Delta K_{\rm s}$ and $\Delta \eta$. The mixtures of ILs and DMSO provide potential industrial applications for the utilization of both ILs and DMSO. The intermolecular interactions and structural effects were analyzed on the basis of the measured and the derived properties.

2. Experimental

2.1. Materials

DMSO (Merck >99% of purity) was stored over freshly activated 3 Å molecular sieves for 48 h and was purified by the standard method described by Riddick et al. [17]. Acetic acid, diethyl amine and triethyl amine were purchased from Spectrochem, India. The purity of the DMSO was verified by measuring the densities (ρ), sound velocity (u) and viscosity (η) which are in good agreement with literature values [17,22]. The purity of the sample was further confirmed by GLC single sharp peaks.

2.2. Synthesis of ILs

Both ILs were synthesized in our laboratory [23,24] as given below and purity of ILs are measured using ¹H NMR. ¹H (400 MHz) spectra were recorded on a JEOL 400 NMR spectrometer in DMSO- d_6 (with TMS for ¹H as internal references).

2.2.1. Synthesis of diethyl ammonium acetate (DEAA)

The synthesis of ILs was carried out in a 250 mL round bottomed flask, which was immersed in a water-bath and fitted with a reflux condenser. Acetic acid (1 mol) was dropped into the diethyl amine (1 mol) at 343.15 K for 1 h. The reaction mixture was heated at 353.15 K with stirring for 2 h to ensure that the reaction had proceeded to completion. The reaction mixture was then dried at 353.15 K until the weight of the residue remained constant. The sample was analyzed by Karl Fisher titration and revealed very low levels of water (below 70 ppm). The yield of DEAA was 118 g. ¹H NMR (CDCl₃): δ (ppm) 1.3 (t, 6H), 1.97 (s, 3H), 2.95 (m, 3H), 9.20 (s, 2H).

2.2.2. Synthesis of triethyl ammonium acetate (TEAA)

A procedure similar to that above for DEAA was followed with the exception of the use of triethyl amine ([amine]) instead of diethyl amine. The yield of TEAA was 98%. ¹H NMR (CDCl₃): δ (ppm) 0.778 (t, 9H), 1.466 (s, 3H), 2.58 (m, 6H), 11.0 (s, 1H).

2.3. Methods

2.3.1. Density measurements

The density measurements were performed with an Anton-Paar DMA 4500 M vibrating-tube densimeter, equipped with a built-in solid-state thermostat and a resident program with accuracy of temperature of ± 0.02 K. Typically, density precisions are ± 0.00005 g cm⁻³. Proper calibration at each temperature was achieved with doubly distilled, deionized water and with air as standards. The excess molar volumes (V^{E}) (± 0.003 cm³ mol⁻¹) were deduced from the densities of the pure compounds and mixture (ρ_{m}) using the standard equations.

2.3.2. Ultrasonic sound velocity measurements

Ultrasonic sound velocities were measured by a single crystal ultrasonic interferometer (model F-05) from Mittal Enterprises, New Delhi, India, at 2 MHz frequency at various temperatures. A thermostatically controlled, well-stirred circulated water bath with a temperature controlled to ± 0.01 K was used for all the ultrasonic sound velocity measurements. The uncertainty in sound velocity is 0.02%.

2.3.3. Viscosity measurements

Viscosity measurements were performed by using vibro viscometer (Model: SV-10 A&D Company Limited, Japan). The instrument has been provided with two sensor plates of gold coating. The sample cell was placed under these sensor plates. Viscosity measurements were taken from the digital display device attached to the vibro viscometer. Viscosity measurements of the sample were taken at heating rate 1 K/15 min for getting the thermodynamic equilibrium. A thermostatically controlled, well-stirred circulated water bath with a temperature controlled to \pm 0.01 K was used for all the viscosity measurements. Typically, the viscosities uncertainty is to be 1%.

