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Thermophysical properties of the thiophene family

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Abstract In this contribution, we have studied the thermophysical properties of three members of the thiophene family (thiophene, 2-methylthiophene, and 2,5-dimethylthiophene) at atmospheric pressure in a wide temperature range. Density, speed of sound, dynamic viscosity, surface tension, and static permittivity have been determined from $T = 278.15$ to $T = 338.15$ K at atmospheric pressure, while the refractive index has been obtained under atmospheric pressure in a temperature range from 283.15 to 338.15 K. Vapour pressures of these compounds have been also measured. Finally, several useful properties like isobaric expansibility, isentropic compressibility, molar refraction, and dipolar moment have been calculated from the experimental data.

Keywords 2,5-Dimethylthiophene · 2-Methylthiophene · Physicochemical properties · Thiophene

Introduction

Thiophene that is a five aromatic ring with an atom of sulphur was discovered as a contaminant in benzene by Victor Meyer in 1882. Thiophene and its derivatives is an important family of compounds that has attracted the attention of researchers due to the large number of applications in different disciplines. In medicine, thiophene derivatives show among others antihypertensive activity [1], anti-inflammatory activity [2], antibacterial activity [3], and antitumour activity [4], while in material science, they have been used, for example, as inhibitors of corrosion of metals [5] or in the fabrication of light-emitting diodes [6–8]. More information about the relevance of thiophenes can be found in the paper of Mancuso and Gabriele [9].

The knowledge of both the thermophysical properties of these compounds and their dependence with structure and intermolecular interactions is fundamental in biochemistry and also in the chemical industry. There are some previous works [10–33] reporting thermophysical properties of thiophenes, but these studies are not systematic, and for most of the properties, there are only measurements at two or three temperatures in a quite limited range of temperature. With the aim of increasing this knowledge, we have determined for thiophene, 2-methylthiophene, and 2,5-dimethylthiophene: densities, speeds of sound, refractive indices, dynamic viscosities, surface tensions, and static permittivities at atmospheric pressure in a wide temperature range ($T = 278.15$–338.15 K) and we have also measured vapour pressures of these compounds.

In addition, we have compared the results obtained for the three members of thiophene family with the homologues compounds of the furan family [34]. These two families of heterocyclic compounds only differ in the heteroatom of the ring: oxygen atom (furans) or sulphur atom (thiophenes). This replacement has structural and energetic effects [35].

We have made a detailed perusal of the literature about thermophysical properties of these compounds. For thiophene, there are some studies reporting properties like

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density, refractive index, dynamic viscosity, and surface tension at several temperatures [10–15]. Zuñiga-Moreno et al. [16] presented a *pVT* characterization; in this study, six density values at atmospheric pressure are included. For speed of sound, Schaaffs [17] presented a value at $T = 293.15$ K, while Weissler [18] and Ulagendran et al. [19] reported the speed of sound at $T = 303.15$ K. In the work of Kobe et al. [20] about ethers and heterocyclic compounds, the refractive index of thiophene at three temperatures (293.15–303.15 K) is reported. Philippe and Piette [21] studied permittivities for solid and liquid thiophene, while in the already mentioned study of Holland and Smyth [12], the permittivities have been studied at several wavelengths and temperatures. With respect to the vapour–liquid equilibrium, we have found ten papers reporting at least vapour pressures values at two temperatures [10, 22–30].

In the case of 2-methylthiophene, Fawcett [31] reported density, refractive index, and dynamic viscosity from $T = 293.15$ to 303.15 K, although for dynamic viscosity, the value at $T = 273.15$ K was also shown; in the same paper, Fawcett presented vapour pressures in the temperature range 371.65–391.55 K. Haines et al. [32] published results for density, refractive index, dynamic viscosity, and surface tension at the same temperatures, and Jeffery et al. [14] determined densities and surface tensions at four temperatures (293.15, 313.15, 333.15, and 358.15 K) and one experimental refractive index at $T = 293.15$ K. On the other hand, White et al. [23] measured vapour pressures from $T = 324.31$ to 390.59 K, Eon et al. [24] showed five values between 333.45 and 373.45 K, and finally, Giles et al. [33] reported two vapour pressures at $T = 373.15$ and 413.15 K.

Last for 2,5-dimethylthiophene, it can be outlined that the studies are more scarce. Jeffery et al. [14] presented experimental densities and surface tensions at four temperatures (293.15, 313.15, 333.15, and 358.15 K) and one experimental refractive index at $T = 293.15$ K. With respect to vapour pressures, Eon et al. [24] provided results from $T = 333.45$ to 373.45 K with steps of 10 K.

Experimental

The thiophene and its derivatives were obtained from Aldrich, and the purities in mass percentage of the chemicals checked by GC chromatography were thiophene (99.9 %), 2-methylthiophene (99.2 %), and 2,5-dimethylthiophene (99.9 %). The gas chromatograph HP7890 was equipped with a flame ionization detector, and the capillary column was Supelco 28049-U (30 m × 0.25 mm). The water content was also determined by a Karl-Fischer titration using an automatic titrator Crison KF 1S-2B, and the water content was found lower than 500 ppm.

In Table 1, the experimental values of density and refractive index of the pure compounds at $T = 293.15$ K are shown along with some literature values [10, 14, 31, 32, 36, 37] for comparison.

Density, ρ, and speed of sound, u, were measured with an Anton Paar DSA 5000 vibrating tube densimeter and sound analyser. The operating frequency for the determination of speed of sound was about 3 MHz. The device is thermostated within ±0.001 K. The uncertainties for density and speed of sound were estimated, respectively, in 1×10^{-5} g cm^{-3} and 0.1 m s^{-1}.

Refractive index at 589.3 nm (sodium D wavelength), n_D, was obtained with an automatic refractometer Abbemat-HP from Dr. Kernchen whose temperature was maintained at ±0.01 K. The uncertainty of the measurements is 1×10^{-5}.

