Fluid Phase Equilibria 267 (2008) 188–192

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Short communication

Estimation of speed of sound of ionic liquids using surface tensions and densities: A volume based approach

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ARTICLE INFO

Article history:
Received 15 October 2007
Received in revised form 10 March 2008
Accepted 12 March 2008
Available online 18 March 2008

Keywords:
Ionic liquid
Speed of sound
Surface tension
Density
Correlation

ABSTRACT

The limited availability of experimental data and their quality have been preventing the development of predictive methods and Computer Aided Molecular Design (CAMD) of ionic liquids (ILs). Based on experimental speed of sound data collected from the literature, the inter-relationship of surface tension (σ), density (ρ), and speed of sound (u) has been examined for imidazolium based ILs containing hexafluorophosphate (PF_6), tetrafluoroborate (BF_4), bis(trifluoromethanesulphonyl) amide (NTf_2), methyl sulphate ($MeSO_4$), ethyl sulphate ($EtSO_4$), and trifluoromethanesulphonate (CF_3SO_3) anions, covering wide ranges of temperature, 278.15–343.15 K and speed of sound, 1129.0–1851.0 m s^{-1}. The speed of sound was correlated with a modified Auerbach's relation, by using surface tension and density data obtained from volume based predictive methods previously proposed by the authors. It is shown that a good agreement with literature data is obtained. For 133 data points of 14 ILs studied a mean percent deviation (MPD) of 1.96% with a maximum deviation inferior to 5% was observed. The correlations developed here can thus be used to evaluate the speeds of sound of new ionic liquids.

1. Introduction

The research areas on ionic liquids (ILs) are growing rapidly and the potential application areas of ILs are numerous. ILs have been accepted as a new green chemical revolution which excited both the academia and the chemical industries. Due to their unique properties, like negligible volatility, wide liquidus range, non-flammability, high thermal conductivity, chemical and physical stability, and high potential for recycling, they received an advantageous edge in various applications and when considered the possibility of tuning the chemical and physical properties of ILs by changing anion–cation combination, this advantage will become a great opportunity to obtain task-specific ILs for a specific applications.

The speed of sound is an important property in the study of physics and chemistry, as speed of sound when used along with other properties, allows the derivation of a wide range of thermophysical properties including isentropic and isothermal compressibilities, isobaric thermal expansion coefficient, thermal pressure coefficient, the Joule–Thomson coefficient, isobaric and isochoric heat capacities, ratio of isobaric and isochoric heat capacities, and the reduced bulk modulus. All of these derivative properties are connected, with speed of sound directly or indirectly, by thermodynamic relationships. They are essential for the accurate design and optimization of several industrial processes. For instance, heat capacities become crucial to calculate the calorific power of a compound and they are extremely important in the chemical and oil industry; knowledge of the inversion curve, defined as the curve where the Joule–Thomson coefficient becomes zero, is essential for the design of throttling processes and so forth.

Experimental data for speed of sound of ionic liquids is very scarce and limited to imidazolium based ionic liquids. When developing ionic liquids for a given purpose, if experimentally measured speed of sound data are not available, theoretical or empirical meth-

Abbreviations: CAMD, Computer Aided Molecular Design; IL, ionic liquid; MPD, mean percentage deviation; QSPR, quantitative structure–property relationship; OF, objective function; [C_4mim][PF_6], 1-butyl-3-methylimidazolium hexafluorophosphate; [C_6mim][PF_6], 1-hexyl-3-methylimidazolium hexafluorophosphate; [C_8mim][PF_6], 1-octyl-3-methylimidazolium hexafluorophosphate; [C_4mim][BF_4], 1-butyl-3-methylimidazolium tetrafluoroborate; [C_2mim][NTf_2], 1-ethyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide; [C_3mim][NTf_2], 1-propyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide; [C_4mim][NTf_2], 1-butyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide; [C_5mim][NTf_2], 1-pentyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide; [C_6mim][NTf_2], 1-hexyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide; [C_8mim][NTf_2], 1-octyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide; [C_1mim][$MeSO_4$], 1,3-dimethylimidazolium methylsulphate; [C_4mim][$MeSO_4$], 1-butyl-3-methylimidazolium methylsulphate; [C_2mim][$EtSO_4$], 1-ethyl-3-methylimidazolium ethylsulphate; [C_2mim][CF_3SO_3], 1-ethyl-3-methylimidazolium trifluoromethansulphonate; [$C_n$mim]$^+$, 1-alkyl-3-methylimidazolium cation.

