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Thermodynamic evaluation of imidazolium based ionic liquids with thiocyanate anion as effective solvent to thiophene extraction

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ABSTRACT

In order to have deep insight on the molecular interactions between thiophene (TS) and ionic liquids, the density, speed of sound and refractive index of binary liquid mixture of TS with 1-hexyl-3-methylimidazolium thiocyanate [HMIM][SCN], and 1-octyl-3-methylimidazolium thiocyanate [OMIM][SCN] at $T = (288.15 \text{ to } 303.15)$ K and at atmospheric pressure have been measured in dilute region of TS. Various thermophysical parameters including partial molar volumes, $\overline{v}_{m,i}$, apparent molar volumes, V , standard partial molar volumes V_ϕ^0, partial molar isentropic compressibility, κ_ϕ^0, excess molar volumes, V^E, excess partial molar volumes, $\overline{v}_{m,i}^E$, and molar refractions, R_D, have been calculated using these data. The densitometric and refractometric non-intrinsic contributions to the partial molar volume, θ^d and θ^r have been obtained using the measured experimental data. Also, interaction volume, V_{int}, and cavity volume, V_{cav}, have been calculated from scaled particle theory (SPT). The results demonstrate that the ionic liquids with shorter alkyl chain length interact effectively with thiophene as according to the calculated interaction volumes and excess partial molar volumes. One would expect that the extraction efficiency of [HMIM][SCN] is slightly better than the other ionic liquid. The calculated quantities such as $\overline{v}_{m,i}^E$ and V_{int} can be used to predict extraction capability of these ionic liquids to thiophene extraction from fuel.

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1. Introduction

The challenge of petroleum industry is to reduce the typical aromatic-sulfur compounds that are found in fuels as thiophene, and its derivatives [1]. Deep desulfurization of fossil fuel has become an important industry subject due to the new legislative regulations to reduce sulfur content in the USA and Europe [2,3]. Nowadays, the hydrodesulfurization (HDS) processes which are employed by refineries to remove organic sulfur from fuels for several decades need high temperature and pressure, larger reactor volumes, and more active catalysts [4,5].

Faced with continuing fuel quality challenges, the scientific fundamental research have begun to pay close attention to extraction of sulfur compounds with ionic liquids, which have the potential for alternative and future complementary technology for deep desulfurization [6]. It may be industrially favorable process because of low temperature, low use of energy and low cost [7].

So, ionic liquids (ILs) are proposed as entrainers for new alternative technologies to the classical hydrodesulfurization process and in order to the deep desulfurization of low level aromatic sulfur compounds. For the application of ILs in refinery processing, the possibility of the entrainer has to be investigated on model fuel, representing the real feed mixtures [8]. In order to solve this problem, the ternary liquid–liquid equilibrium (LLE) desulfurization with ILs [9–11] and activity coefficients at infinite dilution have been proposed as the first information of selectivity [12,13].

Various ionic liquids have been used to desulfurization process. Due to high cost, high viscosity or hydrolysis and production of hazardous substances such as HF, some of them are not appropriate for industrial operation [14]. Recently, the use of ionic liquids with thiocyanate anion because of low cost, low viscosity and non-hazardous hydrolysis productions has been intensified to this process. Some studies by COSMO-RS were conducted on systems that include [BMIM][SCN] + TS + hexane, heptane or decane for calculating infinite dilution activity coefficient and selectivity of the ionic liquid in the extraction of thiophene from hydrocarbons [13]. Dibenzothiophene extraction from dodecane by [BMIM][SCN] ionic liquid has been studied by Wilfred et al. [15]. Vapor–liquid equilibrium of binary systems including 1-ethyl-3-methylimidazolium thiocyanate [EMIM][SCN] with thiophene or pyridine has been studied by Khelassi-Sefaoui et al. [16]. Extract of dibenzothiophene (DBT) from *n*-dodecane with [BMIM][SCN] had been reported with extraction efficiency of more than 65% [17].

However, because there are numerous ionic liquids, it is hard and very time consuming in practice to select appropriate IL for such processes from liquid–liquid equilibrium. In addition, the LLE study consumes large amounts of ionic liquid; as a result, the study will lead to more costs.

Volumetric method provides useful information about interactions and significantly contributes to a better understanding of the interactions between components. Volumetric properties of binary mixtures are complex properties because they depend not only on solute–solute,

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solvent–solvent, and solute–solvent interactions, but also of the structural effects arising from interstitial accommodation due to the difference in molar volume and free volume between components present in the mixture [18]. Moreover, there is interest in using volumetric data to test molecular theories or models of solution to extend our understanding about molecular interactions between components [19] and understand the relation between structure and property, making it easier to search for an optimal ionic liquid for a specific application [20].

This work is a continuation of our studies on the extraction abilities of chosen ILs from model fuel based on our previous fundamental thermodynamic measurements from volumetric properties such as standard partial molar volumes V_ϕ^0, partial molar isentropic compressibility, κ_ϕ^0, excess molar volumes, V^E and excess partial molar volumes, $\bar{v}_{m,i}^E$, measurements in binary systems [21,22].

Literature survey indicates that few studies have been done on the volumetric properties of these types of systems [23]. In this study, it is focused to study the influence of two ionic liquids with different cation alkyl chain length on the thermodynamic properties of binary systems that contain thiophene and ionic liquid.

To achieve this aim, in this work, volumetric, acoustic and refractometric properties of two binary mixtures containing thiophene + 1-hexyl-3-methylimidazolium thiocyanate and 1-octyl-3-methylimidazolium thiocyanate were presented in dilute region of TS at different temperatures and at atmospheric pressure. Therefore, density, speed of sound and refractive index data of binary studied mixtures have been measured and some thermodynamic parameters have been calculated. The results will help us to better understand the influence of ionic liquids on extractive desulfurization process. A specific experimental technique which allows a minimal consumption and loss of IL during the experiments was adopted.

2. Experimental

2.1. Materials

N-methylimidazole, 1-chlorohexane, 1-chlorooctane, sodium thiocyanate, thiophene and ethyl acetate were supplied by Merck Co. and dichloromethane was supplied by CHEM-LAB. These reagents were used without further purification and the ionic liquids were synthesized in our lab. The chemical name, purity in mass fraction and analysis method of the used materials are given in Table 1.

2.2. Synthesis of ionic liquids

The syntheses of the ionic liquids were based on the metathesis reaction of sodium thiocyanate with 1-hexyl-3-methylimidazolium chloride ([HMIM][Cl]) and 1-octyl-3-methylimidazolium chloride ([OMIM][Cl]) [24].

For the synthesis of the ionic liquids, 1-hexyl-3-methylimidazolium chloride, [HMIM][Cl], and 1-octyl-3-methylimidazolium chloride, [OMIM][Cl], two naked round-bottom flask containing 1-methylimidazole were put on a magnetic stirrer and excess amount of 1-chlorohexane/1-chlorooctane was added to the flask dropwise from the dropper funnel in an ice bath. After completion of the haloalkane addition, the entire system has been refluxed for 72 h under argon atmosphere with gradually rising temperature up to 343 K [25]. The major impurities in the thiocyanate based IL was unreacted [HMIM][Cl] or [OMIM][Cl], NaCl and the excess NaSCN. The prepared IL was washed then with the dry dichloromethane. The impure IL is solved in this solvent, but NaSCN and NaCl salts are not soluble and separate from the solution. The unreacted raw materials are evaporated under reduced pressure using a rotary evaporator. The remaining liquid is further dried at about $T = 343$ K under reduced pressure using high vacuum pump. Since ILs are very hygroscopic compounds, to remove trace amount of moisture, both of the obtained imidazolium based ionic liquids were dried overnight at about $T = 353$ K under high vacuum (0.1 Pa) prior to use. Water contents of the prepared ionic liquids were found by Karl Fischer method using a Karl Fischer titrator (751 GPD Titrino-Metrohm, Herisau, Switzerland) which was less than 0.1%. The [HMIM][SCN] and [OMIM][SCN] were analyzed by ^{1}H NMR (Brucker Av-400) and FT-IR (Brucker, tensor27) to confirm the absence of any major impurities (supplementary content). The physical properties of pure chemicals used in this work including experimental densities, speeds of sound, and refractive indices are given in Table 2 and compared with those values reported in the literature.