Surface tension, σ, was measured by the drop volume technique with a tensiometer Lauda TVT-2. The temperature was controlled within ±0.01 K by an external Lauda E-200 thermostat. The uncertainty for measurement of surface tension was 0.05 mN m^{-1}.

Kinematic viscosities, ν, determined with an Ubbelohde capillary viscosimeter controlled through a Schott-Geräte automatic measuring unit model AVS-440. The temperature was kept constant at ±0.01 K by a CT52 Schott-Geräte thermostat. The estimated uncertainty of kinematic viscosity was 0.5 %. The dynamic viscosity, $\eta = \rho \cdot \nu$, was calculated from the experimental values of density and kinematic viscosity. For dynamic viscosity, the estimated uncertainty was also 0.5 %.

Static permittivity, ε, at a frequency of 2 MHz, was determined using a capacitive measurement method between parallel plates. The capacitances were measured by means of an Agilent 4263BA precision LCR meter connected to a four-terminal Agilent 16452A liquid dielectric test fixture through an Agilent 16048A test leads. The temperature was fixed at ±0.01 K by a CT52 Schoot-Geräte thermostat. The uncertainty for the static permittivity is 0.5 %.

Finally, vapour pressures were obtained using a dynamic recirculating still, Fischer–Labodest which was equipped with a Cottrell pump. The temperature was measured by a thermometer model F25 with a PT100 probe from Automatic Systems Laboratories. The pressures were determined using a Digiquartz 735-215A-102 pressure transductor from Paroscientific with a Digiquartz 735 display unit. The uncertainty in temperature and pressure of equilibrium was, respectively, 0.01 K and 50 Pa.

Results

The measured values of density, refractive index, speed of sound, surface tension, kinematic viscosity, static permittivity and vapour pressure and some derived properties

Table 1 Densities, ρ, and refractive indices, n_D, at $T = 293.15$ K and at atmospheric pressure together with some literature values for comparison

Compound	ρ/g cm^{-3}		n_D	
	Exptl.	Lit.	Exptl.	Lit.
Thiophene	1.064530	1.0644 [10] 1.0646 [36]	1.528690	1.5287 [10] 1.52866 [14]
2-Methylthiophene	1.020138	1.01965 [32] 1.020 [37]	1.520017	1.5203 [31] 1.52035 [32]
2,5-Dimethylthiophene	0.985248	0.9848 [14]	1.512876	1.51240 [14]

such as isentropic compressibility, molar refraction and dynamic viscosity for the three members of the thiophene family have been reported in Tables S1–S4 of the supplementary information.

All these properties versus temperature are shown in Figs. 1–9.

The experimental densities have been correlated with temperature using a modified Rackett equation [38] in the form indicated by Spencer and Danner [39]:

$$\rho = \frac{A_R}{B_R^{\left[1+(1-T/C_R)^{D_R}\right]} \quad (1)$$

where A_R, B_R, C_R and D_R are the fitting parameters and T is the temperature.

For the following properties, speed of sound, refractive index, surface tension and static permittivity, a linear dependence has been found with respect to temperature; therefore, we have employed a linear equation to fit the data with temperature:

$$Y = A \cdot T + B \quad (2)$$

where Y is the studied property and A and B are the adjustable parameters.

The best-fitting parameters for Eqs. 1 and 2 along with the corresponding relative root-mean-square deviations, RMSD$_r$, calculated as follows:

$$\mathrm{RMSD_r}(\%) = 100\left(\frac{1}{n}\sum_{i=1}^{n}\left(\frac{Y_{i,\exp} - Y_{i,\mathrm{corr}}}{Y_{i,\exp}}\right)^2\right)^{1/2} \quad (3)$$

are given in Table 2.

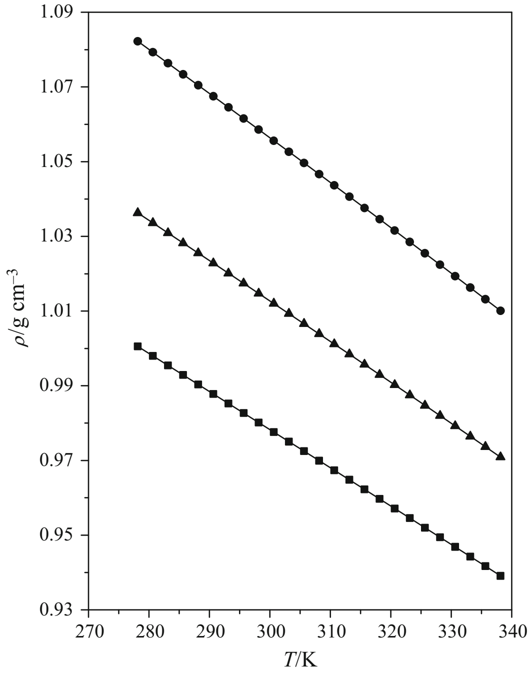

Fig. 1 Density as a function of temperature for studied solvents: (*filled circle*) thiophene, (*filled triangle*) 2-methylthiophene, and (*filled square*) 2,5-dimethylthiophene

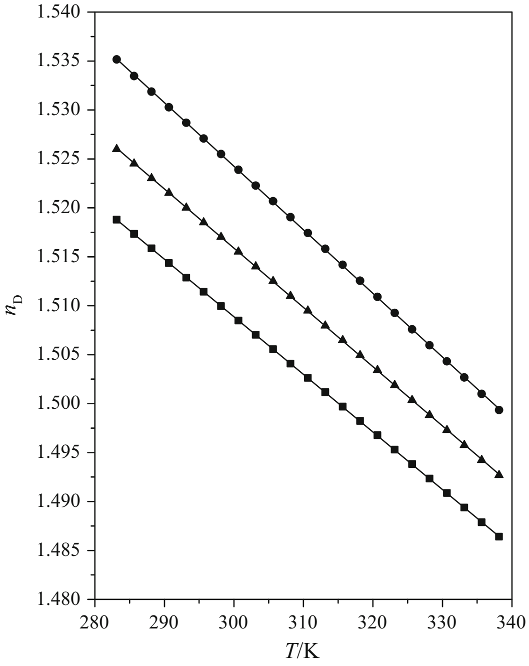

Fig. 2 Refractive index as a function of temperature for studied solvents: (*filled circle*) thiophene, (*filled triangle*) 2-methylthiophene, and (*filled square*) 2,5-dimethylthiophene

