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Thermodynamic study of aspirin in the presence of ionic liquid, 1-hexyl-3-methylimidazolium bromide in acetonitrile at $T = (288.15 \text{ to } 318.15)$ K

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ABSTRACT

In recent years, ionic liquids have received much attention in pharmaceutical processing. Thermophysical properties such as densities, viscosities, speeds of sound and refractive indices for systems containing aspirin (ASA), ionic liquid {1-hexyl-3-methylimidazolium bromide ([HMIm]Br)} and acetonitrile have been measured at $T = (288.15$ K to $318.15)$ K and at atmospheric pressure. The measured data have been applied to calculate the standard partial molar volumes $V_\phi{}^0$, volumes of transfer $\Delta_{tr}V_\phi{}^0$, Hepler's constants $\left(\partial^2 V_\phi{}^0/\partial^2 T\right)_p$, apparent molar isentropic compressibility κ_ϕ, molar refractions R_D, viscosity B-coefficients and solvation numbers. The calculated Hepler's constants $\left(\partial^2 V_\phi{}^0/\partial^2 T\right)_p$ indicate that the ionic liquid behave as structure-maker in the solutions. The results have been interpreted in terms of solute–solvent interactions. Generally it is concluded that dominant interactions between ASA and ionic liquid are ion–polar and polar–polar interactions.

1. Introduction

Pharmaceutical compounds are chemical substances characterized by the specific properties towards a human body [1]. The pharmaceutical industries are undoubtedly experiencing a series of challenges. One of these challenges is the administration of solid form of many drugs due to many well known problems including low solubility, polymorphic conversion, drug delivery, instability and low bioavailability [2].

Many approaches have been proposed to improve the oral bioavailability of such drugs including micronization, complexation with cyclodextrins, salt formation, use of co-solvency, surfactants and nanoparticles, solid dispersion, hydrotropy, etc. Some of these ways may improve the dissolution rate of the drug but these methods are not always practical, for example, salt formation of neutral compounds is not feasible. Moreover, the salts of weak acid and weak base may convert back to their original acid or base forms and lead to aggregation in the gastrointestinal tract [2–4].

Recently to overcome these problems, ionic liquids (ILs) have been recommended as alternative organic solvents in the pharmaceutical industry [5]. They have been widely promoted as “green solvents”, in many fields of chemistry and industry due to their unique physicochemical properties including wide liquid range, high thermal stability, negligible vapor pressure and high ionic conductivity [6,7]. The ionic-liquids have been popularly used as solvents for synthesis, extraction and separation, azeotropic mixtures, catalysis, antimicrobial agent, electrochemistry and nanotechnology [8]. They also have been used in pharmaceutical industry as solvent in the synthesis of drugs or drug intermediates, crystallization, separations, extraction of drugs from natural products, drug delivery, drug detection and as ingredients [9].

Aspirin (ASA) is one of a salicylate drug, often used as an analgesic to relieve minor aches and pains, as an antipyretic to reduce fever, and as an anti-inflammatory medication [10,11]. It is easily hydrolyzed in presence of moisture, forming salicylic acid (SA) which in turn is metabolized to a number of different metabolites [12]. Aspirin is unstable in water, thus it must be solubilized in non-aqueous solvent such as acetonitrile (MeCN). Solvents are used in pharmaceutical processing (reacting, separation and formulation), therefore appropriate selection may enhance the reaction yield and determine the quantity [13].

Acetonitrile is regarded as a key solvent in pharmaceutical industry. Its high popularity is due to its excellent solvation ability with respect to a wide range of polar and non-polar solutes and favorable properties such as low freezing/boiling points, low viscosity [14–20]. Much effort has been put into decreasing the amount of organic solvents involved in drug product manufacturing. Pharmaceutical companies have attempted to exchange more toxic solvents with more environmentally friendly alternatives with similar properties (e.g., replacing benzene with toluene) or have looked for new innovations such as green solvents [21]. The generalized use of ionic liquid as a solvent in pharmaceutical processing needs detailed knowledge of their physicochemical properties when they are mixed with drugs. The study of thermodynamic properties of drugs in ionic liquid mixtures is crucial from a technological

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point of view but it also provides a better understanding of the mechanisms involved when using these new media. For example, volumetric and acoustic properties are powerful tools to study drugs behavior in ionic liquid solutions and were used to provide information on solute–solvent and solute–solvent interactions in the mixtures [22]. Viscometric properties of drug molecules have also important implications for the permeations of drug molecules through biological membrane [23]. The thermodynamic properties of drug in solvent can also provide important information in determining the appropriate solvent in the pharmaceutical industry; consequently many thermodynamic studies have been done on the systems including drug and solvent by Iqbal et al. in some organic solvents such as DMSO, THF, MeCN and alcohols [10,23–26].

Poor solubility of drugs in water can dramatically reduce their bioavailability. For example, aspirin, discovered in 1853 [27], is one of the most prominent and widely used pharmaceuticals with an incredible spectrum of properties, but it is only sparingly soluble in water (0.33 g in 100 mL) or in the acidic environment of the stomach, leading to undissolved particles sticking to the gastrointestinal mucosa and resulting in topical irritation and gastric distress [28,29]. Different strategies using ILs have been studied to help overcome this problem. As previously mentioned, poorly water soluble drugs such as albendazole and danazol groups could be readily dissolved in [Bmim][PF_6] [30], and the solubility could be enhanced by the inclusion of another IL, such as [Hmim]Br. This showed that the usefulness of ILs as solvents can be improved by modulating their aqueous miscibility through the addition of a second IL [31]. In another study, effect of alkyl chain length on the solubility of ibuprofen and paracetamol has been investigated. Results show that the solubility increases with increasing chain length, so the solubility of paracetamol and ibuprofen in [HMIm]PF_6 is higher than [BMIm]PF_6 [32].

Therefore, in the present work the density, speed of sound, viscosity and refractive index data of aspirin as a drug model (solute) in the presence of ionic liquid (1-hexyl-3-methylimidazolium bromide) [HMIm]Br (co-solute) in acetonitrile solutions (MeCN) at different temperatures $T = (288.15, 298.15, 308.15 \text{ and } 318.15)$ K and at atmospheric pressure have been measured. The apparent molar volume, standard partial molar volume and transfer volume have been calculated using density data. Also, the apparent molar isentropic compressibilities have been computed from the experimental speed of sound data. The viscosity *B*-coefficients were calculated using the Jones-Dole equation.The measured experimental refractive index data for the studied solutions were used to calculate molar refraction. All these parameters were used to interpret the solute–solute and solute–solvent interactions and effect of temperature on the solvation properties of ASA in the presence of ionic liquid.

2. Experimental

2.1. Materials

The chemicals used in this work were aspirin, 1-bromohexane, acetonitrile, ethyl acetate, and *N*-methylimidazole were obtained from Merck. A sample description of the chemicals is provided in Table 1. All purities are given in mass percentage. During the course of the experiments, the purity of acetonitrile was checked by density, viscosity and refractive index measurements. The physical properties of acetonitrile and 1-hexyl-3-methylimidazolum bromide are listed in Table 2. The measured values were in agreement with those reported in the literature values at the experimental temperatures [33–46].

Table 1
A sample description of the used chemicals.

Chemical name	CAS number	Mass percentage purity	Purification method	Analysis method
Aspirin	50-78-2	GR > 0.998	–	–
Acetonitrile	75-05-8	GR > 99.99	–	–
[HMIm]Br	Synthetic	>99.88	Extraction and distillation	Karl Fischer titration and ^{1}H NMR
N-methylimidazole	616-47-7	>0.99	–	–
1-Bromohexane	111-25-1	>0.98	–	–
Ethyl acetate	141-78-6	>0.998	–	–

2.2. Synthesis of ionic liquid

1-Hexyl-3-methylimidazolium bromide ([HMIm]Br) in acetonitrile was prepared and purified by using the procedure explained in literature [47,48]. Briefly, [HMIm]Br was synthesized by direct alkylation of *N*-methylimidazole with an excess of 1-bromohexane in a round bottom flask at $T = 298.15$ K for 36 h under a nitrogen atmosphere. The crude product was filtered and then washed three times with fresh 30 ml ethyl acetate each time. The removal of residual reagents ethyl acetate compounds in the ionic liquid was performed at about $T = 333$ K using a rotary evaporator for at least 4 h under reduced pressure. The ionic liquid has no major impurity verified by ^{1}H NMR spectrum. This ionic liquid was used after vacuum desiccation for at least 24 h to remove trace amount of moisture. Water content found in the ionic liquid by Karl Fischer method using a Karl Fischer titrator (751 GPD Titrino-Metrohm, Herisau, Switzerland) was less than 0.12%. Ionic liquid was analyzed by ^{1}H NMR (Brucker Av-300) and FTIR (PerkinElmer, Spectrum RXI) to confirm the absence of any major impurities which found to be in good agreement with those reported in literature [49,50].