2.3. Apparatus and procedure

The density and speed of sound measurement were performed using a vibrating tube densimeter and speed of sound analyzer (DSA5000, Anton Paar Co.). The instrument was automatically thermostatted (built in Peltier method) within $\pm 1.0 \times 10^{-3}$ K. The experimental uncertainty of density and speed of sound measurements were less than 3.0×10^{-5} g · cm^{-3} and 0.1 m · s^{-1}, respectively. The densimeter includes an automatic correction for the viscosity of the sample. The apparatus was calibrated before each series of measurements with double distilled, degassed and deionized water and dried air at atmospheric pressure.

The binary mixtures were prepared in molal base concentration using an analytical balance (AND, GR202, Japan) with precision of $\pm 10^{-5}$ g. The uncertainty for molality of the solutions, m, is 0.0001 (mol · kg^{-1}). All the solutions were kept tightly sealed to minimize evaporation and contamination. Measurements were performed immediately after preparation of solutions.

Densities and speed of sound data of the mixtures containing TS + IL were measured using a method to minimize the IL consumption and loss. First, the solution with the lowest concentration was prepared by mixing known amounts of thiophene and IL in 10 mL Hamilton gas tight syringe containing a small magnetic stirrer for mixing the solution. Prior to each measurement, each binary mixture degassed for half an hour to avoid possible a bubble which would generally result in unstable

Table 1
A brief summary of the purity of the used chemicals.

Chemical name	CAS no	Abbreviation	Supplier	Initial mass fraction purity	Purification method	Mass fraction purity	Analysis method
N-methylimidazole	[616-47-7]		Merck	>0.99	None		
1-Chlorohexane	[111-25-1]		Merck	>0.99	None		
1-Chlorooctane	[111-85-3]		Merck	>0.99	None		
Ethyl acetate	[141-78-6]		Merck	>0.99	None		
Thiophene	[110-02-1]	TS	Merck	>0.995	None		
Sodium thiocyanate	[540-72-7]		Merck	≥0.98	None		
dichloromethane	[75-09-2]		Chem.-Lab		None		
1-Hexyl-3-methyl imidazolium thiocyanate	[85100-78-3]	[HMIM][SCN]	Synthesized		Rotary evaporator/vacuum	>0.98	^{1}H NMR/FT-IR/KF
1-Octyl-3-methyl imidazolium thiocyanate	[61545-99-1]	[OMIM][SCN]	Synthesized		Rotary evaporator/vacuum	>0.98	^{1}H NMR/FT-IR/KF

Table 2
The density (d), speed of sound (u), and refractive index (n_D) of the chemicals used in this work.

Chemical name	$10^{-3}\cdot d/(\mathrm{kg}\cdot\mathrm{m}^{-3})$		n_D		$u/(\mathrm{m}\cdot\mathrm{s}^{-1})$	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
Thiophene	1.058556	1.05884 [4]	1.5252	1.52572 [4]	1278.95 1258.65 (T = 303.15 K)	1258.2 (T = 303.15 K) [51]
[HMIM][SCN]	1.056845	1.05692 [52]	1.5524		1669.47	
[OMIM][SCN]	1.008283	1.00827 [53]	1.5545		1615.08	

densimeter readings. Afterward, about 1.5 mL of mixture was injected to densimeter to measure densities and speed of sound in the temperature range from 288.15 K to 303.15 K. Afterward, the solution was carefully recovered from the densimeter (by suction, using the same syringe as for sampling), and the mass of the remaining solution in the 10 mL gas tight syringe was weighed. Then, an incremental amount of thiophene was added, and the density and speed of sound were measured after complete dissolution and the process was repeated with a minimum IL consumption. Each reported value is an average of three measurements.

Refractive indices of both the solvent and binary mixtures were measured using a digital Abbe refractometer (ATAGO, Dr-A1, Japan) with an uncertainty of $\pm 2\cdot 10^{-4}$ calibrated by doubly distilled water before each series of measurements. The temperature was controlled with bath thermostat (HETO BIRKEROD 01 TE623, Denmark) with a temperature stability of ±0.1 K.

3. Results and discussion

3.1. Volumetric properties

For the determination of the volumetric properties of investigated mixtures, the experimental densities as a function of thiophene molality m for the two binary mixtures (TS + [HMIM][SCN]) and (TS + [OMIM][SCN]) at 288.15, 293.15, 298.15 and 303.15 K were measured. The results are given in Table 3. The apparent molar volume of thiophene in [HMIM][SCN] and [OMIM][SCN] mixtures, V , was calculated from the density values of solution d and solvent d_0 using the following equation [26]:

$$V_\phi = \frac{M}{d} - \left[\frac{(d - d_0)}{m\cdot d\cdot d_0}\right] \tag{1}$$

where M and m are the molar mass and molality of thiophene, respectively. The V values of the investigated mixtures at T = (288.15, 293.15, 298.15 and 303.15) K are presented in Table 4. The V values of thiophene in the [HMIM][SCN] and [OMIM][SCN] mixtures are positive, increase with increase in temperature and decrease by thiophene concentration increment. There is a linear dependence between V and thiophene molality according to the following equation [27]:

$$V_\phi = V_\phi^0 + S_\mathrm{v}\cdot m \tag{2}$$

where V_ϕ^0 is the apparent molar volume at infinite dilution, that has the same meaning as the standard partial molar volume. At infinite dilution, the solute–solute interaction is negligible and therefore, the standard partial molar volume provides valuable information concerning the solute–solvent interactions and S_v is the experimental slope which shows the nature of the solute–solute interactions [28]. The V_ϕ^0 and S_v values, the corresponding standard errors and deviations are given in

Table 3
Density (d), speed of sound (u) and refractive index (n_D) data of thiophene in [HMIM][SCN] and [OMIM][SCN] binary mixtures at T = (288.15 to 303.15) K.[a]