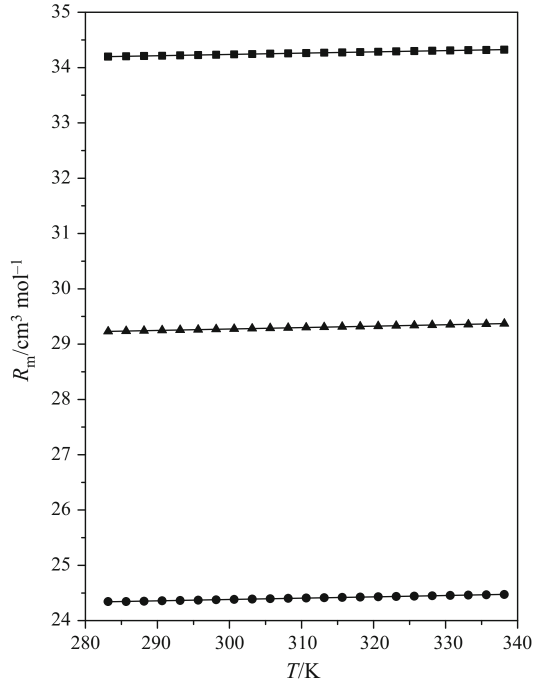

Fig. 3 Molar refraction as a function of temperature for studied solvents: (*filled circle*) thiophene, (*filled triangle*) 2-methylthiophene, and (*filled square*) 2,5-dimethylthiophene

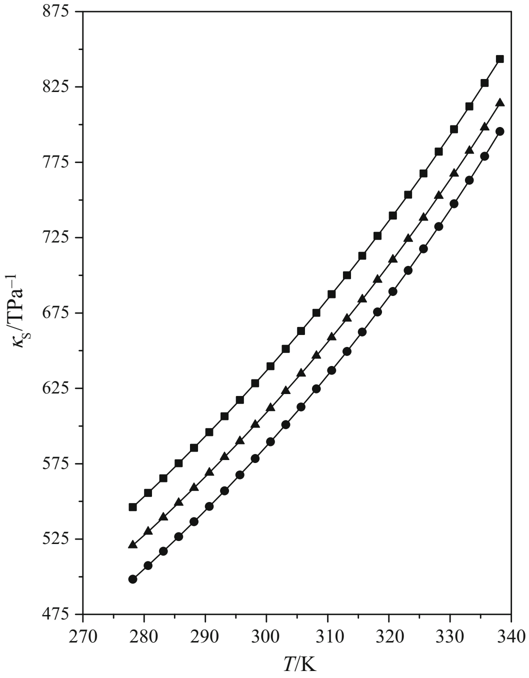

Fig. 5 Isentropic compressibility as a function of temperature for studied solvents: (*filled circle*) thiophene, (*filled triangle*) 2-methylthiophene, and (*filled square*) 2,5-dimethylthiophene

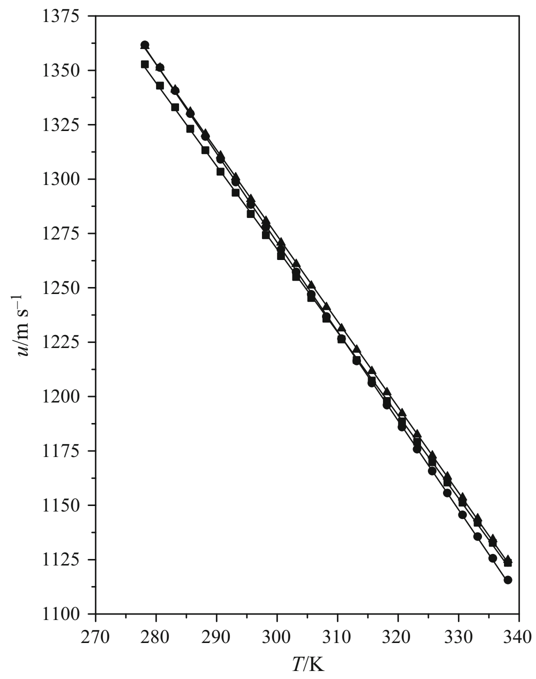

Fig. 4 Speed of sound as a function of temperature for studied solvents: (*filled circle*) thiophene, (*filled triangle*) 2-methylthiophene, and (*filled square*) 2,5-dimethylthiophene

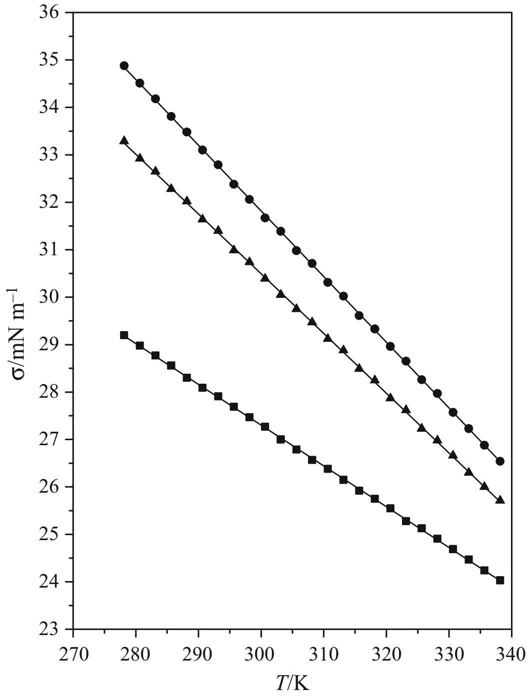

Fig. 6 Surface tension as a function of temperature for studied solvents: (*filled circle*) thiophene, (*filled triangle*) 2-methylthiophene, and (*filled square*) 2,5-dimethylthiophene