2.3. Apparatus and procedure

The solutions were prepared in glass vials and in molal base concentration by weighing using an analytical balance (AND, GR202, Japan) with an uncertainty $\pm 1 \cdot 10^{-8}$ kg and closed tightly with parafilm. The uncertainty for molalities of the solutions is less than $2 \cdot 10^{-4}$ mol·kg^{-1}. The sample density *d* and speed of sound *u* were measured with a vibrating tube densimeter (Anton Paar, DSA 5000 densimeter and speed of sound analyzer, Austria). The apparatus was calibrated with doubly distilled deionized and degassed water and dry air at atmospheric pressure. Density and speed of sound is extremely sensitive to temperature, so it was kept constant within $\pm 1.0 \cdot 10^{-3}$ K using the Peltier technique built in densimeter. In each measurement, the precision of density and speed of sound were $\pm 0.3 \cdot 10^{-3}$ kg.m^{-3} and 0.01 m.s^{-1}, respectively.

The viscosities were measured using an Ubbelohde-type viscometer, which has a flow time of about 200 s for water at 298.15 K. The viscometer was calibrated with doubly distilled deionized water. Viscosity of solutions η is obtained by the following Eq. (1):

$$\frac{\eta}{\rho} = Lt - \frac{K}{t} \tag{1}$$

where ρ is the density, *t* is the flow time of the solution, *L* and *K* are the viscometer constants [51]. A digital stopwatch with a resolution of 0.01 s has been used for the measurement of flow time. The evaluated uncertainty of the experimental viscosity was ±0.005 mPa·s.

Refractive indices (n_D) of the studied solutions were determined using a digital refractometer (ATAGO-DRA1, Japan) with an uncertainty of $\pm 1 \cdot 10^{-4}$. The instrument was calibrated with doubly distilled water before each series of measurements. A procedure called "zero setting" was always performed before the actual measurements of the sample's refractive index, to ensure that the refractometer is working properly. Calibration was made with pure liquids of known refractive index such as hexane. The temperature was controlled using a circulating bath thermostat (Julabo NP, Germany) with a thermal stability of ±0.01 K.

Table 2
Densities, ρ, speeds of sound, u, viscosities, η and refractive indices , n_D data for acetonitrile and ionic liquid at different temperatures.

T (K)	$10^{-3}\,\rho$ (kg·m^{-3})		u (m·s^{-1})		η (m Pa·s)		n_D	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
Acetonitrile								
288.15	0.787395	0.78726 [27] 0.787376 [28]	1319.07		0.388		1.3461	
298.15	0.776615	0.77664 [29] 0.77666 [30]	1211 1278.59	1278.59 [31] [30]	0.344	0.342 [32] 0.341[33] 0.3369[30]	1.3412	1.34163 [34] 1.3411 [33] 1.3414 [35]
308.15	0.765810	0.76586 [34] 0.75942 [36] 0.76589 [27]	1238.34	1238.21[31]	0.313	0.314 [33] 0.317 [33]	1.3371	1.3365 [37]
318.15	0.754851	0.75498 [38]	1198.25	1198.15 [31]	0.289	0.292 [39] 0.2974 [40]	1.3327	1.3327 [37]
[HMIm]Br								
298.15	1.2221	1.2235 [41]						

3. Results and discussion

3.1. Volumetric and ultrasonic properties

The experimental density ρ for the ternary (ASA + [HMIm][Br] + MeCN) solutions, as a function of ionic liquid (0.000, 0.1021, 0.1997 and 0.2890) molality in MeCN and solvent ([HMIm][Br] + MeCN) at different temperatures T = (288.15, 298.15, 308.15 and 318.15) K are reported in Table 3. As it can be seen from this table, the densities and speeds of sound of the investigated solutions decrease with increase in temperature and with acetonitrile content.

The apparent molar volumes V_ϕ of the aspirin at different concentrations of [HMIm]Br in MeCN solutions were calculated using density data through the following equation [52]:

$$V_\phi = \frac{M}{\rho} - \left[\frac{1000(\rho - \rho_0)}{m\rho\rho_0}\right] \tag{2}$$

where M is the molar mass of ASA, ρ and ρ_0 denote the densities of the solution and reference solvent ([HMIm]Br + MeCN) respectively and m presents the molality of the ASA. The values of apparent molar volume V_ϕ of the investigated solutions are given in Table 3. The plot of V_ϕ for ASA at all different molality of ionic liquid at T = 298.15 K and fixed molality of [HMIm]Br in MeCN (0.1997 mol·kg^{-1}) at different temperature T = (288.15, 298.15, 308.15 and 318.15) K are shown in Figs. 1 and 2, respectively. It is observed that, the apparent molar volumes increase with increasing the ionic liquid concentration. The standard partial molar volume V_φ^0 is often obtained from the extrapolation of the apparent molar volume V_ϕ to an infinite dilution using the following linear equation:

$$V_\phi = V_\phi{}^0 + S_V m \tag{3}$$

where m is the molal concentration of ASA and S_V is the experimental slope indicating of solute–solute interactions [53,54]. The values of $V_\phi{}^0$ and S_V along with their standard errors of parameters and standard deviations of apparent molar volume $\sigma(V_\phi)$ are listed in Table 4. This table shows that the standard partial molar volume, $V_\phi{}^0$ increase with an increase in concentration of ionic liquid and temperature. This behavior indicates that stronger interactions between ASA and [HMIm]Br at high concentration of ionic liquid and temperature. The values of S_V also decrease with increasing the molality of ionic liquid. These values for ASA in MeCN are positive and become more negative in the presence of ionic liquid [HMIm]Br. This behavior denotes the presence of solute–solute interactions between aspirin molecules which become weaker with increasing the concentration of ionic liquid.

The temperature dependence of $V_\phi{}^0$ values can be expressed by the Eq. (4):

$$V_\phi{}^0 = A + BT + CT^2 \tag{4}$$

where A, B and C have been evaluated by the least-square fitting of standard partial molar volumes at different temperatures. Differentiation of Eq. (4) with respect to temperature was done to calculate apparent molar isobaric expansions [55]:

$$E_\phi{}^0 = \left(\frac{\partial V_\phi{}^0}{\partial T}\right)_p = B + 2CT. \tag{5}$$

The calculated values of partial molar isobaric expansions $E_\phi{}^0$ are given in Table 4. The values of the partial molar isobaric expansivity $E_\phi{}^0$ are important indicator solute–solvent interactions. These values are also employed in interpreting of the structure-making or breaking properties of various solutes. Positive expansivity (i.e. increasing volume with increasing temperature) is a characteristic property of non-aqueous solutions of hydrophobic solvation [56]. The $E_\phi{}^0$ values are decreasing with increase in temperature. This may be attributed to the fact that molecular motions get fast through enhancement in temperature and the difference in solvent structure between solvation shell and bulk acetonitrile becomes smaller, and consequently the corresponding effect from the overlap of solvation shells becomes weaker [57,58].

The values of the standard partial molar volumes were used to calculate the isobaric thermal expansion coefficient α according to the following equation [55]:

$$\alpha = \frac{E_\varphi^0}{V_\varphi^0}. \tag{6}$$

The coefficient of thermal expansion (α) (Table 4) is basically a measure for the response of a system's volume to an increase temperature. The larger value gets more sensitive in the volume of the systems versus a change of temperature [59,60].