2.3.4. Preparation of samples

Clear solutions were prepared gravimetrically using a Mettler Toledo balance with a precision of ± 0.0001 g. The uncertainty in solution composition expressed in mole fraction was found to be less than 5×10^{-4} . Mixing of the two components was promoted by the movement of a small glass sphere (inserted in the vial prior to the addition of the ILs) as the flask was slowly and repeatedly inverted. After mixing the sample, the bubble-free homogeneous sample was transferred into the U-tube of the densimeter, the sample cell of ultrasonic interferometer or viscometer through a syringe.

3. Results and discussion

To understand the molecular interactions of DMSO with ammonium ILs, we have measured the thermophysical properties such as ρ , uand η over the whole mole fraction range at temperature ranging from 298.15 to 308.15 K under atmospheric pressure. Usually, ILs are miscible with medium- to high-dielectric liquids and immiscible with low dielectric liquids [25]. In the present study, both ILs are completely miscible in DMSO (ε =46.45 at 298.15 K) [17], since DMSO is a high dielectric liquid. Experimental values of ρ , u and η at various temperatures are reported in Table 1 for ILs, DMSO, and their mixtures over the whole composition range. The effect of the ILs on the ρ , u and η in the DMSO has been examined at various temperatures. It was found that the ρ values for the mixtures of DEAA or TEAA with DMSO decrease as both temperature and concentrations of the DEAA or TEAA in DMSO increase at all studied temperatures, as shown in Fig. 1.

Ultrasonic sound velocities are also another important source of information about the properties of different solvents and their mixture. As it can be seen from Fig. 2, the values of *u* sharply decrease as the temperature increases in the ILs with DMSO system. The values of *u* were found to increase with increasing the mole fraction of DEAA and TEAA up to 0.5000 and 0.4000 respectively. At mole fractions < 0.5000 the values sharply increased at all investigated temperatures. To obtain the mechanism events of the ILs role in the molecular interactions with DMSO, we further studied viscosity measurements for DEAA or TEAA with DMSO under the same experimental conditions. From Fig. 3, it is clear that the viscosities increase with increasing the mole fraction of ILs in DMSO whereas the η values decrease as the temperature increases in the two systems. It is obvious that the thermophysical properties reflect the structural properties of liquids and packing factors of the system. There are no previous ρ , u and η data reported in the literature for ammonium ILs + DMSO at various temperatures, for comparison.

Table 1

Mole fraction (x_1) of IL, density (ρ), ultrasonic sound velocity (u), viscosity (η), excess molar volumes (V^{E}) , isentropic compressibility (K_{s}) , and deviation in isentropic compressibility (ΔK_{s}) , deviation in viscosity $(\Delta \eta)$ for the systems of IL with DMSO at T = (298.15, 303.15, 308.15) K and at atmospheric pressure.