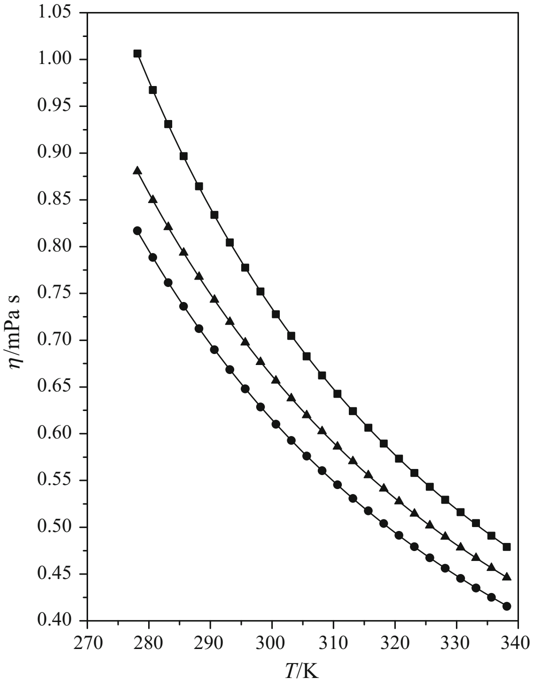

Fig. 7 Viscosity as a function of temperature for studied solvents: (*filled circle*) thiophene, (*filled triangle*) 2-methylthiophene, and (*filled square*) 2,5-dimethylthiophene

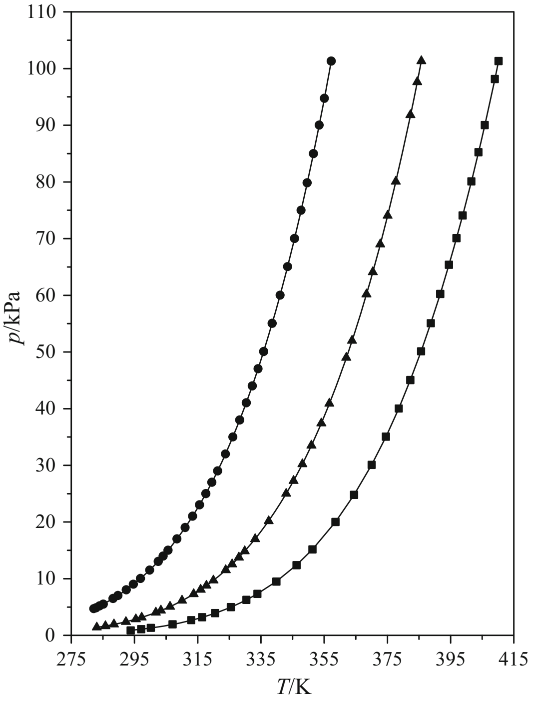

Fig. 9 Vapour pressure as a function of temperature for studied solvents: (*filled circle*) thiophene, (*filled triangle*) 2-methylthiophene, and (*filled square*) 2,5-dimethylthiophene

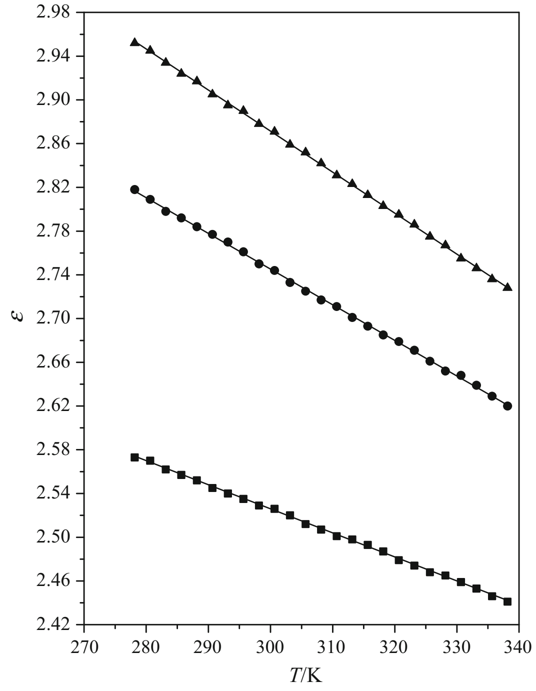

Fig. 8 Static permittivity as a function of temperature for studied solvents: (*filled circle*) thiophene, (*filled triangle*) 2-methylthiophene, and (*filled square*) 2,5-dimethylthiophene

From the dependence of density with temperature, the isobaric expansibility, α_p, can be calculated:

$$\alpha_p = -1/\rho(\partial\rho/\rho T)_p \tag{4}$$

the α_p values at $T = 298.15$ K are reported in Table 3.

The molar refraction, R_m, of thiophene compounds has been obtained using the experimental data of density (molar volume, V_m) and refractive index through the Lorentz–Lorenz relation:

$$R_m = \frac{n_D^2 - 1}{n_D^2 + 2} V_m \tag{5}$$

The isentropic compressibility, κ_S, can be calculated if the ultrasonic absorption is negligible from experimental density and speed of sound values using Newton–Laplace equation:

$$\kappa_S = -1/(\rho \cdot u^2) \tag{6}$$

From experimental surface tension values and their dependence with temperature, the entropy and enthalpy of surface formation per unit surface area, $\Delta S\sigma$ and $\Delta H\sigma$, have been obtained:

Table 2 Fitting parameters and relative root-mean-square deviations, RMSD$_r$, for the measured thermophysical properties