Table 3
Density, ρ, viscosity, η, speeds of sound, u, refractive index, n_D, molar refraction, R_D, apparent molar volume, V_φ, and apparent molar isentropic compressibility, κ_φ, of ternary (ASA [HMIm]Br + MeCN) solutions at T = (288.15 to 318.15) K.

m ($\mathrm{mol \cdot kg^{-1}}$)	$10^{-3}\rho$ ($\mathrm{kg \cdot m^{-3}}$)	u ($\mathrm{m \cdot s^{-1}}$)	η ($\mathrm{m\,Pa \cdot s}$)	n_D	$10^6 V_\varphi$ ($\mathrm{m^3 \cdot mol^{-1}}$)	$10^{14}\kappa_\varphi$ ($\mathrm{m^3 \cdot mol^{-1} \cdot Pa^{-1}}$)	2 ($\mathrm{m^3 \cdot mol^{-1}}$)
T = 288.15 K				m_{IL} = 0.0000 $\mathrm{mol \cdot kg^{-1}}$			
0.0402	0.789756		0.394	1.3467	132.01		11.14
0.0834	0.792285	1320.33	0.398	1.3476	132.59	0.67	11.19
0.1100	0.793822	1320.59	0.402	1.3483	132.91	0.90	11.23
0.1394	0.795495	1320.82	0.405	1.349	133.25	1.13	11.27
0.1708	0.797242	1321.10	0.408	1.3498	133.74	1.29	11.32
0.2076	0.799277	1321.40	0.412	1.3505	134.13	1.44	11.37
0.2453	0.801312	1321.75	0.416	1.3513	134.64	1.57	11.42
0.2705	0.802661		0.419	1.3519	134.90		11.46
0.3006	0.804272		0.422	1.3527	135.14		11.50
T = 298.15 K							
0.0402	0.778992		0.349	1.3422	133.47		11.16
0.0834	0.781508	1279.68	0.353	1.3431	133.82	0.78	11.22
0.1100	0.783035	1279.93	0.355	1.3439	134.12	0.98	11.26
0.1394	0.784705	1280.15	0.358	1.3446	134.36	1.19	11.30
0.1708	0.786446	1280.41	0.362	1.3453	134.82	1.37	11.34
0.2076	0.788483	1280.72	0.365	1.3462	135.12	1.49	11.40
0.2453	0.790515	1281.03	0.369	1.347	135.59	1.64	11.45
0.2705	0.791870		0.371	1.3477	135.79		11.49
0.3006	0.793487		0.375	1.3484	135.97		11.53
T = 308.15 K							
0.0402	0.776765		0.316	1.3378	134.42		11.18
0.0834	0.778997	1239.35	0.319	1.3388	134.89	0.82	11.24
0.1100	0.780722	1239.55	0.322	1.3397	135.13	1.07	11.29
0.1394	0.782274	1239.72	0.325	1.3404	135.40	1.33	11.33
0.1708	0.783955	1239.98	0.328	1.3412	135.79	1.47	11.38
0.2076	0.786172	1240.28	0.331	1.3423	136.10	1.59	11.44
0.2453	0.787787	1240.53	0.334	1.3431	136.52	1.75	11.49
0.2705	0.789305		0.337	1.3438	136.67		11.53
0.3006	0.791221		0.340	1.3446	136.88		11.57
T = 318.15 K							
0.0402	0.765949		0.292	1.3333	135.41		11.21
0.0834	0.768187	1199.15	0.295	1.3345	135.78	0.89	11.28
0.1100	0.769924	1199.33	0.297	1.3352	136.09	1.17	11.32
0.1394	0.771490	1199.48	0.300	1.3359	136.28	1.42	11.36
0.1708	0.773191	1199.72	0.303	1.3367	136.55	1.54	11.40
0.2076	0.775433	1199.93	0.306	1.3377	136.90	1.73	11.46
0.2453	0.777070	1200.22	0.309	1.3388	137.30	1.84	11.52
0.2705	0.778620		0.311	1.3395	137.49		11.56
0.3006	0.780568		0.314	1.3403	137.66		11.61
T = 288.15 K				m_{IL} = 0.1021 $\mathrm{mol \cdot kg^{-1}}$[b]			
0.0000	0.795976	1324.06	0.403	1.3497			
0.0402	0.798226		0.408	1.3504	137.63		11.36
0.0802	0.800448		0.412	1.3514	137.61		11.42
0.1114	0.802164		0.416	1.352	137.58		11.46
0.1395	0.803704	1324.58	0.420	1.3526	137.55	3.05	11.49
0.1702	0.805378	1324.82	0.423	1.3533	137.53	2.95	11.54
0.2107	0.807567	1325.12	0.428	1.3543	137.50	2.89	11.60
0.2405	0.809168	1325.32	0.432	1.3550	137.47	2.87	11.65
0.2687	0.810675	1325.55	0.436	1.3556	137.46	2.84	11.69
0.3044	0.812572	1325.85	0.440	1.3563	137.41	2.80	11.73
T = 298.15 K							
0.0000	0.785235	1283.58	0.364	1.3450			
0.0402	0.787489		0.370	1.3459	138.13		11.38
0.8020	0.789717		0.373	1.3467	138.07		11.44
0.1114	0.791437		0.376	1.3473	138.03		11.48
0.1395	0.792982	1284.04	0.380	1.3479	137.99	3.16	11.51
0.1702	0.794661	1284.25	0.383	1.3487	137.96	3.07	11.56
0.2107	0.796861	1284.52	0.387	1.3495	137.89	3.00	11.61
0.2405	0.798467	1284.74	0.390	1.3503	137.86	2.95	11.66
0.2687	0.799987	1284.96	0.393	1.3507	137.81	2.91	11.70
0.3044	0.801886	1285.26	0.396	1.3515	137.79	2.86	11.74
T = 308.15 K							
0.0000	0.774510	1243.60	0.333	1.3402			
0.0402	0.776765		0.336	1.3412	138.72		11.40
0.0802	0.778997		0.340	1.3421	138.60		11.45
0.1114	0.780722		0.343	1.3427	138.52		11.50
0.1395	0.782274	1243.98	0.346	1.3433	138.43	3.30	11.53
0.1702	0.783955	1244.20	0.349	1.344	138.41	3.17	11.57
0.2107	0.786172	1244.46	0.354	1.3448	138.25	3.07	11.63
0.2405	0.787787	1244.67	0.356	1.3454	138.19	3.01	11.67
0.2687	0.789305	1244.90	0.359	1.3459	138.19	2.96	11.71

(continued on next page)

Table 3 (*continued*)