	T/K = 288.15			T/K = 293.15			T/K = 298.15			T/K = 303.15		
[b]$m/(\mathrm{mol}\cdot\mathrm{kg}^{-1})$	$10^3\cdot d/(\mathrm{kg}\cdot\mathrm{m}^{-3})$	$u/(\mathrm{m}\cdot\mathrm{s}^{-1})$	n_D	$10^3\cdot d/(\mathrm{kg}\cdot\mathrm{m}^{-3})$	$u/(\mathrm{m}\cdot\mathrm{s}^{-1})$	n_D	$10^3\cdot d/(\mathrm{kg}\cdot\mathrm{m}^{-3})$	$u/(\mathrm{m}\cdot\mathrm{s}^{-1})$	n_D	$10^3\cdot d/(\mathrm{kg}\cdot\mathrm{m}^{-3})$	$u/(\mathrm{m}\cdot\mathrm{s}^{-1})$	n_D
[HMIM][SCN] + TS												
0	1.062754	1697.44	1.5547	1.059787	1683.00	1.5534	1.056845	1669.47	1.5524	1.054469	1654.32	1.5512
0.0241	1.062816	1696.43	1.5545	1.059834	1682.11	1.5532	1.056874	1668.60	1.5522	1.054462	1652.90	1.5510
0.0674	1.062929	1694.92	1.5543	1.059919	1680.53	1.5530	1.056928	1667.05	1.5520	1.054450	1652.33	1.5508
0.0927	1.062995	1694.04	1.5542	1.059971	1679.62	1.5529	1.056964	1666.16	1.5519	1.054443	1651.89	1.5507
0.1351	1.063107	1692.58	1.5540	1.060056	1678.10	1.5527	1.057019	1664.67	1.5517	1.054432	1651.10	1.5505
0.1854	1.063240	1690.88	1.5538	1.060162	1676.32	1.5525	1.057093	1662.92	1.5515	1.054421	1650.02	1.5503
0.2329	1.063368	1689.30	1.5536	1.060264	1674.67	1.5523	1.057163	1661.29	1.5513	1.054410	1648.81	1.5501
0.2865	1.063512	1687.53	1.5534	1.060385	1672.83	1.5521	1.057252	1659.48	1.5511	1.054399	1647.26	1.5499
0.3194	1.063603	1686.46	1.5533	1.060458	1671.72	1.5520	1.057305	1658.38	1.5510	1.054392	1646.25	1.5498
0.3505	1.063692	1685.47	1.5532	1.060533	1670.69	1.5519	1.057360	1657.34	1.5509	1.054386	1644.98	1.5497
[OMIM][SCN] + TS												
0	1.014075	1644.30	1.5561	1.011121	1629.31	1.5553	1.008283	1615.08	1.5545	1.005432	1601.27	1.5536
0.0192	1.014135	1643.76	1.5559	1.011182	1628.80	1.5551	1.008344	1614.59	1.5543	1.005493	1600.80	1.5534
0.0401	1.014202	1643.18	1.5558	1.011250	1628.25	1.5550	1.008411	1614.06	1.5542	1.005560	1600.29	1.5533
0.0684	1.014293	1642.40	1.5557	1.011344	1627.50	1.5549	1.008502	1613.35	1.5541	1.005653	1599.61	1.5532
0.1204	1.014470	1640.97	1.5555	1.011522	1626.15	1.5547	1.008676	1612.06	1.5539	1.005826	1598.37	1.5530
0.1526	1.014582	1640.12	1.5554	1.011637	1625.32	1.5546	1.008787	1611.27	1.5538	1.005934	1597.61	1.5529
0.1846	1.014696	1639.26	1.5553	1.011748	1624.52	1.5545	1.008903	1610.49	1.5537	1.006043	1596.88	1.5528
0.2062	1.014773	1638.70	1.5552	1.011829	1623.96	1.5544	1.008976	1609.97	1.5536	1.006118	1596.38	1.5527
0.2556	1.014957	1637.41	1.5550	1.012012	1622.73	1.5542	1.009161	1608.79	1.5534	1.006287	1595.28	1.5526
0.2822	1.015053	1636.74	1.5549	1.012113	1622.07	1.5541	1.009257	1608.16	1.5533	1.006380	1594.68	1.5525
0.3268	1.015222	1635.63	1.5547	1.012278	1620.99	1.5539	1.009421	1607.13	1.5532	1.006539	1593.70	1.5524

[a] Standard uncertainties u for molality, density and speed of sound are $u(m)$= 0.0001 $\mathrm{mol}\cdot\mathrm{kg}^{-1}$; $u(d)$=3.0 × 10^{-5} $\mathrm{g}\cdot\mathrm{cm}^{-3}$ and $u(u)$ = 0.1 $\mathrm{m}\cdot\mathrm{s}^{-1}$.

[b] m is the molal concentration of thiophene.

Table 4
The values of apparent molar volume (V_φ), apparent molar isentropic compressibility (κ_φ) and molar refraction (R_D) of thiophene in [HMIM][SCN] and [OMIM][SCN] mixtures at $T = (288.15$ to $303.15)$ K.

$m/(\mathrm{mol \cdot kg^{-1}})$	T/K = 288.15			T/K = 293.15			T/K = 298.15			T/K = 303.15		
	$10^6 \cdot V_\varphi/(\mathrm{m^3 \cdot mol^{-1}})$	$10^{14} \cdot \kappa_\varphi/(\mathrm{m^3 \cdot mol^{-1} \cdot Pa^{-1}})$	$10^6 \cdot R_D/(\mathrm{m^3 \cdot mol^{-1}})$	$10^6 \cdot V_\varphi/(\mathrm{m^3 \cdot mol^{-1}})$	$10^{14} \cdot \kappa_\varphi/(\mathrm{m^3 \cdot mol^{-1} \cdot Pa^{-1}})$	$10^6 \cdot R_D/(\mathrm{m^3 \cdot mol^{-1}})$	$10^6 \cdot V_\varphi/(\mathrm{m^3 \cdot mol^{-1}})$	$10^{14} \cdot \kappa_\varphi/(\mathrm{m^3 \cdot mol^{-1} \cdot Pa^{-1}})$	$10^6 \cdot R_D/(\mathrm{m^3 \cdot mol^{-1}})$	$10^6 \cdot V_\varphi/(\mathrm{m^3 \cdot mol^{-1}})$	$10^{14} \cdot \kappa_\varphi/(\mathrm{m^3 \cdot mol^{-1} \cdot Pa^{-1}})$	$10^6 \cdot R_D/(\mathrm{m^3 \cdot mol^{-1}})$
[HMIM][SCN] + TS												
0.0241	76.89	3.718	67.77	77.65	3.933	67.83	78.53	4.034	67.92	80.06	3.268	67.95
0.0674	76.86	3.713	67.34	77.64	3.925	67.40	78.51	4.030	67.49	80.05	3.298	67.53
0.0927	76.85	3.713	67.09	77.61	3.920	67.15	78.46	4.026	67.24	80.05	3.350	67.28
0.1351	76.83	3.712	66.68	77.60	3.915	66.74	78.45	4.023	66.83	80.04	3.410	66.87
0.1854	76.82	3.708	66.20	77.57	3.912	66.26	78.40	4.021	66.35	80.03	3.479	66.40
0.2329	76.79	3.703	65.76	77.54	3.906	65.82	78.37	4.018	65.91	80.03	3.551	65.97
0.2865	76.77	3.701	65.27	77.49	3.900	65.33	78.31	4.014	65.43	80.02	3.633	65.49
0.3194	76.76	3.698	64.98	77.47	3.896	65.04	78.29	4.012	65.14	80.02	3.678	65.20
0.3505	76.73	3.694	64.70	77.44	3.892	64.77	78.26	4.011	64.87	80.01	3.751	64.93
[OMIM][SCN] + TS												
0.0192	79.93	4.037	80.05	80.11	4.072	80.19	80.32	4.129	80.32	80.54	4.184	80.44
0.0401	79.88	4.028	79.75	80.06	4.065	79.89	80.30	4.126	80.02	80.52	4.183	80.14
0.0684	79.85	4.023	79.36	80.01	4.066	79.50	80.28	4.121	79.63	80.47	4.174	79.74
0.1204	79.75	4.016	78.65	79.93	4.057	78.78	80.21	4.112	78.91	80.42	4.167	79.03
0.1526	79.70	4.005	78.22	79.87	4.052	78.35	80.16	4.107	78.48	80.39	4.164	78.60
0.1846	79.65	4.001	77.80	79.84	4.045	77.93	80.10	4.101	78.06	80.36	4.156	78.18
0.2062	79.62	3.995	77.52	79.80	4.044	77.65	80.09	4.099	77.78	80.34	4.153	77.89
0.2556	79.55	3.987	76.88	79.74	4.036	77.01	80.00	4.089	77.14	80.31	4.142	77.27
0.2822	79.53	3.981	76.55	79.70	4.032	76.68	79.98	4.086	76.80	80.29	4.140	76.93
0.3268	79.47	3.970	75.99	79.66	4.025	76.12	79.93	4.079	76.25	80.25	4.132	76.38

Table 5
Standard partial molar volumes (V_ϕ^0), experimental slopes (S_v) and standard deviations $\sigma(V_\varphi)$ of thiophene in [HMIM][SCN] and [OMIM][SCN] solutions at $T = (288.15$ to $303.15)$ K.