Property	Compound	Fitting parameters				RMSD$_r$/%
		A_R/g cm^{-3}	B_R	C_R/K	D_R	
ρ/g cm^{-3}	Thiophene	0.452525	0.56904	469.2690	0.67258	0.00
	2-Methylthiophene	0.465084	0.59100	471.0584	0.72535	0.00
	2,5-Dimethylthiophene	0.453113	0.59280	482.85	0.77345	0.00
		A/K^{-1}	B			
n_D	Thiophene	−0.0006497	1.719173			0.00
	2-Methylthiophene	−0.0006055	1.697546			0.00
	2,5-Dimethylthiophene	−0.0005881	1.685302			0.00
		A/m s^{-1} K^{-1}	B/m s^{-1}			
u/m s^{-1}	Thiophene	−4.09956	2500.75			0.05
	2-Methylthiophene	−3.94125	2456.35			0.05
	2,5-Dimethylthiophene	−3.81988	2413.76			0.06
		A/mN m^{-1} K^{-1}	B/mN m^{-1}			
σ/mN m^{-1}	Thiophene	−0.13849	73.37			0.09
	2-Methylthiophene	−0.12593	68.27			0.11
	2,5-Dimethylthiophene	−0.08596	53.09			0.08
		η_0/mPa s	B/K	T_0/K		
η/mPa s	Thiophene	0.03230	735.240	50.61		0.15
	2-Methylthiophene	0.03430	735.670	51.39		0.09
	2,5-Dimethylthiophene	0.03900	659.904	75.14		0.06
		A/K^{-1}	B			
ε	Thiophene	−0.00326	3.724			0.06
	2-Methylthiophene	−0.00375	3.997			0.05
	2,5-Dimethylthiophene	−0.00220	3.186			0.05
		A	B	C		
p/kPa	Thiophene	5.9547	1175.6	213.60		0.12
	2-Methylthiophene	5.9580	1269.0	208.46		0.30
		5.9002	1312.1	199.88		0.30

$$\Delta S_\sigma = -(\partial\sigma/\partial T)_p \tag{7}$$

$$\Delta H_\sigma = \sigma - (\partial\sigma/\partial T)_p \tag{8}$$

the values of these derived properties at $T = 298.15$ K are given in Table 3.

The dependence of the dynamic viscosity with temperature is more complex, presenting the plots a convex shape, so we have employed the Vogel–Fulcher–Tammann equation [40–42] to fit the data:

$$\eta = \eta_0 \cdot \exp[B/(T - T_0)] \tag{9}$$

where T_0, B and η_0 are adjustable parameters. These parameters and the relative root-mean-square derivations are collected in Table 2.

The dipolar moment of a compound in the liquid state can be estimated from experimental data of density, refractive index, and static permittivity can be estimated using the Onsager equation [43]:

$$\mu^2 = \frac{9\kappa TM}{4\pi N_A \rho}\frac{\left(\varepsilon - n_D^2\right)\left(2\varepsilon + n_D^2\right)}{\varepsilon\left(n_D^2 + 2\right)^2} \tag{10}$$

Table 3 Calculated properties at $T = 298.15$ K: isobaric expansibility, α_p, enthalpy of surface formation, $\Delta H\sigma$, entropy of surface formation, $\Delta S\sigma$, dipolar moment, μ, and enthalpy of vaporization, ΔH_{vap}

Compound	α_p/kK^{-1}	$\Delta H\sigma$/mN m^{-1}	$\Delta S\sigma$/mN m^{-1} K^{-1}	μ/D	ΔH_{vap}/kJ mol^{-1}
Thiophene	1.1181	73.37	0.14	0.51	34.229
2-Methylthiophene	1.0700	68.27	0.13	0.65	37.672
2,5-Dimethylthiophene	1.0423	53.09	0.09	0.47	40.463

Table 4 Previously reported vapour pressure data and average absolute deviations in pressure, Δp, between our experimental and literature data

Compound	Temperature range/K	Number of experimental data	Reference	Δp/kPa
Thiophene	344.15–354.6	4	[10]	0.04
	288.15–357.31	15	[22]	0.14
	299.95–353.92	15	[23]	0.07
	333.45–353.45	3	[24]	0.92
	313.15–353.15	9	[25]	0.15
	308.15–318.15	3	[26]	0.03
	328.01–356.73	8	[27]	0.12
	323.15–338.15	2	[28]	0.04
	308.14–335.87	8	[29]	0.33
	273.15–363.15	10	[30]	0.43
2-Methylthiophene	371.65–385.65	5	[31]	0.14
	324.31–385.28	16	[23]	0.13
	333.45–373.45	5	[24]	0.24
	373.15	1	[33]	0.03
2,5-Dimethylthiophene	333.45–373.45	5	[24]	0.24

in this equation, M is the molar mass, N_A is the Avogadro constant, and κ is the Boltzmann constant. The calculated dipolar moments at $T = 298.15$ K are shown in Table 3.

Finally, the vapour pressures have been correlated with temperature using the Antoine equation:

$$\log p = A - \frac{B}{C + t} \tag{11}$$

where A, B and C are adjustable parameters, p is the vapour pressure in kPa, and t is temperature in Celsius degrees, the parameters are collected in Table 2. From the slope of the vapour pressure plot, the enthalpy of vaporization can be easily determined using the Clausius–Clapeyron equation. The values of this property at $T = 298.15$ K are reported in Table 3.

Discussion

In this section, we have performed a detailed analysis of several thermophysical properties of thiophene compounds taking into account the structure and molecular interactions. The knowledge of these properties let find out the behaviour at the molecular level.

The density values decrease when the temperature increases, due to the thermal expansion and the weakening of intermolecular interactions. The sequence of the density values is thiophene > 2-methylthiophene > 2,5-dimethylthiophene. The highest value for thiophene can be explained by an easier accommodation of the molecules, because thiophene has not any methyl group attached to the ring, and therefore, there is not remarkable steric hindrance. This density sequence is the same than for furan family, but the values for thiophene compounds are higher; these higher density values are due to a better packing of the molecules in the thiophene family.

Our experimental density values for thiophene are in excellent agreement with the values reported by Fawcett and Rasmussen [10], Haines et al. [11], Timmermans and Hennaut-Roland [13] and Jeffery et al. [14] with an average absolute deviation in density below 0.0002 g cm^{-3}, but the comparison with the results of Holland and Smyth [12], Ohsmyanski et al. [15] and Zuñiga-Moreno et al. [16] is not so favourable with a deviation of 0.0018 g cm^{-3}. For 2-methylthiophene and 2,5-dimethylthiophene, our densities are in accordance with those reported in the literature [14, 30, 31] with average absolute deviations in density: 0.0006 and 0.0002 g cm^{-3}, respectively.