x_1	$\rho/$	и/	η	$V^{\rm E}/$	$K_{\rm s}/$	$\Delta K_{\rm s}/$	$\Delta \eta /$
-	g.cm ⁻³	$m.s^{-1}$	mPa.s	cm ³ .mol ⁻¹	T.Pa ⁻¹	T.Pa ⁻¹	mPa.s
deaa w	ith DMSO a	it 298.15	K				
0	1.09537	1496	1.99	0	408	0	0
0.0144	1.09397	1500	2.24	-0.032	406	-1.4	0.044
0.0290	1.0925	1507	2.53	-0.060	403	-3.8	0.123
0.0440	1.09091	1513	2.81	-0.081	401	-6.1	0.187
0.0752	1.08771	1522	3.39	-0.123	397	-8.7	0.319
0.1077	1.08443	1532	3.98	-0.16	393	-12	0.442
0 1 5 9 4	1 07915	1546	4 91	-0.192	388	-16	0.630
0 2149	1 07365	1560	5.81	-0.208	383	- 19	0.732
0.2747	1.07305	1572	674	-0.206	370	- 21	0.752
0.2/4/	1.06704	1572	7.71	0.200	272	-21	0.805
0.3400	1.00204	1500	0.70	-0.19	270	-21	0.034
0.4103	1.05611	1587	8.70	-0.164	370	-20	0.815
0.5136	1.04826	1593	10.09	-0.126	376	-17	0.720
0.6299	1.04053	1595	11.56	-0.091	3//	- 12	0.518
0.6756	1.03779	1596	12.13	-0.081	378	-9.7	0.431
0.7186	1.03529	1597	12.66	-0.067	379	-8.0	0.344
0.7542	1.03333	1597	13.11	-0.059	379	-6.4	0.283
0.7977	1.03104	1598	13.67	-0.051	380	-4.8	0.217
0.8465	1.02858	1599	14.29	-0.041	380	-2.9	0.136
0.8868	1.02662	1601	14.83	-0.031	380	-1.9	0.097
0.9373	1.02427	1604	15.50	-0.019	379	-1.0	0.042
0 9747	1 02257	1606	16.01	-0.008	379	-0.24	0.013
1	1 02146	1608	1636	0	378	0	0
1	1.02140	1000	10.50	0	570	0	0
	th DMCO	+ 202 15	V				
DEAA W	1 002 41	1472	1 70	0	422	0	0
0	1.09241	1472	1.79	0	422	0	0
0.0144	1.09103	14/8	2.04	-0.037	420	- 2.3	0.080
0.0290	1.08949	1485	2.32	-0.065	416	- 5.2	0.186
0.0440	1.08791	1491	2.61	-0.09	413	- 7.3	0.298
0.0752	1.08475	1500	3.13	-0.143	410	-9.7	0.449
0.1077	1.08129	1512	3.67	-0.176	404	-14	0.604
0.1594	1.07591	1526	4.41	-0.212	399	-17	0.732
0.2149	1.07019	1540	5.17	-0.224	394	-20	0.834
0.2747	1.06427	1554	5.92	-0.218	389	-22	0.875
0 3400	1 05815	1564	672	-0.197	386	-22	0.900
0.4103	1.05209	1572	7.51	-0.172	385	-21	0.858
0.5136	1 04405	1582	8 64	-0.135	383	- 19	0.764
0.5150	1.03612	1502	0.04	_ 0.099	383	_ 15	0.565
0.0233	1.03012	1500	10.20	0.035	202	- 15	0.303
0.0/00	1.03331	1591	10.28	-0.089	382	- 13	0.484
0./186	1.03077	1592	10.73	-0.078	383	-11	0.425
0.7542	1.02877	1593	11.10	-0.071	383	-9	0.373
0.7977	1.02644	1594	11.54	-0.065	383	-7	0.297
0.8465	1.0239	1595	12.02	-0.052	384	-4.6	0.199
0.8868	1.0219	1597	12.44	-0.045	384	-3.4	0.141
0.9373	1.01946	1599	12.96	-0.027	383	-1.5	0.063
0.9747	1.01773	1602	13.36	-0.017	383	-0.53	0.019
1	1.01652	1604	13.64	0	382	0	0
DEAA w	ith DMSO a	t 308.15	К				
0	1.08608	1460	1.65	0	432	0	0
0.0144	1.08482	1469	1.90	-0.043	427	-4.2	0.104
0.0290	1.08333	1474	2.18	-0.071	425	-5.8	0.234
0.0440	1.08187	1480	2.48	-0.101	422	-7.9	0.382
0.0752	1 07892	1490	2.95	-0.164	418	-11	0.534
0 1077	1.07555	1502	3.45	-0.198	412	- 15	0 704
0 1594	1 07020	1516	4 11	-0.235	407	-18	0.228
0.1334	1.07023	1520	A 77	_0.233	402		0.000
0.2145	1.004/1	1530	5.40	0.240	206	21	0.332
0.2/4/	1.05884	1544	5.40	- 0.230	202	- 23	0.954
0.3400	1.05285	1554	6.08	-0.216	292	- 23	0.968
0.4103	1.0469	1562	6.74	-0.191	392	- 22	0.914
0.5136	1.03899	1574	7.69	-0.151	388	-20	0.812
0.6299	1.0312	1582	8.70	-0.113	387	-16	0.637
0.6756	1.02846	1584	9.10	-0.105	387	-14	0.572
0.7186	1.02597	1586	9.46	-0.094	387	-12	0.495
0.7542	1.02402	1588	9.76	-0.087	387	-10	0.432
0.7977	1.0217	1589	10.14	-0.077	388	-8.1	0.369
0.8465	1.01925	1590	10.52	-0.070	388	-5.4	0.253
0.8868	1.0173	1592	10.86	-0.063	388	-3.8	0.182
0.9373	1.01492	1594	11.27	-0.049	388	-1.6	0.079
0.9747	1.01315	1594	11.6	-0.028	388	-0.79	0.027
1	1.01187	1599	11.83	0	387	0	0
				-		-	-