T/K	$10^6 \cdot V_\phi^0/(\mathrm{m^3 \cdot mol^{-1}})$	$10^6 \cdot S_v/(\mathrm{m^3 \cdot mol^{-2} \cdot kg})$	$10^6 \cdot \sigma(V_\varphi)/(\mathrm{m^3 \cdot mol^{-1}})$
		[HMIM][SCN] + TS	
288.15	76.89 ± 0.01	−0.44 ± 0.01	0.01
293.15	77.68 ± 0.01	−0.64 ± 0.02	0.01
298.15	78.55 ± 0.01	−0.82 ± 0.03	0.01
303.15	80.06 ± 0.01	−0.14 ± 0.01	0.01
		[OMIM][SCN] + TS	
288.15	79.95 ± 0.01	−1.52 ± 0.04	0.01
293.15	80.11 ± 0.01	−1.46 ± 0.05	0.02
298.15	80.36 ± 0.01	−1.34 ± 0.04	0.01
303.15	80.54 ± 0.01	−0.94 ± 0.04	0.01

Table 5. The standard deviation values have been calculated by Eq. (3) for the concentration range studied of TS.

$$\sigma(V_\phi) = \frac{\sqrt{\left(V_\phi^{\,\mathrm{exp}} - V_\phi^{\mathrm{cal}}\right)^2}}{n-2} \qquad (3)$$

where n is the number of experimental data.

The S_v values for (TS + [HMIM][SCN])/(TS + [OMIM][SCN]) mixtures are negative at all experimental temperature which indicates relatively weak TS-TS interactions in ionic liquids. The V_ϕ^0 values of TS in both solvents are positive with the order of [HMIM][SCN] < [OMIM][SCN] which represents the presence of stronger solute–solvent interactions between TS and [HMIM][SCN] rather than [OMIM][SCN][29]. The increasing V_ϕ^0 values of thiophene in ILs at higher temperature suggest weak solute–solvent interactions between thiophene and ILs at higher temperature. At lower temperatures, the interaction between thiophene and the ionic liquids may be favored due to the slower molecular movement of ions and thiophene that would lead to a smaller value for V_ϕ^0. The effect of temperature on the V_φ values of thiophene in [HMIM][SCN] and [OMIM][SCN] liquid binary mixtures is depicted in Fig. 1.

Since apparent molar volumes at infinite dilution provide information about solute–solvent molecular interactions, they can be used to the development of molecular models for expression of the thermodynamic behavior of solutions [23]. The thermodynamic features of all the solvation processes of non-polar molecules are influenced by the

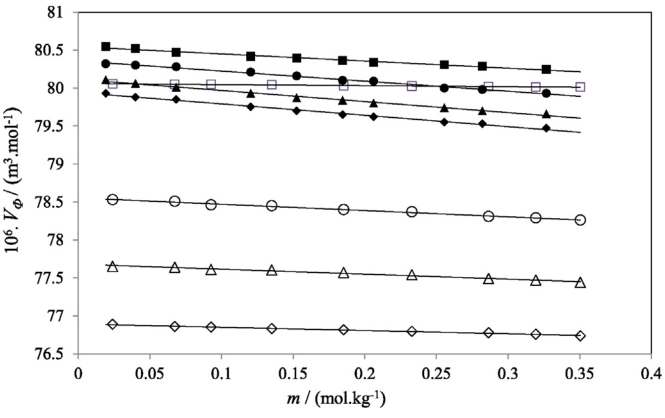

Fig. 1. Apparent molar volume of thiophene, V_φ as a function of its molality, m, at different temperatures in [HMIM][SCN]; ◊, 288.15 K, Δ, 293.15 K, ○, 298.15 K and □, 303.15 K and [OMIM][SCN]; ◆, 288.15 K, ▲, 293.15 K, ●, 298.15 K and ■, 303.15 K, —, calculated from E. (1).

thermodynamics of cavity creation and a suitable cavity has to be created for the insertion of a solute molecule. Cavity creation is studied by means of theoretical statistical mechanical approaches and/or computer simulations in which one of them is Scaled Particle Theory (SPT). Based on the scaled particle theory, which assumes the solute dissolution as a step-wise process: creating a cavity in the solvent for the solute molecule and allowing solute molecule to interact with surrounding solvent molecules, a thermodynamic model can be written in the following equation [30]:

$$V_{\phi}^{0} = V_{cav} + V_{\text{int}} + k_T \cdot R \cdot T \tag{4}$$

where V_{cav} is the partial molar volume of cavity formation, V_{int} is the volume change due to the solute–solvent interactions, k_T is the coefficient of isothermal compressibility of the solvent, R is the universal gas constant and T is the absolute temperature. The cavity volume is calculated by the relation given in Eq. (5) [31]:

$$V_{\text{cav}} = k_T \cdot R \cdot T \cdot \left(\frac{y}{1-y} + \frac{3 \cdot y \cdot z \cdot (1+z)}{(1-y)^2} + \frac{9 \cdot y^2 \cdot z^2}{(1-y)^3} + \frac{\pi \cdot \sigma_2^3 \cdot N_A}{6} \right) \tag{5}$$

and

$$y = \frac{\pi \cdot N_A \cdot \sigma_1^3}{6 \cdot V} \tag{6}$$

where N_A is Avogadro's constant and y is the ratio of the volume occupied by one mole of hard sphere solute particles to the molar volume of solvent, Eq. (6), and z is the ratio of the hard sphere diameters of solute σ_2 and solvent σ_1.

$$z = \frac{\sigma_2}{\sigma_1} \tag{7}$$

The molecular volume and diameter values of thiophene and ionic liquids were calculated using an equation provided by Abraham and Zissimos [32]. Isothermal compressibility factor for pure ionic liquids was calculated using Equation [33]:

$$k_T = k_S + \frac{\alpha^2 \cdot T \cdot V}{C_P}. \tag{8}$$

The C_P values in Eq. (8) have been calculated from the equation proposed by Ahmadi et al. [34]. Interaction volumes of TS in both ionic liquid mixtures have negative values as shown in Table 6 and are larger (more negative) for the TS + [HMIM][SCN] mixture and ionic liquids used in this study, interact effectively with thiophene. This can lead to their good efficiency of the TS extraction. According to the values of interaction, one would expect the extraction efficiency of ionic liquid with hexyl cations alkyl chain length, is slightly more than the other one.

Considering the following relation the temperature dependence of V_{ϕ}^{0} values for the thiophene in [HMIM][SCN] and [OMIM][SCN] mixtures could be expressed as [35]:

$$V_{\phi}^{0} = A + BT + CT^2 \tag{9}$$

Table 6
Cavity volumes V_{cav} and interaction volumes V_{int} of thiophene in ([HMIM][SCN]/[OMIM][SCN]) solutions at $T = 298.15$ K.

Systems	$10^6 \cdot V_{cav}/(\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$	$10^6 \cdot V_{int}/(\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$
(Thiophene + [HMIM][SCN])	222.36	−147.31
(Thiophene + [OMIM][SCN])	103.95	−24.62

Table 7
Partial molar expansibility (E_{ϕ}^{0}), isobaric thermal expansion (α) for thiophene in [HMIM][SCN] and [OMIM][SCN] at $T = (288.15$ to $303.15)$ K.