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doi:10.1016/j.fluid.2008.03.008

ods must be used to establish if the speed of sound are within acceptable limiting values defined in the design specifications. For this purpose prediction methods for speed of sound of ILs are required.

While much work has been devoted to the wide range of applications of ILs, the basic understanding and study of their structure–property relationships is of equivalent importance but has lagged behind. Very few works have systematically studied the qualitative and/or quantitative relationships between the structures of ILs and their fundamental properties, such as melting point, viscosity, density, surface tension, thermal and electrochemical stability, solvent properties, and speed of sound. To better understand the nature of ionic liquids and rationally expand their applications, knowledge of their physical properties is required. At present, however, data for many other physico-chemical properties of ionic liquids are in short supply, or too unreliable to allow similar structure–property relationship studies.

We already succeeded in developing rapid and facile predictive methods for density [1], surface tension [2] and viscosity [3] of ILs in a wide temperature range. In continuation of our study on rapid predictive methods, here it will be shown that using the previously predicted methods for surface tension and density data, it is possible to obtain a good description of the speed of sound of ionic liquids.

2. Results and discussion

A data base of experimental speed of sound (u) data available in the open literature was collected and is reported in Table 1. Unfortunately only data for imidazolium based ionic liquids was available and thus only the applicability of present correlations studied to imidazolium based ionic liquids could be tested. A global number of 133 data points for 14 imidazolium based ILs containing PF_6 (hexafluorophosphate), BF_4 (tetrafluoroborate), Tf_2N (bis(trifluoromethylsulphonyl)amide), $MeSO_4$ (methylsulphate), $EtSO_4$ (ethylsulphate), and CF_3SO_3 (trifluoromethanesulphonate) as anions [4–20], covering wide ranges of temperature, 278.15–343.15 K and speed of sound, 1129.0–1851.0 m s^{-1}, were used in this study.

The speed of sound (u) in m s^{-1} units can be estimated using the theoretical Auerbach's relation [21]

$$u = \left(\frac{\sigma}{6.33 \times 10^{-10} \cdot \rho} \right)^{a} \quad (1)$$

where $a = 2/3$, σ and ρ are the surface tension in Nm^{-1} units and density in kg m^{-3} units, respectively. Oswal et al. used Auerbach's relation to estimate speed of sound of alkyl alkanoates [22] and alkyl amines [23]. Aminabhavi et al. [24] used Auerbach's relation