Table 1 (continued)							
X1	0/	u/	n/	V ^E /	K./	$\Delta K_c/$	$\Delta n/$
1	$g.cm^{-3}$	m.s ⁻¹	mPa.s	cm ³ .mol ⁻¹	$T.Pa^{-1}$	$T.Pa^{-1}$	mPa.s
	U. D. KOO	. 200 4 5	17				
IEAA W	ith DMSO a	t 298.15	K 1.00	0	400	0	0
0 00000	1.09537	1496	1.99	0	408	0	0 0000
0.0236	1.09091	1516	2.48	0.027	399	- 6.3	-0.033
0.0351	1.08886	1536	2.72	0.039	389	- 15	-0.046
0.0607	1.08437	1564	3.26	0.071	377	-24	-0.074
0.0879	1.07976	1594	3.84	0.115	364	-33	-0.095
0.1152	1.07550	1616	4.42	0.153	356	-38	-0.118
0.1610	1.06891	1650	5.41	0.214	344	-45	-0.143
0.2116	1.06230	1684	6.52	0.283	332	-51	-0.152
0.2699	1.05553	1710	7.81	0.356	324	-52	-0.154
0.3553	1.04713	1734	9.71	0.435	318	-49	-0.143
0.4353	1.04061	1746	11.49	0.478	315	-42	-0.132
0.4831	1.03730	1754	12.56	0.480	314	-38	-0.122
0.5464	1.03336	1764	13.97	0.473	311	-33	-0.112
0.6163	1.02965	1772	15.53	0.438	309	-27	-0.098
0.6796	1.02673	1784	16.94	0.387	306	-22	-0.09
0.7164	1.02519	1790	17.76	0.350	304	-20	-0.084
0.7846	1.02260	1800	19.28	0.273	302	-14	-0.074
0.8163	1.02149	1808	19.99	0.234	299	-13	-0.064
0.8504	1 02043	1816	20.75	0.180	297	-11	-0.058
0.9064	1.01865	1874	220.73	0.100	295	-66	-0.039
0.9466	1.01738	1832	22.01	0.100	203	_ 1 2	-0.027
1	1.01586	18/0	22.51	0.000	201	-4.2	0.027
1	1.01500	1040	24.12	0	251	0	0
TEAA w	ith DMSO a	t 303.15	K	0	422	0	0
0	1.09241	14/2	1.79	0	422	0	0
0.0236	1.08785	1494	2.20	0.021	412	-7.7	-0.022
0.0351	1.08569	1514	2.39	0.035	402	-16	-0.035
0.0607	1.08111	1542	2.82	0.061	389	-26	-0.063
0.0879	1.07654	1574	3.29	0.089	375	-37	-0.078
0.1152	1.07207	1596	3.76	0.129	366	-42	-0.094
0.1610	1.06526	1630	4.55	0.186	353	-49	-0.123
0.2116	1.05844	1660	5.44	0.251	343	-52	-0.134
0.2699	1.05128	1686	6.48	0.334	335	-53	-0.136
0.3553	1.04255	1712	8.01	0.411	327	-50	-0.129
0.4353	1.03571	1726	9.45	0.458	324	-43	-0.115
0.4831	1.03221	1734	10.31	0.465	322	-40	-0.109
0.5464	1.02812	1744	11.45	0.456	320	-35	-0.098
0.6163	1.02429	1758	12.71	0.412	316	-29	-0.084
0.6796	1.02123	1768	13.85	0.359	313	-24	-0.074
0.7164	1.01964	1776	14.51	0.320	311	-22	-0.071
0.7846	1.01692	1788	15.74	0.239	308	-16	-0.058
0.8163	1.01578	1792	16.31	0.196	307	-14	-0.052
0.8504	1 01465	1800	16.93	0.142	304	-12	-0.040
0.9064	1.01264	1808	17.94	0.090	302	-74	-0.031
0.0466	1.01204	1816	18.67	0.037	300	-16	-0.017
1	1.01150	1010	10.07	0.037	200	-4.0	- 0.017
1	1.00958	1024	15.04	0	290	0	0
TEAA w	ith DMSO a	t 308.15	К				
0	1.08608	1460	1.65	0	432	0	0
0.0236	1.08162	1484	1.98	0.012	420	-8.1	-0.012
0.0351	1.07944	1504	2.13	0.026	410	-18	-0.028
0.0607	1.07492	1530	2.48	0.045	397	-27	-0.049
0.0879	1 07034	1564	2.86	0.071	382	- 39	-0.063
0.1152	1.06586	1588	3 24	0.109	372	-46	-0.005
0.1610	1.00500	1622	3.80	0.159	350	- 53	_ 0.091
0.1010	1.05208	16/8	4.61	0.133	350	- 57	-0.051
0.2110	1.05208	1674	5.45	0.234	2/1	57	0.104
0.2055	1.04508	1609	5.45	0.297	225	- 57	- 0.105
0.5555	1.03015	1712	0.09	0.560	222	- 35	-0.105
0.4353	1.02926	1712	7.80	0.431	331	-4/	-0.093
0.4831	1.02566	1724	8.56	0.445	328	-44	-0.086
0.5464	1.02154	1/32	9.49	0.434	326	- 38	-0.072
0.6163	1.01766	1744	10.51	0.391	323	- 33	-0.064
0.6796	1.01461	1754	11.44	0.332	320	-28	-0.051
0.7164	1.01300	1764	11.98	0.291	317	-26	-0.044
0.7846	1.01026	1772	12.98	0.208	315	-20	-0.031
0.8163	1.00909	1776	13.44	0.165	314	-17	-0.030
0.8504	1.00784	1780	13.94	0.126	313	-14	-0.023
0.9064	1.00585	1786	14.76	0.068	312	-7.7	-0.015
0.9466	1.00451	1792	15.35	0.024	311	- 5.1	-0.006
1	1.00261	1798	16.13	0	309	0	0