T/K	$10^6 \cdot E_{\phi}^{0}/(\mathrm{m}^3 \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1})$	$10^4 \cdot \alpha/(\mathrm{K}^{-1})$
	[HMIM][SCN] + TS	
288.15	0.211	27.411
293.15	0.209	26.886
298.15	0.207	26.342
303.15	0.205	25.606
	[OMIM][SCN] + TS	
288.15	0.053	6.572
293.15	0.045	5.585
298.15	0.037	4.597
303.15	0.029	3.618

where A, B and C are empirical parameters and T is the temperature. The limiting apparent molar expansibility can be obtained by differentiating Eq. (9) with respect to temperature at constant pressure [36],

$$E_{\phi}^{0} = \left(\frac{\partial V_{\phi}^{0}}{\partial T} \right)_P. \tag{10}$$

The calculated E_{ϕ}^{0} values are given in Table 7. According to this table, we note that at each temperature, E_{ϕ}^{0} values for thiophene in the studied mixtures are positive value and decrease with rising temperature. In fact expansibility of solutions is greater than expansibility of solvents. This result shows that on heating, some solvent molecules may be released from the solvation layers. This would increase the solution volume a little more rapidly than that of the solvent and so E_{ϕ}^{0} would be positive [26].

The values of the isobaric thermal expansion coefficients of thiophene at infinite dilution (α) can be determined using the following equation [37] and their values are also given in Table 7.

$$\alpha = \frac{E_{\phi}^{0}}{V_{\phi}^{0}} \tag{11}$$

The isobaric thermal expansion coefficient is basically a measure for the response of system's volume to an increase in temperature. According to Table 7, with increasing temperature, α decreases in all studied mixtures.

Excess molar volumes, V^E, were then calculated from density measurements according to the following equation [38]:

$$V^E = \left(\frac{\mathrm{M}_1 \cdot \mathrm{X}_1 + M_2 \cdot \mathrm{X}_2}{d} \right) - \left(\frac{\mathrm{M}_1 \cdot \mathrm{X}_1}{d_1} + \frac{\mathrm{M}_2 \cdot \mathrm{X}_2}{d_2} \right) \tag{12}$$

where x_i, M_i, d_i are, respectively, mole fraction, molar mass, and the density of component i; and d is the experimental density of the binary mixture. It can be observed from the experimental results that the excess molar volumes V^E are positive over the entire studied mole fraction range and for a temperature range from (288.15 to 303.15) K in [OMIM][SCN] and become more positive with increasing concentration of thiophene (Table 8), while in the [HMIM][SCN] excess molar volumes V^E are negative in temperature range of 288.15 to 298.15 and become slightly positive in the 303.15 K. Fig. 2 shows and compares the excess molar volume of thiophene, V^E versus its mole fraction, x_t, in [OMIM][SCN], ♦, and [HMIM][SCN], ▲, at $T = 298.15$ K. The positive values indicate a predominance of the expansive effect associated with dissociation of the ion pairs forming the ionic liquid, rather than a volume contraction contribution [39]. This is due to the development of new heteromolecular interactions and the molecular packing. The attractive interactions between [HMIM][SCN] + TS binary system components are sufficient to cause volume contraction,

Table 8

Excess molar volumes (v_m^E), partial molar volumes ($\bar{v}_{m,1}$) and excess partial molar volumes ($\bar{v}_{m,1}^E$) of x thiophene + (1 − x) [HMIM][SCN]/[OMIM][SCN] at T = (288.15 to 303.15) K and atmospheric pressure.

	T/K = 288.15			T/K = 293.15			T/K = 298.15			T/K = 303.15		
x	v_m^E/(cm^3 · mol^{-1})	$\bar{v}_{m,1}$(cm^3 · mol^{-1})	$\bar{v}_{m,1}^E$/(cm^3 · mol^{-1})	v_m^E/(cm^3 · mol^{-1})	$\bar{v}_{m,1}$/(cm^3 · mol^{-1})	$\bar{v}_{m,1}^E$/(cm^3 · mol^{-1})	v_m^E/(cm^3 · mol^{-1})	$\bar{v}_{m,1}$/(cm^3 · mol^{-1})	$\bar{v}_{m,1}^E$/(cm^3 · mol^{-1})	v_m^E/(cm^3 · mol^{-1})	$\bar{v}_{m,1}$/(cm^3 · mol^{-1})	$\bar{v}_{m,1}^E$/(cm^3 · mol^{-1})
[HMIM][SCN] + TS												
0.0241	−0.009	76.71	−1.900	−0.008	77.49	−1.556	−0.005	78.38	−1.119	0.001	79.38	−0.561
0.0674	−0.026	76.42	−2.182	−0.021	77.18	−1.862	−0.015	78.10	−1.399	0.002	79.43	−0.509
0.0927	−0.036	76.26	−2.348	−0.029	77.00	−2.042	−0.021	77.93	−1.564	0.002	79.46	−0.481
0.1351	−0.052	75.98	−2.628	−0.043	76.70	−2.345	−0.031	77.66	−1.840	0.003	79.50	−0.438
0.1854	−0.072	75.65	−2.961	−0.059	76.34	−2.707	−0.044	77.33	−2.170	0.004	79.55	−0.390
0.2329	−0.090	75.33	−3.277	−0.075	75.99	−3.050	−0.056	77.02	−2.480	0.004	79.59	−0.350
0.2865	−0.111	74.98	−3.632	−0.094	75.61	−3.436	−0.072	76.67	−2.829	0.005	79.63	−0.308
0.3194	−0.124	74.76	−3.849	−0.105	75.37	−3.672	−0.081	76.45	−3.042	0.005	79.65	−0.285
0.3505	−0.137	74.55	−4.054	−0.117	75.15	−3.895	−0.090	76.25	−3.243	0.006	79.67	−0.265
[OMIM][SCN] + TS												
0.0192	0.006	79.95	1.346	0.005	80.11	1.069	0.004	80.37	0.871	0.003	80.50	0.562
0.0401	0.013	79.92	1.315	0.010	80.08	1.035	0.008	80.32	0.822	0.006	80.46	0.519
0.0684	0.021	79.88	1.277	0.016	80.03	0.991	0.013	80.25	0.758	0.009	80.40	0.462
0.1204	0.034	79.82	1.215	0.026	79.96	0.92	0.021	80.14	0.648	0.014	80.30	0.360
0.1526	0.041	79.79	1.181	0.031	79.92	0.881	0.025	80.08	0.585	0.017	80.23	0.297
0.1846	0.047	79.76	1.151	0.036	79.89	0.845	0.027	80.02	0.526	0.019	80.17	0.237
0.2062	0.051	79.74	1.133	0.038	79.87	0.824	0.029	79.98	0.487	0.020	80.13	0.197
0.2556	0.057	79.70	1.096	0.042	79.82	0.779	0.031	79.90	0.405	0.023	80.04	0.106
0.2822	0.061	79.69	1.079	0.044	79.80	0.758	0.032	79.86	0.363	0.023	80.00	0.059
0.3268	0.066	79.66	1.055	0.047	79.77	0.727	0.033	79.79	0.297	0.024	79.92	−0.019

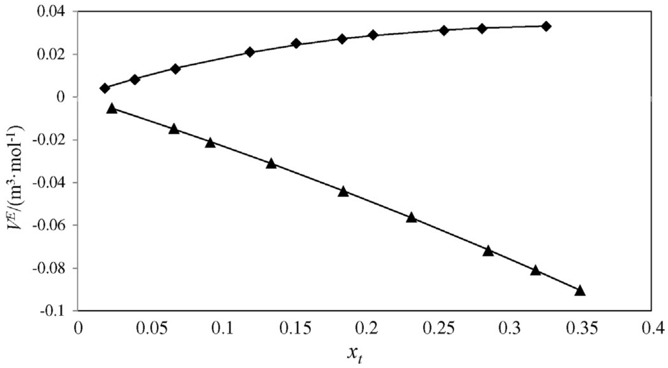

Fig. 2. Plot of excess molar volume, V^E of binary mixtures of thiophene, in [OMIM][SCN], ◆, and [HMIM][SCN], ▲, versus its mole fraction, x_t, at T = 298.15 K.

while TS + [OMIM][SCN] exhibits mostly positive values of the excess volume.