m $(\mathrm{mol\cdot kg^{-1}})$	$10^{-3}\rho$ $(\mathrm{kg\cdot m^{-3}})$	u $(\mathrm{m\cdot s^{-1}})$	η (m Pa·s)	n_D	10^6V_φ $(\mathrm{m^3\cdot mol^{-1}})$	$10^{14}\kappa_\varphi$ $(\mathrm{m^3\cdot mol^{-1}\cdot Pa^{-1}})$	*2* $(\mathrm{m^3\cdot mol^{-1}})$
0.3044	0.791221	1245.20	0.362	1.3467	138.10	2.89	11.75
$T = 318.15$ K							
0.0000	0.763695	1203.64	0.306	1.3354			
0.0402	0.765949		0.309	1.3365	139.39		11.42
0.0802	0.768187		0.313	1.3374	139.11		11.47
0.1114	0.769924		0.315	1.3380	138.88		11.51
0.1395	0.771490	1203.96	0.317	1.3386	138.66	3.44	11.55
0.1702	0.773191	1204.15	0.320	1.3393	138.52	3.28	11.59
0.2107	0.775433	1204.37	0.324	1.3401	138.25	3.15	11.65
0.2405	0.777070	1204.54	0.327	1.3407	138.11	3.09	11.69
0.2687	0.778620	1204.74	0.330	1.3412	137.98	3.01	11.73
0.3044	0.780568	1204.95	0.333	1.3419	137.81	2.95	11.76
$T = 288.15$ K				$m_{IL} = 0.1997\ \mathrm{mol\cdot kg^{-1}}$			
0.0000	0.803310	1327.31	0.424	1.3525			
0.0437	0.805731		0.431	1.3539	138.06		11.59
0.0827	0.807870		0.435	1.3548	138.00		11.65
0.1137	0.809565		0.438	1.3554	137.97		11.69
0.1404	0.811018	1327.56	0.441	1.3560	137.89	3.46	11.73
0.1709	0.812665	1327.71	0.444	1.3567	137.82	3.39	11.77
0.2105	0.814798	1327.92	0.448	1.3575	137.74	3.32	11.82
0.2437	0.816568	1328.11	0.451	1.3582	137.68	3.27	11.87
0.2742	0.818190	1328.28	0.454	1.3589	137.63	3.24	11.92
0.2990	0.819499	1328.42	0.458	1.3595	137.60	3.22	11.95
$T = 298.15$ K							
0.0000	0.792661	1287.02	0.383	1.3482			
0.0437	0.795078		0.388	1.3492	138.89		11.60
0.0827	0.797212		0.391	1.3501	138.86		11.66
0.1137	0.798902		0.395	1.3507	138.85		11.70
0.1404	0.800353	1287.34	0.398	1.3513	138.76	3.55	11.74
0.1709	0.801998	1287.50	0.401	1.3521	138.68	3.47	11.79
0.2105	0.804132	1287.75	0.405	1.3528	138.56	3.37	11.84
0.2437	0.805899	1287.94	0.408	1.3534	138.51	3.33	11.88
0.2742	0.807532	1288.11	0.411	1.3541	138.37	3.29	11.93
0.2990	0.808863	1288.26	0.414	1.3548	138.22	3.25	11.97
$T = 308.15$ K							
0.0000	0.781960	1247.26	0.350	1.3434			
0.0437	0.784372		0.353	1.3445	139.76		11.62
0.0827	0.786504		0.356	1.3455	139.68		11.68
0.1137	0.788204		0.359	1.346	139.49		11.72
0.1404	0.789655	1247.58	0.363	1.3467	139.41	3.67	11.76
0.1709	0.791309	1247.77	0.366	1.3474	139.24	3.54	11.80
0.2105	0.793449	1248.02	0.369	1.3482	139.10	3.43	11.86
0.2437	0.795245	1248.18	0.372	1.3489	138.87	3.38	11.90
0.2742	0.796883	1248.37	0.375	1.3497	138.74	3.32	11.95
0.2990	0.798209	1248.48	0.378	1.3502	138.65	3.31	11.99
$T = 318.15$ K							
0.0000	0.771215	1207.32	0.322	1.3388			
0.0437	0.773612		0.324	1.3397	141.01		11.63
0.0827	0.775739		0.327	1.3407	140.76		11.69
0.1137	0.777439		0.330	1.3413	140.46		11.73
0.1404	0.778908	1207.67	0.333	1.3419	140.10	3.75	11.77
0.1709	0.780566	1207.85	0.335	1.3426	139.89	3.61	11.82
0.2105	0.782734	1208.07	0.339	1.3434	139.53	3.48	11.87
0.2437	0.784532	1208.22	0.342	1.3442	139.31	3.44	11.92
0.2742	0.786189	1208.37	0.345	1.3449	139.09	3.39	11.96
0.2990	0.787538	1208.50	0.348	1.3455	138.89	3.34	12.00
$T = 288.15$ K				$m_{IL} = 0.2890\ \mathrm{mol.kg^{-1}}$			
0.0000	0.811651	1330.89	0.424	1.3497			
0.0418	0.813915		0.434	1.3546	139.34		11.70
0.0796	0.815965		0.437	1.3554	139.01		11.77
0.1117	0.817693		0.441	1.356	138.83		11.81
0.1414	0.819295	1331.03	0.444	1.3566	138.61	3.77	11.84
0.1695	0.820800	1331.10	0.448	1.3572	138.47	3.73	11.89
0.2169	0.823343	1331.20	0.452	1.3583	138.14	3.67	11.95
0.2373	0.824436	1331.26	0.455	1.3586	138.01	3.65	11.99
0.2730	0.826328	1331.34	0.458	1.3593	137.87	3.62	12.03
0.3117	0.828384	1331.43	0.462	1.3602	137.64	3.60	12.07
$T = 298.15$ K							
0.0000	0.801045	1290.88	0.389	1.3450			
0.0418	0.803310		0.393	1.3500	140.04		11.72
0.0796	0.805358		0.396	1.3507	139.76		11.78
0.1117	0.807079		0.399	1.3515	139.67		11.83
0.1414	0.808676	1291.09	0.402	1.3521	139.48	3.87	11.86
0.1695	0.810170	1291.21	0.406	1.3527	139.42	3.81	11.91
0.2169	0.812701	1291.39	0.410	1.3536	139.13	3.74	11.96

Table 3 (*continued*)

m $(\mathrm{mol\cdot kg^{-1}})$	$10^{-3}\rho$ $(\mathrm{kg\cdot m^{-3}})$	u $(\mathrm{m\cdot s^{-1}})$	η (m Pa·s)	n_D	$10^6 V_\varphi$ $(\mathrm{m^3\cdot mol^{-1}})$	$10^{14}\kappa_\varphi$ $(\mathrm{m^3\cdot mol^{-1}\cdot Pa^{-1}})$	2 $(\mathrm{m^3\cdot mol^{-1}})$
0.2373	0.813791	1291.47	0.412	1.354	138.99	3.71	12.01
0.2730	0.815687	1291.61	0.416	1.3547	138.79	3.67	12.05
0.3117	0.817712	1291.74	0.420	1.3554	138.68	3.64	12.08
$T = 308.15$ K							
0.0000	0.790450	1251.00	0.371	1.3402			
0.0418	0.792705		0.372	1.3452	141.15		11.73
0.0796	0.794747		0.376	1.3461	140.80		11.79
0.1117	0.796474		0.380	1.3469	140.54		11.84
0.1414	0.798058	1251.37	0.383	1.3475	140.46	3.98	11.88
0.1695	0.799562	1251.48	0.386	1.3481	140.26	3.91	11.92
0.2169	0.802089	1251.66	0.390	1.3491	139.97	3.84	11.98
0.2373	0.803183	1251.74	0.392	1.3496	139.79	3.80	12.03
0.2730	0.805075	1251.90	0.396	1.3504	139.60	3.76	12.07
0.3117	0.807128	1252.05	0.400	1.3511	139.34	3.74	12.10
$T = 318.15$ K							
0.0000	0.779781	1211.27	0.342	1.3354			
0.0418	0.782025		0.343	1.3407	142.31		11.75
0.0796	0.784055		0.346	1.3415	142.01		11.81
0.1117	0.785773		0.349	1.3421	141.73		11.85
0.1414	0.787371	1211.65	0.352	1.3427	141.39	4.07	11.89
0.1695	0.788859	1211.80	0.355	1.3434	141.31	3.99	11.94
0.2169	0.791385	1212.01	0.359	1.3444	140.95	3.91	11.99
0.2373	0.792469	1212.11	0.361	1.3448	140.82	3.87	12.04
0.2730	0.794355	1212.26	0.364	1.3456	140.62	3.84	12.08
0.3117	0.796399	1212.45	0.368	1.3464	140.36	3.78	12.12

Standard uncertainties u(T) = 0.01 K, u(m) = ±2.10^{-4} mol·kg^{-1}, u(d) = ±5.10^{-3} kg·m^3, u(u) = ±0.01 m·s^{-1}, u$_c$(η) = ±0.005 mPa·s and u$_c$(n_D) = ±1.10^{-4} and the estimated uncertainty u$_c$ (V_φ) = ±0.06.10^{-6} m^3.mol^{-1},u$_c$ (κ_φ) = ±0.02.10^{-14}m^{3}mol.Pa^{-1}, u$_c$ (R_D) = ±0.04.10^{-6} m^3.mol^{-1}, respectively.

[b] m_{IL} is the molality of ASA where the solvent is (MeCN + [HMIm]Br).