The extent of deviation of liquid mixtures from ideal behavior is best expressed by excess functions. Among them, the excess volumes can be interpreted in three areas, namely physical, chemical, and



Fig. 1. Densities for the mixtures of ILs with DMSO vs. mole fraction of IL x_1 for (a) DEAA { (x_1) 298.15 K (\bigcirc) +, or (x_1) 303.15 K (\triangle) +, or (x_1) 308.15 K (\square) + DMSO (x_2)}, (b) TEAA { (x_1) 298.15 K (\bigcirc) +, or (x_1) 303.15 K (\triangle) +, or (x_1) 308.15 K (\square) +, DMSO (x_2)}, at various compositions and atmospheric pressures. The solid line represents the smoothness of these data.

structural effects [1–3]. The excess volumes were determined from the densities of pure compounds (ρ_1 and ρ_2) and of mixture (ρ_m) using the following equation:

$$V^{\rm E} = V_m - (x_1 V_1 + x_2 V_2) \tag{1}$$

or

$$V^{\rm E} = \frac{x_1 M_1 + x_2 M_2}{\rho_{\rm m}} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2}\right) \tag{2}$$

where V_m , V_1 and V_2 are molar volumes of the mixture and pure components; M_1 , M_2 and x_1 , x_2 are the molar masses and mole fractions of ILs and DMSO, respectively. In recent years, the ultrasonic studies have been adequately employed in understanding the nature of molecular interaction in solvent mixed systems. Isentropic compressibilities (K_s) of the binary mixtures were calculated using the relation from sound velocity (u) and density (ρ);

$$K_{\rm s} = u^{-2} \rho^{-1}.$$
 (3)