Table 1
Prediction of speed of sound of imidazolium based ionic liquids

Ionic liquid	Mw (g mol^{-1})	Calculated parachor	Molecular volume (Å^3)	Temperature range (K)	Data points	Mean percent deviation (%)	Reference
[C_4mim][PF_6]	284.18	534.62	345	298.15	1	0.06	[4]
				298.15	1	0.11	[5]
				293.15–303.15	3	0.14	[6]
				293.15–303.15	3	0.14	[7]
				298.15	1	0.14	[8]
				298.15–318.15	5	0.44	[9]
				293.15	1	0.91	[10]
				283.16–323.25	8	1.55	[11]
[C_6mim][PF_6]	312.24	614.42	401	293.15–303.15	3	2.17	[6]
				293.15–303.15	3	2.17	[7]
				298.15	1	2.17	[5]
[C_8mim][PF_6]	340.29	694.22	457	293.15–303.15	3	4.04	[6]
				293.15–303.15	3	4.04	[7]
				298.15	1	4.08	[5]
[C_4mim][BF_4]	226.03	473.50	311	293.15	1	3.56	[10]
				283.15–323.15	5	3.87	[11]
				298.15–318.15	5	4.35	[12]
[C_2mim][Tf_2N]	391.32	631.86	430	293.15	1	4.91	[10]
[C_3mim][Tf_2N]	405.34	671.76	458	298.15–338.15	5	2.92	[13]
[C_4mim][Tf_2N]	419.37	711.66	486	293.15	1	1.34	[10]
				283.15–323.15	5	1.84	[14]
[C_5mim][Tf_2N]	433.40	751.56	514	298.15	1	0.85	[10]
				288.15–338.15	6	0.82	[13]
[C_6mim][Tf_2N]	447.42	791.46	542	293.15	1	0.48	[10]
				283.15–343.15	8	1.07	[15]
[C_8mim][Tf_2N]	475.48	871.26	598	293.15	1	2.42	[10]
[C_1mim][$MeSO_4$]	208.24	453.90	270	293.15–303.15	3	3.61	[6]
				293.15–303.15	3	3.61	[7]
				283.15–343.15	13	3.63	[16]
[C_4mim][$MeSO_4$]	250.32	555.60	354	293.15–303.15	3	0.12	[6]
				278.15–343.15	14	0.36	[17]
[C_2mim][$EtSO_4$]	236.29	515.7	326	288.15–343.15	12	0.59	[18]
				298.15	1	1.16	[19]
[C_2mim][CF_3SO_3]	260.24	475.43	311	278.15–338.15	7	3.78	[20]
Total				278.15–343.15	133	1.96	

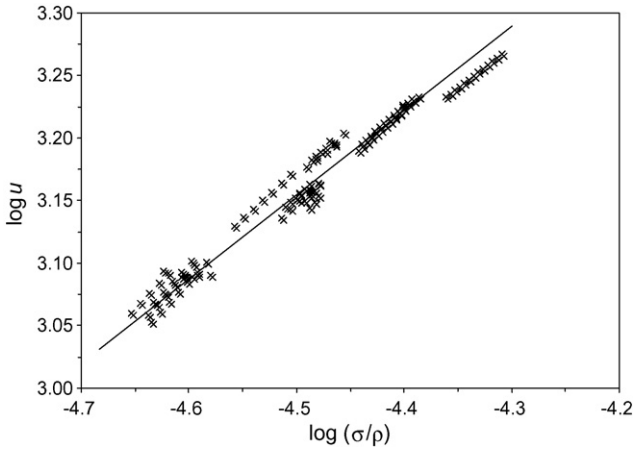

Fig. 1. Relationship between $\log u$ and $\log(\sigma/\rho)$ for imidazolium based ionic liquids: (×) experimental data points; solid line, correlation using Eq. (1) with $a = 0.6714$.

to estimate speed of sound of binary mixtures of 2-methoxyethanol with aliphatic alcohols. Recently Blairs [25] modified the Auerbach's relation for the estimation of unknown sound velocities of metallic liquids using available surface tension and density values. Eq. (1) predicts that a plot of $\log u$ against $\log(\sigma/\rho)$ should be linear with the slope equal to 2/3. To examine the functional dependence of u and σ/ρ, a double logarithmic plot was drawn in Fig. 1 using speed of sound data from literature [4–20] and surface tension and density data obtained using our predictive methods [1,2], briefly described below. The resulting linear correlation, not presented in the figure, can be expressed as

$$\log u_{\text{exp}} = (0.6199 \pm 0.0092) \cdot \log\left(\frac{\sigma}{\rho}\right) + (5.9447 \pm 0.0414) \quad (2)$$

with a correlation coefficient $R^2 = 0.9717$ at 95% confidence level. This shows that although Eq. (1) in its original form is not able to describe the experimental sound velocities a modified version of it, following the approach of Blairs [25] or Oswal et al. [22,23], could be used to correlate the sound velocities of ionic liquids.