According to Hepler's equation [61]:

$$\left({}^{\partial C_p}\!\big/_{\partial P}\right)_T = -T\left({}^{\partial^2 V_\varphi^o}\!\big/_{\partial T^2}\right)_p = -2CT. \tag{7}$$

The sign of second derivatives of the standard partial molar volume with respect to the temperature $\left(\partial^2 V_\phi{}^0/\partial T^2\right)_p$ reflect the structure making and breaking ability of a solute in the solution [62]. If the sign of $\left(\partial^2 V_\phi{}^0/\partial T^2\right)_p$ is negative, the solute is a structure breaker; otherwise, it is a structure maker. The values of $\left(\partial^2 V_\phi{}^0/\partial T^2\right)_p$ related to investigated solutions summarized in Table 4 have positive values. Therefore, the ASA is predominantly a structure maker and this tendency is enhanced with increasing [HMIm]Br concentration. This behavior may be explained the favorable solvation of ASA molecules by ionic liquid.

The transfer volumes $\Delta_{tr}V_\phi{}^0$ of the ASA from acetonitrile to ([HMIm]Br + MeCN) solutions were calculated as follows [55]:

$$\Delta_{tr}V_\phi{}^0 = V_\phi{}^0(\text{in [HMIm]Br} + \text{MeCN}) - V_\phi{}^0(\text{in MeCN}). \tag{8}$$

The types of the interaction present in the studied solutions are as the following:

(a) Polar–ionic group interactions between the COOH and OCH$_3$ groups of ASA, and the ions of [HMIm]Br. (b) Polar–polar group interactions between the Polar groups of ASA and the imidazolium ring of [HMIm]Br through the hydrogen bonding. (c) Polar–nonpolar group

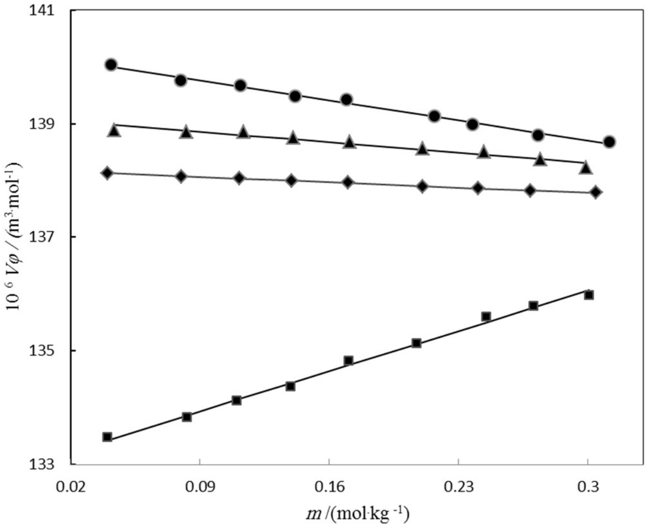

Fig. 1. Apparent molar volumes of ASA in several concentrations of ([HMIm]Br + MeCN) solutions at T = 298.15 K: (♦) 0.1021; (■) 0.0000; (▲ (0.1997; (●) 0.2890 mol·kg^{-1}.

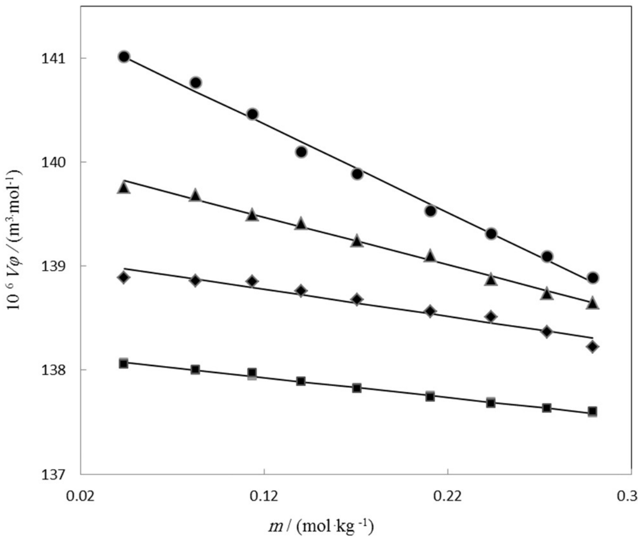

Fig. 2. Apparent molar volumes of ASA in ([HMIm]Br + MeCN) solutions with 0.1997 molality at different temperatures: at (♦) 298.15 K; (■) 288.15 K; (▲) 308.15 K; (●) 318.15 K.

Table 4

The standard partial molar volumes, $V_{\varphi}{}^{0}$, and Slopes, S_V, transfer volumes, $\Delta V_{tr}{}^{0}$, apparent molar isobaric expansions, $E_{\phi}{}^{0}$, Hepler's constant $(\partial^2 V_{\phi}{}^{0}/\partial T^2)$ and standard deviations, $\sigma(V_{\varphi})$ of ASA in different molalities of [HMIm]Br in MeCN solutions at $T = (288.15$ to $318.15)$ K.

m_{IL}[a] (mol·kg^{-1})	T (K)	$10^6V_{\varphi}^0$ (m^3.mol^{-1})	10^6S_v (m^3·mol^{-1}·kg)	$10^6\sigma(V_{\varphi})$	$10^6\Delta_{tr}V_{\varphi}^0$ (m^3·mol^{-1})	10^6E_0 (m^3·mol^{-1}·K^{-1})	$10^4\alpha$ (K^{-1})	$10^6(\partial^2V_{\varphi}^0/\partial T^2)$
0.0000								
	288.15	132.43 ± 0.03	9.88 ± 0.17	0.06	–	0.151	1.139	0.0020
	298.15	133.02 ± 0.05	10.11 ± 0.27	0.07	–	0.127	0.957	
	308.15	134.07 ± 0.04	9.64 ± 0.23	0.06	–	0.104	0.775	
	318.15	135.06 ± 0.03	8.85 ± 0.18	0.05	–	0.08	0.595	
0.1021								
	288.15	137.67 ± 0.01	−0.82 ± 0.03	0.01	5.24	0.043	3.154	0.0013
	298.15	138.18 ± 0.01	−1.32 ± 0.03	0.01	5.16	0.056	4.083	
	308.15	138.79 ± 0.03	−2.34 ± 0.13	0.03	4.72	0.069	5.001	
	318.15	139.56 ± 0.04	−5.98 ± 0.2	0.05	4.53	0.082	5.905	
0.1997								
	288.15	138.16 ± 0.01	−1.91 ± 0.06	0.02	5.73	0.074	5.322	0.0022
	298.15	139.09 ± 0.04	2.60 ± 0.23	0.04	6.07	0.095	6.832	
	308.15	140.02 ± 0.03	−4.57 ± 0.15	0.03	5.95	0.117	8.322	
	318.15	141.38 ± 0.05	−8.48 ± 0.24	0.05	6.32	0.138	9.763	
0.2890								
	288.15	139.52 ± 0.04	−6.19 ± 0.19	0.05	7.09	0.065	4.657	0.0025
	298.15	140.22 ± 0.04	−5.05 ± 0.19	0.05	7.20	0.089	6.380	
	308.15	141.35 ± 0.04	−6.46 ± 0.19	0.05	7.28	0.114	8.063	
	318.15	142.54 ± 0.05	−7.16 ± 0.26	0.07	7.48	0.138	9.714	

[a] m_{IL} is the molality of ILwhere the solvent is (MeCN + [HMIm]Br).

interactions between the COOH, COCH$_3$ group of ASA and the nonpolar groups (alkyl chain) of [HMIm]Br. (d) Nonpolar–nonpolar groups interactions between the nonpolar groups of ASA and alkyl group attached to imidazolium ring of [HMIm]Br.

The values of $\Delta_{tr}V_{\phi}{}^{0}$ obtained by this procedure are summarized in Table 4. According to the cosphere overlap model [63], the values of $\Delta_{tr}V_{\phi}{}^{0}$ have positive values which indicate dominance of the polar–polar and ion–polar interactions between ASA and the [HMIm]Br.