Fig. 2. Ultrasonic sound velocities for the mixtures of ILs with DMSO vs. mole fraction of IL x_1 for (a) DEAA {(x_1) 298.15 K (\bigcirc) +, or (x_1) 303.15 K (\triangle) +, or (x_1) 308.15 K (\square) + DMSO (x_2)}, (b) TEAA {(x_1) 298.15 K (\bigcirc) +, or (x_1) 303.15 K (\triangle) +, or (x_1) 308.15 K (\square) + DMSO (x_2)}, at various compositions and atmospheric pressures. The solid line represents the smoothness of these data.

Deviations in isentropic compressibility (ΔK_s) were evaluated using the following relation.

$$\Delta K_{\rm s} = K_{\rm s} - x_1 K_{\rm s1} - x_2 K_{\rm s2} \tag{4}$$

where K_{s1} , and K_{s2} are the isentropic compressibilities of the pure components 1 and 2, respectively. The deviations in viscosity ($\Delta \eta$) were calculated by the following equation.

$$\Delta \eta = \eta - \sum_{i=1}^{N} x_i \eta_i \tag{5}$$

where η and η_i denote the viscosity of the mixture and the pure component, respectively.

The composition dependence of the $V^{\rm E}$, $\Delta K_{\rm s}$ and $\Delta \eta$ properties represents the deviation from ideal behavior of the mixtures and provides an indication of the interactions between IL and DMSO.



Fig. 3. Viscosities for the mixtures of ILs with DMSO vs. mole fraction of IL x_1 for (a) DEAA { (x_1) 298.15 K (\bigcirc) +, or (x_1) 303.15 K (\triangle) +, or (x_1) 308.15 K (\bigcirc) + DMSO (x_2)}, (b) TEAA { (x_1) 298.15 K (\bigcirc) +, or (x_1) 303.15 K (\triangle) +, or (x_1) 308.15 K (\bigcirc) +, DMSO (x_2)}, at various compositions and atmospheric pressures. The solid line represents the smoothness of these data.

The following Redlich–Kister expression was used to correlate these properties:

$$Y = x_1 x_2 \left(\sum_{i=0}^{n} a_i (x_1 - x_2)^i \right)$$
(6)

where *Y* refers to V^{E} , ΔK_{s} or $\Delta \eta$. a_i are adjustable parameters and can be obtained by least-squares analysis. Values of the fitted parameters are listed in Table 2 along with the standard deviations of the fit. The values of V^{E} , ΔK_{s} and $\Delta \eta$ for the binary mixtures at various temperatures as function of ILs concentrations are included in Table 1. Figs. 4, 5 and 6 display the experimental data for the binary mixtures, and the fitted curves, along with the excess properties of V^{E} , ΔK_{s} and $\Delta \eta$ for the ILs with DMSO as function of IL concentrations at different temperatures, respectively.

As seen from the experimental results in Fig. 4, the values of $V^{\rm E}$ for DEAA or TEAA with DMSO are negative or positive, respectively in the entire range of composition. It is more interesting to note that the $V^{\rm E}$ values in DEAA + DMSO or TEAA + DMSO systems have minimum or maximum values at mole fractions of this ILs of about $x_1 \approx 0.2000$ or $x_1 \approx 0.5000$ at investigated temperatures, respectively. The minimum

Table 1	2
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Estimated parameters of Eq. (6) and standard deviation, σ for the systems of ILs with DMSO at various temperatures.