Partial molar volumes for all components were calculated using excess molar volumes by the following equation:

$$\bar{v}_{m,1} = v_m^E + v_1^* + x_2 \cdot \left(\frac{\partial v_m^E}{\partial x_1}\right) \tag{13}$$

$$\bar{v}_{m,2} = v_m^E + v_2^* - x_1 \cdot \left(\frac{\partial v_m^E}{\partial x_1}\right) \tag{14}$$

where v_1^* and v_2^* are the molar volumes of the pure components. According to Table 8, it can be seen that the partial molar volumes for thiophene in [OMIM][SCN] and [HMIM][SCN] shows decreasing trend with increasing TS concentration.

The excess partial molar volumes, $\bar{v}_{m,i}^E$, have frequently been used to give an insight on solute–solvent interactions. The excess partial molar volumes of a component in a binary mixture can be determined from the relation [40]:

$$\bar{v}_{m,i}^E = \bar{v}_{m,i} + v_i^*. \tag{15}$$

The partial molar volumes and excess partial molar volumes of all binary mixtures are given in Table 8. Fig. 3 shows a clear difference in the values of the excess partial molar volumes of TS in the mixtures with [HMIM][SCN] and [OMIM][SCN] at T = 298.15 K. The positive $\bar{v}_{m,1}^E$ quantities are indicative of absence of specific interactions, and enhancement of self-associated structure of TS (entropy-decreasing)

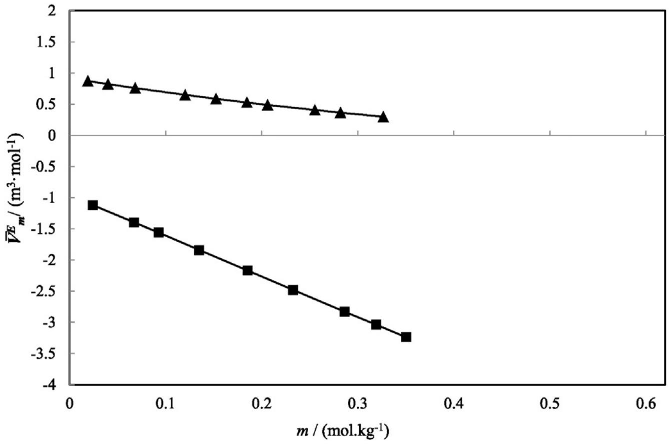

Fig. 3. Variation of excess partial molar volumes of binary mixtures of thiophene with [OMIM][SCN], ▲, and [HMIM][SCN], ■, at 298.15 K.

[40]. The $\overline{v}_{m,1}^{E}$ follows the order: [OMIM][SCN] > [HMIM][SCN]. Negative $\overline{v}_{m,1}^{E}$ value of [HMIM][SCN] shows that the solute–solvent interactions at infinite dilution are comparatively strong with TS.

3.2. Acoustic properties

Acoustic studies have been utilized to better understand the nature of interactions in the mixture [41]. Measurement of speed of sound in the mixture helps in clarifying the solute–solute and solute–solvent interactions. Speed of sound values are given in Table 3. The isentropic compressibility, κ_s is also computed from the Laplace–Newton's equation [42]:

$$\kappa_s = \frac{1}{d \cdot u^2} \tag{16}$$

where u $(\mathrm{m \cdot s^{-1}})$ is speed of sound of the solution. The apparent molar isentropic compressibility of thiophene, κ_ϕ is computed from the following equation based on measured speed of sound and density of solutions [43],

$$\kappa_\phi = \frac{(\kappa_s \cdot d - \kappa_{s0} \cdot d)}{m \cdot d \cdot d_0} + \frac{\kappa_s \cdot M}{d} \tag{17}$$

where κ_{s0} and κ_s are the isentropic compressibility of solvents ([HMIM][SCN] and [OMIM][SCN]) and solutions, respectively. The values of κ_φ for thiophene in [HMIM][SCN] and [OMIM][SCN] ionic liquid mixtures at $T = (288.15 \text{ to } 303.15)$ K are listed in Table 4. It is observed that the κ_φ values of thiophene solutions have the order: [HMIM][SCN] < [OMIM][SCN] and there is a linear dependence between κ_φ and thiophene molality as the following equation:

$$\kappa_\phi = \kappa_\phi^0 + S_K \cdot m_s \tag{18}$$

where κ_ϕ^0 is the apparent molar isentropic compressibility at infinite dilution (the standard partial molar isentropic compressibility) and S_K is the experimental slope. The positive values of κ_φ are attributed to repulsive interactions between the solute and solvent [44].

There are two factors that contribute to κ_ϕ^0, (a) large molecules can have some solvent intrinsic compressibility (positive effect) due to the intermolecular free space that makes the solution more compressible [44], and (b) penetration (negative effect) of the solvent molecules into the intra-molecular free space due to the interaction of thiophene with the neighboring IL molecules. The solute solvation causes expanding in the solution volume, resulting in a less compact and more compressible medium.

The values of κ_ϕ^0 and S_K obtained for the studied solutions at the experimental temperatures are listed in Table 9. According to this table, the values of κ_ϕ^0 in [HMIM][SCN] are positive and become more positive with the order of [HMIM][SCN] < [OMIM][SCN]. The more positive κ_ϕ^0 values of thiophene in [OMIM][SCN] are attributed to the strong repulsive interactions due to lack of solvation of thiophene. The plot of κ_φ versus thiophene molality at [HMIM][SCN] and [OMIM][SCN] at $T = (288.15, 293.15, 298.15 \text{ and } 303.15)$ K is depicted in Figs. 4 and 5.

Table 9
The values of partial molar isentropic compressibility (κ_ϕ^0), experimental slope (S_k) and standard deviations $\sigma(\kappa_\varphi)$ of thiophene in [HMIM][SCN] and [OMIM][SCN] solutions at $T = (288.15 \text{ to } 303.15)$ K.

T/K	$10^{14} \cdot \kappa_\phi^0$/ $(\mathrm{m^3 \cdot mol^{-1} \cdot Pa^{-1}})$	$10^{14} \cdot S_\mathrm{k}$/ $(\mathrm{m^3 \cdot mol^{-2} \cdot Pa^{-1} \cdot kg})$	$10^{14} \cdot \sigma(\kappa_\varphi)$/ $(\mathrm{m^3 \cdot mol^{-1} \cdot Pa^{-1}})$
[HMIM][SCN] + TS			
288.15	3.720 ± 0.001	−0.068 ± 0.004	0.001
293.15	3.933 ± 0.001	−0.117 ± 0.005	0.001
298.15	4.034 ± 0.001	−0.068 ± 0.004	0.001
303.15	3.212 ± 0.009	1.484 ± 0.039	0.013
[OMIM][SCN] + TS			
288.15	4.038 ± 0.001	−0.206 ± 0.006	0.002
293.15	4.074 ± 0.001	−0.151 ± 0.005	0.002
298.15	4.132 ± 0.001	−0.164 ± 0.002	0.001
303.15	4.188 ± 0.001	−0.172 ± 0.005	0.001