The speed of sound is a very interesting property because observable thermodynamic properties of a fluid can be estimated from its value using conventional thermodynamic calculations [44]. For speed of sound, the values decrease with increasing temperature as expected. It is noticeable that the speeds of sound for the three compounds are quite similar. At low temperatures, the highest u value is for thiophene, followed by 2-methylthiophene and 2,5-dimethylthiophene, while at high temperatures, the sequence is 2-methylthiophene $\approx$ 2,5-dimethylthiophene $>$ thiophene. The speeds of sound for thiophene family are higher than for furan family. The values obtained for thiophene have been compared with literature data, and our experimental values are in excellent agreement with the values reported by Schaaffs [17] and by Weissler [18] with average absolute deviations of 2.3 and 0.9 m s^{-1}, respectively, but with the value given by Ulagendran et al. [19], the agreement is not good, being the deviation around 9 m s^{-1}. Furthermore, using the experimental data for density and speed of sound, we have obtained the corresponding isentropic compressibilities, κ_S, and this property gives knowledge about molecular structure. Now, the κ_S values for the three members studied are different and they increase with temperature. The highest κ_S value is for 2,5-dimethylthiophene which presents the worst molecular packing due to the presence of two methyl groups attached to the ring followed by 2-methylthiophene and thiophene. Now, the values for furan family are higher than for thiophene family showing that the members of the furan family have a poorly packed structure, confirming the suppositions made in the density results discussion.

The refractive index decreases with increasing temperature. The n_D values follow the order: thiophene $>$ 2-methylthiophene $>$ 2,5-dimethylthiophene. With respect to the influence of molecular structure on refractive indices, the better molecular packing in the case of thiophene leads to higher refractive index values. Finally, the values of thiophene family are higher than furan family probably due to the larger polarizability of the sulphur atom in comparison with the oxygen one [12]. Our refractive index results for thiophene are in good agreement with those of Fawcett and Rasmussen [10], and Haines et al. [11] being the average absolute deviation, 0.00015, Holland and Smyth [12] reported the square of refractive indices and the deviation is higher, 0.00134, although the refractive index value at $T = 293.15$ K is in accordance with our value, and finally, our results are similar to the values given by Kobe et al. [20] at the temperatures 293.15 and 303.15 K (deviation 0.00034), but the value at $T = 298.15$ K is not similar, probably due to a type-mistake. In the case of 2-methylthiophene, the comparison with literature data is favourable because the average absolute deviation with the values of Fawcett [31], and Haines et al. [32] is around 0.00039. On the other hand, the refractive index at $T = 293.15$ K reported by Jeffery et al. [14] for the three thiophenes shows a good correspondence with our values with a deviation of 0.00021.

Very important structural information about the studied compounds can be obtained through molar refraction, R_m. This property increases with the temperature. Molar refraction is considered the hard core volume of a mole of molecules [45]; therefore, from this value, the unoccupied part of the molar volume, the free molar volume, can be calculated. The sequence for molar refraction is 2,5-dimethylthiophene $>$ 2-methylthiophene $>$ thiophene. At $T = 298.15$ K, values for free volume are 55.107, 67.474, and 80.235 $cm^3\ mol^{-1}$ for thiophene, 2-methylthiophene, and 2,5-dimethylthiophene, respectively. Highest free volume values indicate that the molecular organization is more compressible as it also confirmed by the isentropic compressibility values of our compounds. It can be also outlined that the free volumes of thiophene family are very similar to those of furan family.

The surface tension depends on the interactions between the molecules of the liquid, that is, this property shows the extent of the cohesive forces in the bulk phase. When the temperature increases, these cohesive forces diminish, so, the surface tension decreases as it shows experimentally. The highest value for surface tension is for thiophene, followed by 2-methylthiophene and 2,5-dimethylthiophene, and the better packing of molecules in thiophene leads to strong cohesive forces and consequently higher surface tension. As we have mentioned, a linear dependence for surface tension and temperature has been found; therefore, the entropy of surface formation per unit surface area is constant in the studied range of temperature. Thiophene presents the highest values for the properties of surface formation per unit surface followed by 2-methylthiophene and 2,5-dimethylthiophene that present similar values. On the other hand, the surface tension for thiophene family is higher than for furan family, due to the higher attractive forces acting in the thiophenes. The surface tension results for thiophene reported here are in good agreement with those of Timmermans and Hennaut-Roland [13] and Haines et al. [11] being the average absolute deviations 0.19 and 0.12 mN m^{-1}, respectively, but they are not in accordance with the results of Jeffery et al. [14] showing a deviation of 1.33 mN m^{-1}, being our results higher. For 2-methylthiophene, the deviations with the results of Haines et al. [32] and Jeffery et al. [14] are 0.34 and 0.65 mN m^{-1}, respectively. Finally, for 2,5-dimethylthiophene the average absolute deviation with the values provided by Jeffery et al. [14] is 1.8 mN m^{-1}, and our results are higher again.

The dynamic viscosity decreases with temperature, and the values for the three thiophenes follow the sequence 2,5-

dimethylthiophene > 2-methylthiophene > thiophene. Values for dynamic viscosities increase when the number of methyl groups attached to the thiophene ring increases because the molecule is heavier and more difficult to transport. The viscosity of the homologue furan compounds is lower; apart from a higher molecular mass of the thiophenes derivates, this behaviour can be explained taking into account that the intermolecular interactions, mainly the dispersion forces, in thiophene family are stronger than in the furan family. Our viscosity results for thiophene present slight absolute average deviations, around 0.015 mPa s, with published values [11–13, 15], although the viscosities reported by Fawcett and Rasmussen [10] are in a better agreement with our results, 0.008 mPa s. For 2-methylthiophene, the average absolute deviation with the results of Fawcett [31] is 0.006 mPa s, while the deviation with the values of Haines et al. [32] is 0.017 mPa s.