Y	Systems	T/K	<i>a</i> ₀	<i>a</i> ₁	<i>a</i> ₂	σ
$V^{\rm E}/{\rm cm^3}~{\rm mol^{-1}}$	DEAA	298.15	-0.4838	0.7511	-0.9841	0.004
	+ DMSO	303.15	-0.4666	0.7961	-1.2930	0.007
		308.15	-0.4871	0.8779	-1.5653	0.010
	TEAA	298.15	1.9146	-0.0213	-0.8072	0.006
	+ DMSO	303.15	1.8657	-0.1575	-1.2415	0.003
		308.15	1.7747	-0.1238	-1.4718	0.002
$\Delta K_{\rm s}/{\rm T.Pa^{-1}}$	DEAA	298.15	-73.832	64.310	-9.428	0.8
	+ DMSO	303.15	-76.837	70.138	-18.253	0.8
		308.15	-66.989	87.562	-72.990	2.8
	TEAA	298.15	-163.43	168.21	-71.42	3.0
	+ DMSO	303.15	-167.71	185.51	-104.69	3.0
		308.15	-191.30	168.77	-65.56	2.2
$\Delta \eta$ /mPa.s	DEAA	298.15	3.0399	-2.0619	-0.8967	0.04
	+ DMSO	303.15	3.2095	-2.9280	0.5433	0.03
		308.15	3.5455	-3.0034	0.7425	0.05
	TEAA	298.15	-0.4829	0.4310	-0.5648	0.003
	+ DMSO	303.15	-0.4418	0.3787	-0.2921	0.004
		308.15	0.4745	-0.3927	0.1573	0.007



Fig. 4. Excess molar volumes ($V^{\mathbb{E}}$) for the mixtures of ILs with DMSO vs. mole fraction of IL x_1 for (a) DEAA{(x_1) 298.15 K (\bigcirc) +, or (x_1) 303.15 K (\triangle) +, DMSO (x_2)}, (b) TEAA {(x_1) 298.15 K (\bigcirc) +, or (x_1) 303.15 K (\triangle) +, DMSO (x_2)}, at various compositions and atmospheric pressures. Solid (-) lines correlated by Redlich–Kister equation.



Fig. 5. Deviation in isentropic compressibilities (ΔK_s) for the mixtures of ILs with DMSO vs. mole fraction of IL x_1 for (a) DEAA { $(x_1) 298.15 \text{ K} (\bigcirc) +, \text{ or } (x_1) 303.15 \text{ K} (\triangle) +, \text{ or } (x_1) 308.15 \text{ K} (\Box) +, DMSO (x_2)$ }, (b) TEAA { $(x_1) 298.15 \text{ K} (\bigcirc) +, \text{ or } (x_1) 303.15 \text{ K} (\triangle) +, \text{ or } (x_1) 308.15 \text{ K} (\Box) + DMSO (x_2)$ }, at various compositions and atmospheric pressures. Solid (-) lines correlated by Redlich–Kister equation.

increases and as temperature increases for DEAA + DMSO system at all temperatures. This behavior can be explained in terms of hydrogen bonding that is certainly more T-dependent than coulombic interactions. The minimum can be due to hydrogen bonds between DMSO molecules and DEAA, which is schematically shown in Scheme 1. The negative excess molar volumes reveal that a more efficient packing or attractive interaction occurred when DEAA and DMSO were mixed. The interactions between the DMSO molecules and the ions of these ILs are due to ion-dipole interactions. This will reduce the hydrogen bond between the cation and anion in the ionic liquid, which contribute to the negative V^{E} values. On the other hand, the TEAA + DMSO mixture reveals the positive values of V^E. The observed positive values show that there exist no specific interactions between unlike molecules and also the compact structure of the polar component (DMSO) due to dipolar association has been broken by these ILs. The magnitude and sign of $V^{\rm E}$ values are a reflection of the type of



Fig. 6. Deviation in viscosities $(\Delta \eta)$ for the mixtures of ILs with DMSO vs. mole fraction of IL x_1 for (a) DEAA { (x_1) 298.15 K (\bigcirc) +, or (x_1) 303.15 K (\triangle) +, or (x_1) 308.15 K (\square) + DMSO (x_2)}, (b) TEAA { (x_1) 298.15 K (\bigcirc) +, or (x_1) 303.15 K (\triangle) +, or (x_1) 308.15 K (\square) +, DMSO (x_2)}, at various compositions and atmospheric pressures. Solid (-) lines correlated by Redlich–Kister equation.

interactions taking place in the mixture, which are the result of different effects containing the loss of the DMSO dipole interaction from each other (positive V^{E}) and the breakdown of the ionic liquid ionpair (positive V^{E}). The interaction between the ion-pair of ILs increases as compared to IL + DMSO interactions, which leads to positive contribution. This phenomenon is explicitly explained in Scheme 1.