The transfer volumes of solutions may also be displayed by the McMillan Mayer theory of solutions [64], which permits the formal separation of the effects due to interactions between the pairs of the solute molecules and those due to interactions between three or more solute molecules by the following equation:

$$\Delta V_{tra}^{0} = 2V_{AI}m_I + 3V_{AII}m_I^2 + \ldots. \tag{9}$$

where A stands for the aspirin and I stands for the ionic liquid. V_{AI} and V_{AII} are the pair and triplet volumetric interaction parameters, respectively. These volumetric interaction parameters were evaluated by the least square fitting method and given in Table 5. The V_{AI} and V_{AII} values for ASA are positive and negative, respectively. The large positive V_{AI} values suggest that the interactions between ASA and ionic liquid are mainly pairwise.

Based on the speed of sound and density values reported in Table 3, the isentropic compressibilities, $\kappa_s(Pa^{-1})$ were calculated from the Laplace–Newton's equation [51]:

$$\kappa_s = \frac{1}{\rho u^2}. \tag{10}$$

The variation of κ_s values as a function of ASA concentration and temperature are depicted in Figs. 3 and 4, respectively. The values of κ_s are linear in all concentrations. The isentropic compressibility is the sum of two contributions, κ_{s1} (solvent intrinsic) and κ_{s2} (solute intrinsic). The κ_{s1} is the isentropic compressibility due to the compression of solvent (acetonitrile) and κ_{s2} is compressibility due to the compression of the solvation shell of solute (ASA and IL) or penetration of solvent molecules in to IL free volume. The κ_s values are linear and increase with an increase in temperature of binary and ternary systems due to an increase in thermal agitation, resulting in the solvent molecules being release from solute thereby increasing the solution volume making the solution more compressible. For the binary and ternary systems κ_s increase with an increase in contribution of solvent due to the combined effect of desolvation of ions and contributing to the structure of acetonitrile molecules because (solvent intrinsic) dominates over the (solute intrinsic) effect.

The apparent molar isentropic compressibility κ_{φ} is computed from the following relation [65]:

$$\kappa_{\phi} = \frac{(\kappa_s\rho_0 - \kappa_{s0}\rho)}{m\rho\rho_0} + \frac{\kappa_s M}{\rho}. \tag{11}$$

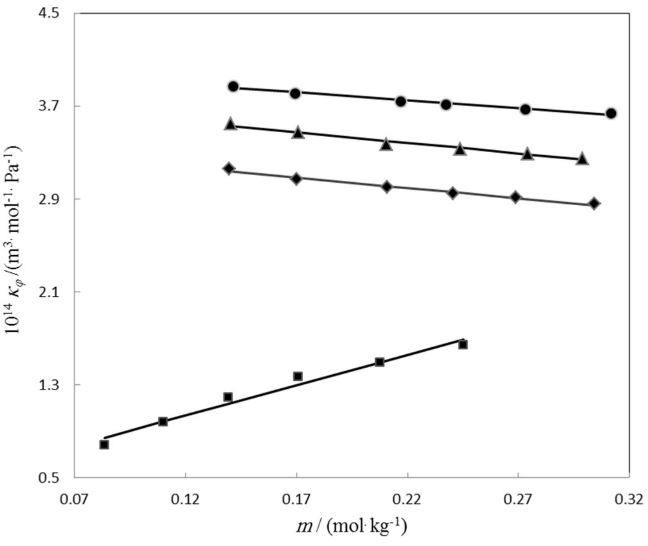

Fig. 3. The isentropic compressibility of ASA in several concentrations of ([HMIm]Br + MeCN) solutions at $T = 298.15$ K: (♦) 0.1021; (■) 0.0000; (▲ (0.1997; (●) 0.2890 mol·kg^{-1}.

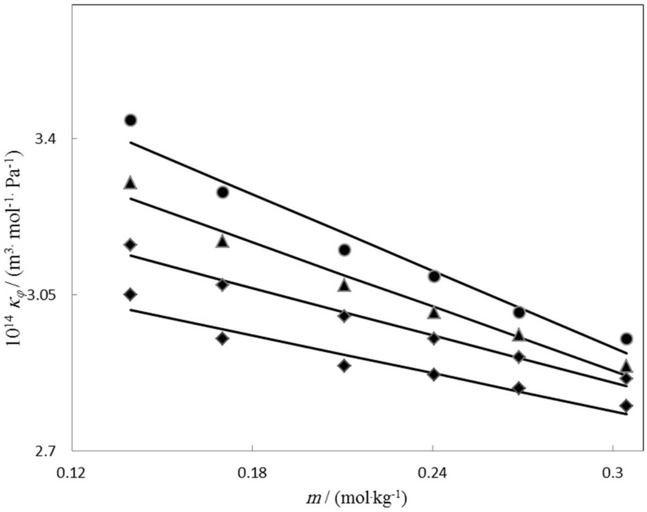

Fig. 4. The isentropic compressibility of ASA in ([HMIm]Br + MeCN) solutions with 0.1021 molality at different temperatures: at (♦) 288.15 K; (■) 298.15 K; (▲) 308.15 K; (●) 318.15 K.

where κ_{s0} and κ_s are the isentropic compressibility of pure solvent and mixture, respectively[35].

The limiting value of isentropic compressibility κ_φ^0 is often obtained from the extrapolation of the κ_φ to an infinite dilution using the following linear equation:

$$\kappa_\varphi = \kappa_\varphi^0 + S_k m. \tag{12}$$

The parameter κ_φ^0 is the limiting value of apparent molar isentropic compressibility of ASA at each experimental temperature and S_k is the experimental slopes indicative of solute–solute interactions [66]. The values of κ_φ shown in Table 3. The values of κ_φ^0 and S_k obtained for each mixture at the experimental temperatures are listed in Table 5.

In dilute concentration of ASA in acetonitrile observed the negative values. For the binary system these values increase with an increase in temperature, i.e., the (ion + solvent) interaction of both systems are weaker and therefore acetonitrile molecules are released into bulk solution, thereby making the solvent more compressible.

Weak and strong attractive interactions between solute and solvent cause to the positive and negative κ_φ values. For the binary system κ_φ values are small and increase with an increase in temperature, i.e., the (ion + solvent) interaction of both systems are weaker and therefore acetonitrile molecules are released into bulk solution, thereby making the solvent more compressible. The κ_φ^0 values are a result of two efforts: solvent intrinsic compressibility due to the intermolecular free which makes the solution more compressible (positive effect) and solute intrinsic penetration of the solvent molecules into the intra-ionic free space (negative effect) [67].

3.2. Viscosity B-coefficients

The measured viscosities η for (ASA + [HMIm]Br + MeCN) ternary solutions at different temperatures T = (288.15, 298.15, 308.15 and 318.15) K are tabulated in Table 3. The results obtained from this table show an increase in the viscosities of the solutions with an increase in the concentration of the ionic liquid. This is due to the fact that with the increase of ionic liquid concentration, the number of collision between the molecules increases resulting in a loss of kinetic energy, therefore, the molecules tend to stack together to induce the increase in the viscosity. The plot of viscosities of ASA at all different molality of ionic liquid [HMIm]Br in MeCN at T = 298.15 K and fixed molality of [HMIm]Br (0.1997 mol·kg⁻¹) at different temperature T = (288.15, 298.15, 308.15 and 318.15) K are shown in Figs. 5 and 6, respectively.

Table 5
Pair volumetric interaction parameters, V_{AI}, and triplet volumetric interaction parameters, V_{AII} of ASA in ([HMIm]Br + MeCN) solutions at T = (288.15 to 318.15) K.

T (K)	$10^6 V_{AI}$ (m³·mol⁻²·kg)	$10^6 V_{AII}$ (m³·mol⁻³·kg²)
288.15	27.18	−53.64
298.15	27.73	−39.20
308.15	25.20	−29.87
318.15	25.17	−28.66

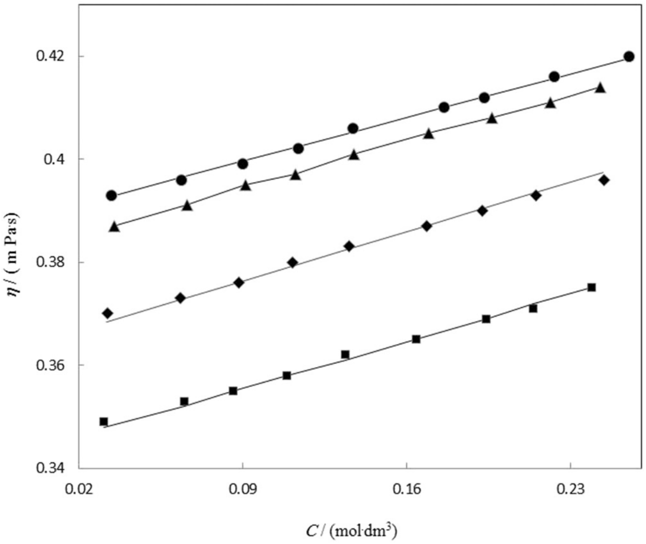

Fig. 5. Viscosity of ASA in several concentrations of ([HMIm]Br + MeCN) solutions at T = 298.15 K: (♦) 0.1021; (■) 0.0000; (▲ (0.1997; (●) 0.2890 mol·kg⁻¹.