Results for static permittivity show that this property decreases with temperature. The highest ε values are for 2-methylthiophene, followed by thiophene and 2,5-dimethylthiophene. Our static permittivities for thiophene are in good agreement with the values reported by Philippe and Piette [21] and Holland and Smyth [12] with average absolute deviations of 0.033 and 0.004, respectively. With respect to calculated dipole moments at $T = 298.15$ K, their values follows the sequence 2-methylthiophene > thiophene > 2,5-dimethylthiophene, and the less symmetrical molecule, 2-methylthiophene, shows the higher dipole moment. These dipole moments are slightly lower than those of the furan family [34] (at $T = 298.15$ K, furan: 0.73 D, 2-methylfuran: 0.76 D, and 2,5-dimethylfuran: 0.59 D).

As expected, the vapour pressure values decrease as the number of methyl groups attached to the thiophene ring increases. At a given temperature, the sequence for vapour pressure is thiophene > 2-methylthiophene > 2,5-dimethylthiophene. As we have already mentioned, the enthalpies of vaporization, ΔH_{vap}, have also been calculated, and the biggest values are presented by 2,5-dimethylthiophene followed by 2-methylthiophene and thiophene. We can also outline that the members of the furan family are more volatile than the corresponding members of the thiophene family; for example, the vapour pressure of furan at $T = 293.15$ K is around eight times higher than the vapour pressure of thiophene. The explanation of this fact can be found again in the higher attractive forces (dispersion forces) operating in the thiophene compounds. This higher strength of the dispersion forces is due to the larger polarizability of the sulphur atom in comparison with the oxygen one, as we have already mentioned. In Table 4, the comparison between our experimental values and those found in the literature is provided; in general, our results are in agreement with previously published vapour pressures [10, 22–31, 33].

Conclusions

In this work, we have presented a thermophysical study for thiophene, 2-methylthiophene, and 2,5-dimethylthiophene. The knowledge of density, speed of sound, refractive index, surface tension, dynamic viscosity, static permittivity, and vapour pressure along with their derived properties provides information at a molecular level about intermolecular interactions and structure of this family of compounds. The number of methyl groups connect to aromatic ring is a very important factor to explain the results.

In most of the properties, except vapour pressure, molar refraction and isentropic compressibility, the obtained values decrease when the temperature increases. Thiophene presents the highest values for density, refractive index, surface tension and vapour pressure. It is noticeable that speed of sound values are quite similar for the three studied compounds, and on the other hand, static permittivities show a interesting behaviour being the values for thiophene intermediate between the values of 2-methylthiophene and 2,5-dimethylthiophene.

Finally, with respect to the comparison of the thermophysical properties of furan and thiophene families, the observed differences mainly arise from the higher attractive forces operating in the thiophene compounds.

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References

1. Russell RK, Press JB, Rampulla RA, McNally JJ, Falotico R, Keiser JA, Bright DA, Tobia A. Thiophene systems 9. Thienopyrimidinedione derivatives as potential antihypertensive agents. J Med Chem. 1988;31:1786–93.
2. Pillai AD, Rathod PD, Xavier FP, Pad H, Sudarsanam V, Vasu KK. Tetra substituted thiophenes as anti-inflammatory agents: exploitation of analogue-based drug design. Bioorg Med Chem. 2005;13:6685–92.
3. Tehranchian S, Akbarzadeh T, Fazeli MR, Jamalifar H, Shafiee A. Synthesis and antibacterial activity of 1-[1,2,4-triazol-3-yl] and 1-[1,3,4-thiadiazol-2-yl]-3-methylthio-6,7-dihydro-benzo[c]thiophen-4(5H)ones. Bioorg Med Chem Lett. 2005;15:1023–5.
4. Chen Z, Ku TC, Seley-Radtke KL. Thiophene-expanded guanosine analogues of gemcitabine. Bioorg Med Chem Lett. 2015;25:4274–6.
5. Benabdellah M, Aouniti A, Dafali A, Hammouti B, Benkaddour M, Yahyi A, Ettouhami A. Investigation of the inhibitive effect of triphenyltin 2-thiophene carboxylate on corrosion of steel in 2 M H_3PO_4 solutions. Appl Surf Sci. 2006;252:8341–7.