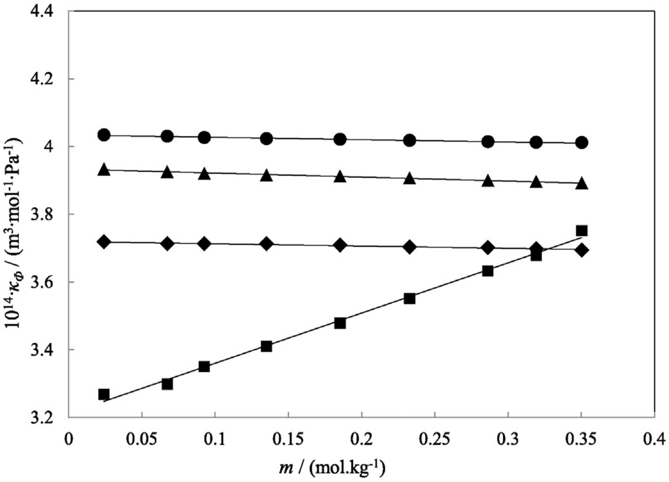

Fig. 4. Apparent molar isentropic compressibility, κ_φ of binary mixtures of thiophene in [HMIM][SCN] at different temperatures ◆, 288.15 K, ▲, 293.15 K, ●, 298.15 K and ■, 303.15 K, —, calculated from Eq. (18) as a function of its molality, m.

Isentropic compressibility, k_s, a parameter describing the elastic properties of the medium, can be sometimes directly interpreted in terms of the liquid structure. Ultrasonic measurements are often applied for investigating phenomena of solvation of electrolytes, both in aqueous and non-aqueous systems [45]. From compressibility data one can easily determine the solvation numbers applying the idea of Pasynski. According to it, solvation should imply a decrease of compressibility of solution compared to that of solvent. Such decrease is always observed in water, both in electrolytic and polar non-electrolytic solutes [45]. Solvated molecules become less compressible. If one follows the Pasynski's assumption that they are completely non-compressible, simple derivation leads to:

$$s_n = \frac{n_1}{n_2} \cdot \left(1 - \frac{\kappa_s}{k_s^0}\right) \tag{19}$$

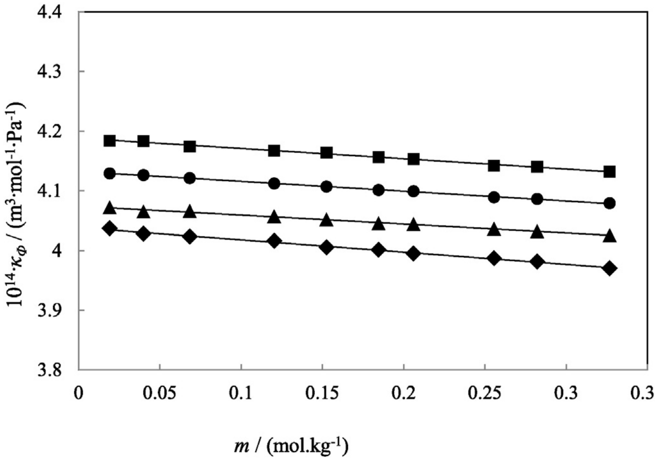

Fig. 5. Apparent molar isentropic compressibility, κ_φ of binary mixtures of thiophene in [OMIM][SCN] at different temperatures ◆, 288.15 K, ▲, 293.15 K, ●, 298.15 K and ■, 303.15 K, —, calculated from Eq. (18) as a function of its molality, m.

Table 10
Solvation number, S_n, values of thiophene in [HMIM][SCN] and [OMIM][SCN] mixtures at T = (288.15, 293.15, 298.15 and 303.15) K.

	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15
$m/(\text{mol} \cdot \text{kg}^{-1})$	S_n	S_n	S_n	S_n
[HMIM][SCN] + TS				
0.0241	−0.191	−0.188	−0.188	−0.192
0.0674	−0.179	−0.187	−0.187	−0.115
0.0927	−0.177	−0.186	−0.186	−0.109
0.1351	−0.175	−0.185	−0.185	−0.107
0.1854	−0.173	−0.184	−0.184	−0.110
0.2329	−0.171	−0.182	−0.183	−0.116
0.2865	−0.170	−0.181	−0.182	−0.123
0.3194	−0.169	−0.180	−0.181	−0.128
0.3505	−0.168	−0.179	−0.181	−0.136
[OMIM][SCN] + TS				
0.0192	−0.123	−0.116	−0.112	−0.108
0.0401	−0.122	−0.116	−0.112	−0.108
0.0684	−0.121	−0.115	−0.111	−0.107
0.1204	−0.120	−0.114	−0.110	−0.106
0.1526	−0.119	−0.114	−0.109	−0.106
0.1846	−0.118	−0.113	−0.109	−0.105
0.2062	−0.118	−0.113	−0.108	−0.104
0.2556	−0.117	−0.112	−0.107	−0.103
0.2822	−0.116	−0.111	−0.107	−0.103
0.3268	−0.115	−0.110	−0.106	−0.102

where n_1 and n_2 are the number of moles of solvent and solute in solution, respectively, k_s is compressibility of the solution and $k^0{}_s$ is that of pure solvent. The calculated solvation number, S_n, values of thiophene in [HMIM][SCN] and [OMIM][SCN] mixtures at T = (288.15, 293.15, 298.15 and 303.15) K are given in Table 10. Solvation number values for TS + ionic liquid mixture are negative and with increasing concentrations of TS, values approach to positive values. Negative values have the physical means to weaken the local structure of the solvent in close to solute molecules. Similar results have been reported for aqueous mixtures [45]. In general, it can be said that the negative solvation is equivalent to the weakening of the interaction between molecules by adding solute.

3.3. Refractometric properties

The refractive index is a measure of the electronic polarizability of a molecule and can provide beneficial information of the forces between various component molecules in the liquid mixtures [46]. The refractive indices n_D for the binary mixtures of (TS + [HMIM][SCN]/[OMIM][SCN]) as a function of thiophene molality m are given in Table 3 at T = (288.15, 293.15, 298.15 and 303.15) K. The values of the refractive indices for the studied mixtures containing TS in the ionic liquids decrease with increasing TS. The molar refractions R_D are calculated for the investigated mixtures using Lorentz–Lorenz equation [47]:

$$R_D = \frac{(n_D)^2 - 1}{(n_D)^2 + 2} \cdot \left(\frac{x_{ts} \cdot M_{ts} + x_{sol} \cdot M_{sol}}{d} \right) \tag{20}$$

where n_D is refractive index of mixture, x_{ts} and x_{sol} are the mol fraction of thiophene and solvent, M_{ts} and M_{sol} are molar mass of thiophene and solvent respectively. The components with high molar refraction and subsequently large polarizability should be capable of having particularly strong dispersion forces for species with high polarizabilities [47]. Fig. 6 shows the variation of molar refraction of TS in the mixture with [OMIM][SCN] and [HMIM][SCN] at 298.15 K.