The Jones–Dole empirical Eq. (13) describes the relative viscosities of electrolyte solutions as functions of their concentrations [68]

$$\frac{\eta}{\eta_0} = 1 + Ac^{1/2} + Bc. \tag{13}$$

The A-coefficient (also called Falkenhagen coefficient, reflecting solute–solute interactions) can be calculated theoretically but are usually small (negligible for nonelectrolytes) [69]. Generally, viscosity B-coefficients reflect the solute–solvent interactions. In fact, when

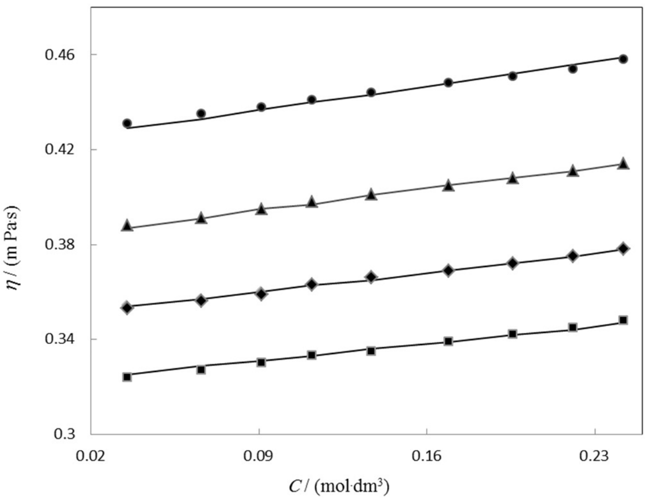

Fig. 6. Viscosity of ASA in ([HMIm]Br + MeCN) solutions with 0.1997 molality at different temperatures: at (♦) 298.15 K; (■) 288.15 K; (▲) 308.15 K; (●) 318.15 K.

A-coefficients are neglected in Eq. (13), this equation is equivalent to the under viscosity equation:

$$\frac{\eta}{\eta_0} = 1 + Bc \tag{14}$$

where η and η_0 are the viscosities of (ASA + [HMIm]Br + MeCN) ternary solutions and reference solvent ([HMIm]Br + MeCN), respectively, c is the molar concentration of ASA in the ternary solution. The viscosity *B*-coefficients were obtained from the slope of linear plot of $(\eta/\eta_0 - 1)$ vs. c by the least square method. The calculated viscosity *B*-coefficients and the corresponding standard deviations of viscosity data $\sigma(\eta)$ for all ternary solutions (ASA + [HMIm]Br + MeCN) are given in Table 7. The viscosity *B*-coefficient is valuable to provide information concerning the solvation of the solutes and their effects on the structure of the solvent in the near environment of the solute molecules. The viscosity *B*-coefficient is also a measure of the effective solvodynamic volume of solvated species and depends on the basis of shape, size and solute–solvent interactions [70]. The values of viscosity *B*-coefficients decrease with increasing in concentration of ionic liquid. Positive values of *B*-coefficients suggest the presence of solute–solvent interactions, but these types of interactions are weakened with an increase of ionic liquid concentration, indicating the dominance of interactions between ASA and ionic liquid. In general, It can be concluded that the addition of [HMIm]Br to binary solutions (ASA + MeCN) lead to preferential interaction between ionic liquid with ASA molecules and strengthening in structure making tendency of the solutions studied.

Solvation number of a solute can be interpreted in term of $\left(B/V_\phi{}^0\right)$. The calculated solvation number $\left(B/V_\phi{}^0\right)$ of ASA in ([HMIm]Br + MeCN) solutions are listed in Table 7. The high $\left(B/V_\phi{}^0\right)$ value is an indication of the formation of a primary salvation shell and the $\left(B/V_\phi{}^0\right)$ ratio lies between 0 and 2.5 for unsolvated spherical species [71]. The observed values of solvation number <2.5 at all temperatures indicate that ASA are not very solvated because a value higher than solvation number >2.5 is an indication of solvated spherical species The values $B/V_\phi{}^0$ are lower than 2.5 and decrease with increasing concentration of [HMIm]Br indicating desolvation of ASA by the ionic liquid.

The viscosities data are analyzed on the basis of transition state treatment of relative viscosity of suggested by Feakins et al. [72]. The viscosity *B*-coefficient in terms of this theory is given by following equation:

$$B = \left(\overline{V}_1^0 - \overline{V}_2^0\right) + \overline{V}_1^0\left(\frac{\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}}{RT}\right) \tag{15}$$

where $\left(\overline{V}_{_1}^0 = \sum \frac{x_i M_i}{\rho}\right)$ is the mean volume of the solvent and $\left(\overline{V}_2^0 = V_\varphi^0\right)$ is the limiting partial molar volume of the pure solute. The term $\overline{V}_1^0$ is the molar volume of the pure solvent. The terms x_i and M_i denote, the mole fractions and molar masses of solvent, d is the density of the reference solvent ([HMIm]Br + MeCN). The free energy of activation per mole of the solvent $\Delta\mu_1^{0\neq}$ and $\Delta\mu_2^{0\neq}$ is calculated according to Eyring's simple model by following equation listed in Table 7

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT \ln \frac{\eta_1 V_1^0}{hN_A} \tag{16}$$

$$\Delta\mu_2^{0\neq} = \Delta G_2^{0\neq} = \frac{RT}{V_1^0}\left[B - \left(\overline{V}_1^0 - \overline{V}_2^0\right)\right] \tag{17}$$

where h is the Planck constant, N_A is the Avogadro number, η_0 is the viscosity of the solvent, and the other symbols have their usual meanings [72]. The values of $\Delta\mu_1^{0\neq}$ and $\Delta\mu_2^{0\neq}$ are listed in Table 7. It is clear from Table 7 that the values of $\Delta\mu_2^{0\neq}$ are positive and larger than $\Delta\mu_1^{0\neq}$ indicating stronger interactions between solute (ASA) and cosolute (ionic liquid) and formation of the transition state is less favored in the presence of ionic liquid. This means that formation of transition state is accompanied by the rupture and distortion of the intermolecular bonds in solvent structure. The values of $\Delta\mu_2^{0\neq}$ are smaller at high concentrations of ionic liquid. This implies that structure making ability of ASA intensified with increase in ionic liquid concentration. The calculated viscosity *B*-coefficients and positive activation free energies of the solvent $\Delta\mu_1{}^{0\neq}$ and solute $\Delta\mu_2{}^{0\neq}$ indicated that the presence of solute–cosolute interactions and the structure making effect of ionic liquid on the acetonitrile

Table 6
The limiting value of isentropic compressibility, κ_φ^0, slope, S_k and standard deviations, $\sigma(\kappa_\varphi)$, of ASA in different molalities of ([HMIm]Br + MeCN) solutions at $T = (288.15$ to $318.15)$ K.

m_{IL}[a] (mol·kg^{-1})	T (K)	$10^{14}\kappa_\varphi^0$ (m^3·mol^{-1}·Pa^{-1})	$10^{14}S_k$ (m^3·mol^{-2}·kg·Pa^{-1})	$10^{14}\sigma(\kappa_\varphi)$
0.0000				
	288.15	0.29	5.48	0.07
	298.15	0.41	5.21	0.06
	308.15	0.45	5.55	0.09
	318.15	0.52	5.68	0.09
0.1021				
	288.15	3.21	−1.42	0.02
	298.15	3.38	−1.77	0.02
	308.15	3.60	−2.40	0.03
	318.15	3.79	−2.87	0.04
0.1997				
	288.15	3.65	−1.49	0.02
	298.15	3.78	−1.81	0.02
	308.15	3.93	−2.18	0.04
	318.15	4.05	−2.44	0.04
0.2890				
	288.15	3.90	−1.03	0.01
	298.15	4.05	−1.35	0.02
	308.15	4.16	−1.43	0.02
	318.15	4.28	−1.66	0.02

[a] m_{IL} is the molality of ILwhere the solvent is (MeCN + [HMIm]Br).