Fig. 5 illustrates the deviation in isentropic compressibility (ΔK_s) values over the whole composition range at various temperatures, for all investigated systems as a function of ILs concentration. It is clear that different phenomena of ΔK_s were observed for the various ILs with DMSO. The graphical representations in Fig. 5, the ΔK_s values are negative over the entire composition range at all the temperature range and approach the minimum at $x_1 \approx 0.3500$ and $x_1 \approx 0.2700$ for the system DEAA and TEAA with DMSO respectively. Clearly, we observed only negative ΔK_s values for the DEAA + DMSO and TEAA + DMSO at all studied temperature range, respectively. The negative values of the ΔK_s of the DEAA or TEAA with DMSO imply that solvent molecules around the solute are less compressible than the solvent molecules in the bulk solutions.



Scheme 1. Schematic depiction of hydrogen bonding interactions between DEAA + DMSO and TEAA + DMSO, where colorrepresentations are as follows, green = carbon, white = hydrogen, red = oxygen and yellow = sulfur.

The DEAA + DMSO system shows the positive viscosity deviation at all investigated temperatures whereas the TEAA + DMSO mixture reveals the negative viscosity deviation at all studied temperatures, as shown in Fig. 6. In fact, temperature influences strongly on the viscosity deviation. As the temperature increases, the deviations also increase towards the positive values for TEAA + DMSO system. Apparently, the viscosity of the pure ILs and their mixtures decreases quickly when the temperature increases. This behavior agrees with several reported literature that with increase in temperature the negative values $\Delta \eta$ are progressively reduced and even reach positive deviation [14,15,26-28]. The minima lie at a mole fraction of approximately 0.2600 for TEAA + DMSO and maximum mole fraction of about 0.3500 for DEAA + DMSO at 298.15 K. The change in the magnitude of the positive $\Delta \eta$ values as a function of temperature can be attributed to the decrease in hydrogen bonding. By increasing the temperature the interactions become very weak due to weakening of the dipolar association by the IL as well as the dissociation of the ionic liquid ion-pair.

4. Conclusions

The work performed intends to map the thermophysical behavior of two important ILs with DMSO at various temperatures. The values of ρ , u and η for ILs with DMSO have been reported at 298.15 to 308.15 K under atmospheric pressure. From these measurements, we have predicated V^{E} , ΔK_{s} and $\Delta \eta$ at each temperature as a function of IL concentration. The values of V^{E} values for DEAA or TEAA with DMSO are negative and positive at all the ranges of composition, respectively, indicating negative deviations and positive deviations from ideal behavior. We observed negative ΔK_s values over the whole composition range for the DEAA + DMSO and TEAA + DMSO at all studied temperature range. The DEAA + DMSO system shows the positive viscosity deviation while TEAA + DMSO system reveals the negative viscosity deviation at all investigated temperatures. In general, the Redlich Kister polynomial was used to correlate the results and provides a good description for $V^{\rm E}$, $\Delta K_{\rm s}$ and $\Delta \eta$ with composition for both systems.

List of symbol

- *u* ultrasonic sound velocity
- x_i mole fraction of component *i*
- V_m molar volume of the mixture
- V_i molar volume of component *i*
- M_i molar mass of component *i* V^E excess molar volume
- *V*^E excess molar volume
- *K*_s isentropic compressibility
- $\Delta K_{\rm s}$ deviation in isentropic compressibility
- *a_i* binary constant of Redlich–Kister equation

Greek letters

- ρ density
- η viscosity
- $\Delta \eta$ deviation in viscosity
- σ stand deviation

Subscripts

cal	calculated	from	Eq.	(6)

exp experimental

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