6. Barbarella G, Melucci M, Sotgiu G. The versatile thiophene: an overview of recent research on thiophene-based materials. Adv Mater. 2005;17:1581–93.
7. Perepichka IF, Perepichka DF, Meng H, Wudl F. Light-emitting polythiophenes. Adv Mater. 2005;17:2281–305.
8. Kim C, Choi KS, Oh JH, Hong HJ, Han SH, Kim SY. The effects of octylthiophene ratio on the performance of thiophene based polymer light-emitting diodes. Sci Adv Mater. 2015;7:2401–9.
9. Mancuso R, Gabriele B. Recent advances in the synthesis of thiophene derivatives by cyclization of functionalized alkynes. Molecules. 2014;19:15687–719.
10. Fawcett FS, Rasmussen HE. Physical properties of thiophene. J Am Chem Soc. 1945;67:1705–9.
11. Haines WE, Helm RV, Bailey CW, Ball JS. Purification and properties of ten organic sulfur compounds. J Phys Chem. 1954;58:270–8.
12. Holland RS, Smyth CP. Microwave adsorption and molecular structure in liquids X. The relaxation times of nine heterocyclic molecules. J Phys Chem. 1955;59:1088–92.
13. Timmermans J, Hennaut-Roland M. Work of the International Bureau of Physico-Chemical Properties physical constants of twenty organic compounds. J Chim Phys Phys Chim Biol. 1959;56:984–1023.
14. Jeffery GH, Parker R, Vogel AI. Physical properties and chemical constitution. Part XXXII. Thiophen compounds. J Chem Soc. 1961;570–575.
15. Oshmyansky Y, Hanley HJM, Ely JF, Kidnay AJ. The viscosities and densities of selected organic compounds and mixtures of interest in coal liquefaction studies. Int J Thermophys. 1986;7:599–608.
16. Zuñiga-Moreno A, Galicia-Luna L, Betancourt-Cárdenas FF. Compressed liquid densities and excess volumes of $CO_2{}^+$ thiophene binary mixtures from 313 to 363 K and pressures up to 25 MPa. Fluid Phase Equilib. 2005;236:193–204.
17. Schaaffs W. Investigations on the velocity of sound and constitution I. The velocity of sound in organic liquids. Z Phys Chem. 1944;194:28–38.
18. Weissler A. Ultrasonic investigation of molecular properties of liquids. IV. Cyclic compounds. J Am Chem Soc. 1949;71:419–21.
19. Ulagendran V, Kumar R, Jayakumar S, Kannappan V. J Mol Liq. 2009;148:67–72.
20. Kobe KA, Ravicz AE, Vohra SP. Critical properties and vapor pressures of some ethers and heterocyclic compounds. Ind Eng Chem Chem Eng Data Ser. 1956;1:50–6.
21. Philippe R, Piette AM. Recherches de stoechiométrie VII. Contribution à l'étude de la constante diélectrique des composés organiques purs. Bull Soc Chim Belg. 1955;64:600–27.
22. Waddington G, Knowlton JW, Scott DW, Oliver GD, Todd SS, Hubbard WN, Smith JC, Huffman HM. Thermodynamic properties of thiophene. J Am Chem Soc. 1949;71:797–808.
23. White PT, Barnard-Smith DG, Fidler FA. Vapor pressure-temperature relationships of sulfur compounds related to petroleum. Ind Eng Chem. 1952;44:1430–8.
24. Eon C, Pommier C, Guiochon G. Vapor pressures and second virial coefficients of some five-membered heterocyclic derivatives. J Chem Eng Data. 1971;16:408–10.
25. Diaz Peña M, Crespo Colin A, Compostizo A, Escudero I. Liquid-vapor equilibria in binary systems formed by methylcyclohexane with chlorobenzene, fluorobenzene and thiophene. J Chem Eng Data. 1980;25:17–21.
26. Triday JO, Rodriguez P. Vapor-liquid equilibria for the system benzene-thiophene-methanol. J Chem Eng Data. 1985;30:112–6.
27. Erlin S, Zaytseva A, Uusi-Kyyny P, Younghun K, Keskinen KI, Aittamaa J. Vapor-liquid equilibrium for binary system of 1-propanethiol, thiophene, and diethyl sulfide with toluene at 90.03 kPa. J Chem Eng Data. 2006;51:1372–6.
28. Sapei E, Zaytseva A, Uusi-Kyyny P, Keskinen KI, Aittamaa J. Vapor-liquid equilibrium for binary system of thiophene + *n*-hexane at (338.15 and 323.15) K and thiophene + 1-hexene at (333.15 and 323.15) K. J Chem Eng Data. 2006;51:2203–8.
29. Uusi-Kyyny P, Pokki J-P, Sapei E, Pakkanen M, Alopaeus V. Vapor-liquid equilibrium for thiophene + butane, + trans-but-2-ene, + 2-methylpropane, and + 2-methylpropene. J Chem Eng Data. 2011;56:614–21.
30. Khelassi-Sefaoui A, Mutelet F, Mokbel I, Jose J, Negadi L. Measurement and correlation of vapour pressures of pyridine and thiophene with [EMIM][SCN] ionic liquid. J Chem Thermodyn. 2014;72:134–8.
31. Fawcett FS. Physical properties of 2- and 3-methylthiophene. J Am Chem Soc. 1946;68:1420–2.
32. Haines WE, Helm RV, Cook GL, Ball JS. Purification and properties of ten organic sulfur compounds-Second series. J Phys Chem. 1956;60:549–55.
33. Giles NF, Wilson GM. Phase equilibria on four binary systems: 1,2-dichloroethane + trans-1,2-dichloroethylene, 1-octene + 2-methyl thiophene, 2-ethyl thiophene + 2,2,4-trimethylpentane, and cyclopropanecarbonitrile + water. J Chem Eng Data. 2006;51:1973–81.
34. Lomba L, Aznar I, Gascón I, Lafuente C, Giner B. Thermophysical study of the furan family. Thermochim Acta. 2015; 617:54–64.
35. Freitas VLS, Ribeiro da Silva MDMC. Oxygen and sulfur heterocyclic compounds. J Thermal Anal Calorim. 2015;121: 1059–71.
36. Appleby WG, Sartor AF, Lee SH, Kapranos SW. Alkylation of thiophene with olefins. J Am Chem Soc. 1948;70:1552–5.
37. Zhao C, Li J, Qi R, Chen J, Luan Z. Pervaporation separation of n-heptane/sulfur species mixtures with polydimethylsiloxane membranes. Sep Purif Technol. 2008;63:220–5.
38. Rackett HG. Equation of state for saturated liquids. J Chem Eng Data. 1970;15:514–7.
39. Spencer C, Danner R. Improved equation for prediction of saturated liquid density. J Chem Eng Data. 1972;17:236–41.
40. Vogel H. The temperature dependence law of the viscosity of fluids. Phys Zeit. 1921;22:645–6.
41. Fulcher GS. Analysis of recent measurements of the viscosity of glasses. J Am Ceram Soc. 1923;8:339–55.
42. Tammann G, Hesse W. Die abhangigkeit der viskositat von der temperaturvon unterkilhlten fliissigkeiten. Zeit Anorg Allg Chem. 1926;156:254–7.
43. Onsager L. Electric moments of molecules in liquids. J Am Chem Soc. 1936;58:1486–93.
44. Bagheri-Chokami Y, Farahani N, Mirkhani SA, Ilani-Kashkouli P, Gharagheizi F, Mohammadi AH. A chemical structure-based model for estimating speed of sound in liquids. J Thermal Anal Calorim. 2014;116:529–38.
45. Brocos P, Piñeiro A, Bravo R, Amigo A. Refractive indices, molar volumes and molar refractions of binary liquid mixtures: concepts and correlations. Phys Chem Chem Phys. 2003;5: 550–7.