Table 7
The viscosity *B*-coefficients, free energy of activation per mole of solvent $(\Delta\mu_1{}^{0\neq})$ and the solute $(\Delta\mu_2{}^{0\neq})$ and solvation number of ASA in different molalities of [HMIm]Br in MeCN solutions at $T = (288.15$ to $318.15)$ K.

m_{IL} (mol·kg^{-1})	T (K)	B (dm^3 mol^{-1})	$\Delta\mu_1^{o\ *}$ (KJ·mol^{-1})	$\Delta\mu_2^{o\ *}$ (KJ·mol^{-1})	$^B/_{V_\varphi^0}$
0.0000					
	288.15	0.376 ± 0.005	–	–	2.74
	298.15	0.375 ± 0.003	–	–	2.71
	308.15	0.368 ± 0.005	–	–	2.65
	318.15	0.359 ± 0.005	–	–	2.58
0.1021					
	288.15	0.373 ± 0.004	9.53	27.16	2.84
	298.15	0.371 ± 0.003	9.65	27.37	2.82
	308.15	0.368 ± 0.005	9.76	27.53	2.74
	318.15	0.363 ± 0.002	9.89	27.78	2.66
0.1997					
	288.15	0.337 ± 0.003	9.67	28.68	2.45
	298.15	0.335 ± 0.003	9.79	29.14	2.41
	308.15	0.334 ± 0.004	9.91	29.61	2.39
	318.15	0.327 ± 0.005	10.00	29.75	2.33
0.2890					
	288.15	0.321 ± 0.003	9.72	27.79	2.30
	298.15	0.312 ± 0.003	9.84	27.05	2.23
	308.15	0.307 ± 0.004	10.01	28.44	2.17
	318.15	0.299 ± 0.004	10.21	28.56	2.10

solvent which these types of interactions are intensifier with an increase of ionic liquid concentration.

3.3. Refractometric results

Experimental refractive index data n_D for (ASA + [HMIm]Br + MeCN) ternary solutions were measured as a function of the ionic liquid concentration at $T = (288.15 \text{ to } 318.15)$ K. The values of measured n_D were tabulated in Table 3.

The molar refraction R_D is calculated using Lorentz–Lorenz equation [73] according to

$$R_D = \left[\frac{n_D - 1}{n_D^2 + 2}\right]\left(\sum_{i=1}^{3}\frac{x_i M_i}{\rho}\right) \quad (18)$$

where x_i and M_i is the mole fraction and molecular weight of components, respectively and ρ is density of (ASA + [HMIm]Br + MeCN) solutions at a fixed concentration of [HMIm]Br. The calculated molar refractions of the investigated solutions are given in Table 3. The plot of R_D values in all different molality of ionic liquid ([HMIm]Br + MeCN) at $T = 298.15$ K and fixed molality of [HMIm]Br ($0.1997 \text{ mol}\cdot\text{kg}^{-1}$) at different temperature $T = (288.15, 298.15, 308.15 \text{ and } 318.15)$ K are shown in Figs. 7 and 8, respectively. Since R_D value is directly proportional to molecular polarizability and therefore this quantity is a measure and ability of the molecular orbitals to deform under an electrical field [74]. Furthermore, when the structure of a molecule becomes more complex, its electron cloud becomes more decentralized, and the polarizability of the molecule increased. As it can be seen from this table, the R_D values increase with increasing amount of [HMIm]Br in the ternary solutions studied due to its electron cloud becomes more decentralized which indicating high polarizability of ASA in the presence of [HMIm]Br.

4. Conclusions

Densities, speeds of sound, viscosities and Refractive indices for the ternary solutions of (ASA + [HMIm]Br + MeCN) have been measured at different temperatures $T = (288.15, 298.15, 308.15 \text{ and } 318.15)$ K. The calculated volumetric and acoustic parameters such as standard apparent molar volumes $V_\phi{}^0$, transfer volumes $\Delta_{tr}V_\varphi{}^0$ and the limiting value of apparent molar isentropic compressibility κ_φ^0 indicating dominance of polar–polar and ion–polar interactions between the ASA and the ionic liquid. The decrease of the solvation numbers and expansivities with increase in temperature suggest that the solute–solvent interactions are intensified as temperature increases.

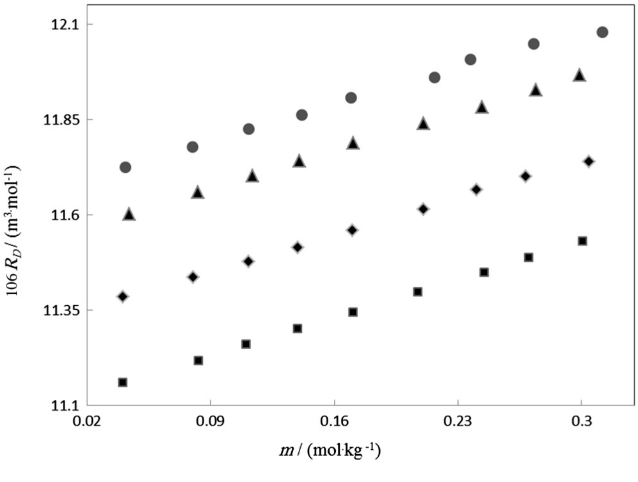

Fig. 7. The molar refraction R_D of ternary (ASA [HMIm]Br + MeCN) solutions at $T = 298.15$ K in several concentrations of the ionic liquid : (♦) 0.0000; (■) 0.1021; (▲ (0.1997; (●) 0.2890 $\text{mol}\cdot\text{kg}^{-1}$.

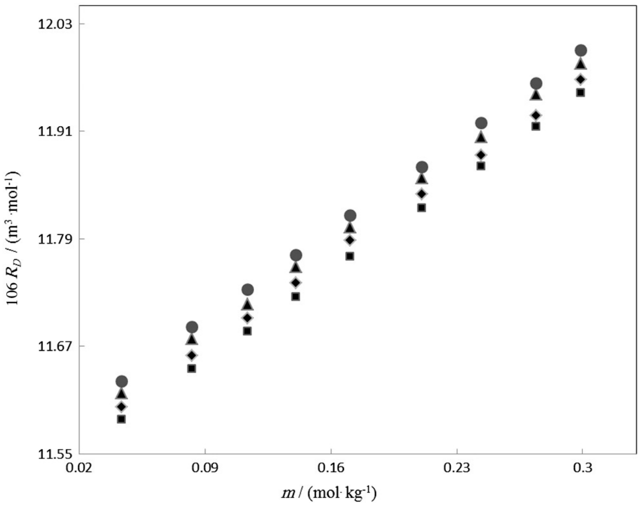

Fig. 8. The molar refraction R_D of ternary (ASA[HMIm]Br + MeCN) solutions with 0.1997 molality of the ionic liquid at different temperatures: at (♦) 298.15 K; (■) 288.15 K; (▲) 308.15 K; (●) 318.15 K.

The positive κ_φ values are attributed to the weak attractive interactions between ASA and acetonitrile. More positive value of κ_φ at high concentration of the ionic liquid shows that strong interaction between ASA and IL cause that acetonitrile molecules to be released into bulk solution, thereby making the solvent more compressible.

The viscosity B-coefficient, free energy of activation per mole of the solvent $\Delta\mu_1^{0\,*}$ and the solute $\Delta\mu_2^{0\,*}$ and molar refraction R_D at infinite dilution provides important information relating to interactions of ASA with the ionic liquid. In general, this ionic liquid has a desolvation effect on the non–aqueous ASA solutions which was enhanced with increasing the ionic liquid concentrations.

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