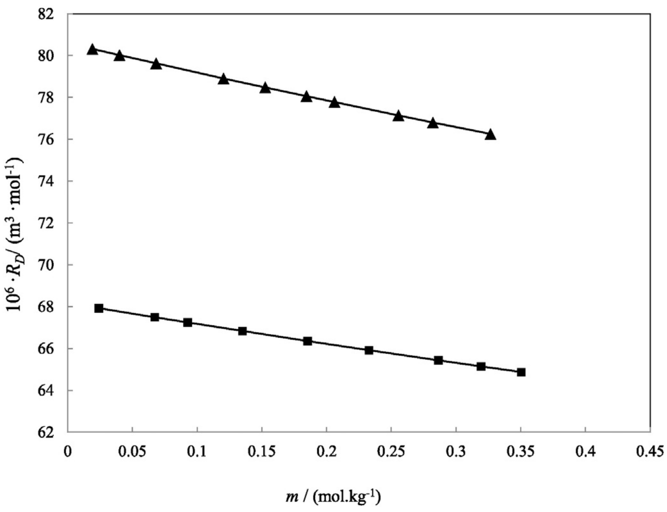

Fig. 6. Variation of molar refractions, R_D, of binary mixtures of (thiophene + [OMIM][SCN], ▲, + [HMIM][SCN], ■) at 298.15 K.

The apparent molar volumes at infinite dilution which are calculated at the volumetric section, include 2 contributions respectively. First one is intrinsic contribution and the other is non-intrinsic contribution. Also according to the equation presented by Alvarado, non-intrinsic contribution data can be calculated from refractometric method [48]. This non-intrinsic contribution related to the volume, indicates solvation shell geometry packing, as well as specific and non-specific intermolecular attractive interactions. As it was explained in the mentioned study, since the apparent molar volumes at infinite dilution contain the volume effects associated with the kinetics contribution, in this condition this quantity is not suitable for comparison with the values obtained from the theoretical models. In order to eliminate the effects of solute transfer from a fixed position in a medium to fixed position in a new medium with different density, Ben Naim standard conditions should be considered. The corrected limiting partial molar volume, hereafter referred as the partial molar volume at Ben-Naim standard conditions, is defined as $v_\phi^{BN}/(\text{cm}^3 \cdot \text{mol}^{-1})$:

$$v_\phi^{BN} = v_\phi^0 - \beta_T \cdot R \cdot T \tag{21}$$

where β_T/kPa^{-1} is the isothermal compressibility of the solvent, R the gas constant and T/K the absolute temperature. Assuming the Ben-Naim standard conditions it has been defined the densitometric non-intrinsic contribution to the partial molar volume, $\theta^d/(\text{cm}^3 \cdot \text{mol}^{-1})$,

$$\theta^d = v_\phi^{BN} - v_i. \tag{22}$$

Table 11
Standard partial molar volume, V_ϕ^0, partial molar volume at Ben-Naim standard conditions, v_ϕ^{BN}, densitometric non-intrinsic contribution to the partial molar volume, θ^d, and refractometric non-intrinsic contribution to the partial molar volume, θ^r, of thiophene in two studied solvents at T = (288.15, 293.15, 298.15 and 303.15) K.

T/K	$10^6 \cdot V_\phi^0$/ $(\text{m}^3 \cdot \text{mol}^{-1})$	$10^6 \cdot v_\phi^{BN}$/ $(\text{m}^3 \cdot \text{mol}^{-1})$	$10^6 \cdot v_i$/ $(\text{m}^3 \cdot \text{mol}^{-1})$	$10^6 \cdot \theta^d$/ $(\text{m}^3 \cdot \text{mol}^{-1})$	$10^6 \cdot \theta^r$/ $(\text{m}^3 \cdot \text{mol}^{-1})$
		[HMIM][SCN] + TS			
288.15	76.894 ± 0.003	73.397	135.561	−62.16	−71.06
293.15	77.678 ± 0.005	74.165	135.561	−61.40	−70.30
298.15	78.552 ± 0.006	75.047	135.561	−60.51	−69.47
303.15	80.059 ± 0.004	76.584	135.561	−58.98	−68.01
		[OMIM][SCN] + TS			
288.15	79.946 ± 0.009	78.912	167.092	−88.18	−105.45
293.15	80.112 ± 0.010	79.082	167.092	−88.01	−105.26
298.15	80.359 ± 0.007	79.334	167.092	−87.76	−105.04
303.15	80.544 ± 0.008	79.514	167.092	−87.58	−104.85

They also derived a new expression for θ based on measurements of the refraction index of solutions as a function of the concentration of the solute under Ben-Naim standard conditions as follows:

$$\theta^r = \frac{R_{2m}^{\infty}}{\psi_1} - \left(\frac{6000 \cdot n_{D_1}}{\left(n_{D_1}^2 + 2\right)^2}\right) \cdot \frac{1}{\psi_1} \cdot \left(\frac{\partial n_D}{\partial C_2}\right)_{C_2 \to 0} - v_i - R \cdot T \cdot \beta_1 \quad (23)$$

where $R_{2m}^{\infty} = \frac{4 \cdot \pi \cdot N_A \cdot \overline{\alpha}_2}{3} / (\mathrm{cm}^3 \cdot \mathrm{mol}^{-1})$ is the dynamic apparent molar refraction of solute, $\psi_1 = \frac{(n_{D1}^2 - 1)}{(n_{D1}^2 + 2)}$ is the specific refraction of the solvent, n_{D1} and n_D are the refraction indexes of solvent and solution, respectively and $\overline{\alpha}_2$ is the electronic polarizability of solvent and was determined by the Hérail and coworkers method [49]. The θ^d quantity contains the volumetric contribution from the intermolecular packing (repulsive interactions) and the (solute + solvent) attractive interactions. By definition, repulsive interactions contribution to non-intrinsic volume is positive, and attractive interactions contribution is negative. The results of densitometric and refractometric method are given in Table 11. The densitometric result contains information about short-range and long-range intermolecular interactions, while the refractometric result only contains information about short-range intermolecular interactions [50]. Due to more negative values of θ^d for both binary systems at lower temperatures, it can be said that the repulsive interactions between thiophene and ionic liquids are getting stronger at higher temperature.

4. Conclusions

Experimental density, speed of sound and refractive index were measured for the binary mixtures of (thiophene + [HMIM][SCN]) and (thiophene + [OMIM][SCN]) at different temperatures. The various volumetric, acoustic and refractometric parameters were obtained. The V_ϕ^0 values of thiophene in all the solutions are positive with the order of [HMIM][SCN] < [OMIM][SCN] which represents the presence of stronger solute–solvent interactions between thiophene and [HMIM][SCN] rather than [OMIM][SCN]. Negative values of $\overline{v}_{m,1}^E$ in TS + [HMIM][SCN] mixture would indicate that molecular interactions between different molecules are stronger than interactions between molecules in the same pure liquid and that attractive forces dominate the behavior of the solutions. The positive $\overline{v}_{m,1}^E$ quantities in TS + [OMIM][SCN] mixture are indicative of absence of considerable interactions, and enhancement of self-associated structure of TS. The $\overline{v}_{m,1}^E$ follows the order: [OMIM][SCN] > [HMIM][SCN]. Most positive $\overline{v}_{m,1}^E$ value of [OMIM][SCN] shows that the solute–solvent interactions at infinite dilution are weakest with TS, whereas negative value of $\overline{v}_{m,1}^E$ of [HMIM][SCN] with TS shows a comparatively stronger solute–solvent interaction. According to the values of κ_ϕ^0, its value in [HMIM][SCN] is positive and becomes more positive with the order of [HMIM][SCN] < [OMIM][SCN]. The more positive κ_ϕ^0 values of thiophene in [OMIM][SCN] are attributed to the repulsive interactions due to lack of solvation of thiophene. Solvation number values are negative for TS + ionic liquid mixture and with increasing concentrations of TS, values approach to positive values. Negative values have the physical means to weaken the local structure of the solvent in close to solute molecules. From interaction volumes V_{int} and due to larger negative values of V_{int} for (TS + [HMIM][SCN]) system, it can be said that between the studied systems the attractive interactions between [HMIM][SCN] and thiophene are more than [OMIM][SCN]. Generally it can be concluded that thiophene-ionic liquid interactions are stronger with [HMIM][SCN].

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