Recently, we proposed an extension of the Ye and Shreeve method [26] for the estimation of ionic liquids densities [1] in a wide range of temperatures (273.15–393.15) K and pressures (0.10–100) MPa, according to Eq. (3) that can be used for the estimation of the speed of sound (u) using Eq. (1) above.

$$\rho = \frac{\text{Mw}}{NV(a + bT + cP)} \quad (3)$$

where ρ is the density in kg m^{-3}, Mw is molecular weight in kg mol^{-1}, N is the Avogadro constant, V is the molecular volume in Å^3, T is the temperature in K and P is the pressure in MPa. The coefficients a, b and c were estimated by fitting Eq. (3) to our previously published experimental data [27,28]. A total amount of circa 800 density data points was used. The values of coefficient a, b and c obtained are $8.005 \times 10^{-1} \pm 2.333 \times 10^{-4}$, $6.652 \times 10^{-4} \pm 6.907 \times 10^{-7}$ K^{-1} and $-5.919 \times 10^{-4} \pm 2.410 \times 10^{-6}$ MPa^{-1}, respectively, at 95% confidence level. The mean percentage deviation (MPD) of calculated densities from the experimental densities is 0.29%. For the density calculation, volume parameters (V) of ions and groups were either directly taken from literature [26] or calculated following the Jenkins' procedure [29]. Volume contributions for ILs used are shown in Table 1.

Using estimated densities and parachors (P_{ch}), the prediction of surface tension for imidazolium based ionic liquids can be done [2] using Eq. (4),

$$\sigma = \left(\frac{P_{\text{ch}} \cdot \rho}{\text{Mw}}\right)^4 \quad (4)$$

The parachors were calculated from Knotts et al. [30] parachor QSPR (quantitative structure–property relationship) correlation using the parameter table estimated from the second training set containing experimental surface tension values with an uncertainty less than 1%. A global number of 361 data points for 38 imidazolium based ILs containing BF_4, PF_6, Tf_2N (bis(trifluoromethylsulphonyl)imide), TfO (trifluoromethanesulphonate), $MeSO_4$ (methylsulphate), $EtSO_4$ (ethylsulphate), Cl, I, I_3, $AlCl_4$, $FeCl_4$, $GaCl_4$ and $InCl_4$ as anions were used in that study. For the studied ILs the mean percentage deviation was 5.75% with a maximum deviation inferior to 16%, which are much lower than the value reported by Knotts et al. [30] for multifunctional compounds in their study. The parachors used are shown in Table 1.

Using these models for the estimation of the densities and surface tensions of the ionic liquids for which sound velocities were available in the literature, and using the original form of the Auerbach equation where only the exponent is taking as adjustable parameter, the experimental sound velocities were correlated by minimizing objective function (O.F.),

$$\text{O.F.} = \frac{100 \times \sum_{i=1}^{N_p} \left| ((\sigma/6.33 \times 10^{-10} \cdot \rho)^a - u_{\text{exp}})/u_{\text{exp}} \right|_i}{N_p} \quad (5)$$

The mean percent deviation, defined as,

$$\text{MPD}\ (\%) = \frac{100 \times \sum_{i=1}^{N_p} \left| (u_{\text{cal}} - u_{\text{exp}})/u_{\text{exp}} \right|_i}{N_p} \quad (6)$$

where N_p represents the number of data points were estimated for each system and are reported in Table 1.

The experimental speed of sound data can be described with success, as shown in Fig. 1, by using $a = 0.6714 \pm 0.0002$ in Eq. (1), for the imidazolium based ILs containing PF_6, BF_4, Tf_2N, $MeSO_4$, $EtSO_4$, and CF_3SO_3 anions. The experimental speed of sound (Y) of imidazolium based ILs displays a good agreement with the corresponding calculated speed of sound (X) as shown in Fig. 2 where $Y = (0.9952 \pm 0.0022)\,X$ ($R^2 = 0.9623$ at 95% level of confidence). Relative deviations between the calculated and experimental speed of sound data as a function of temperature, for ionic liquids containing $[C_4mim]^+$ (1-butyl-3-methylimidazolium cation) and different anions are shown in Fig. 3. For the 133 data points of 14 ionic liquids

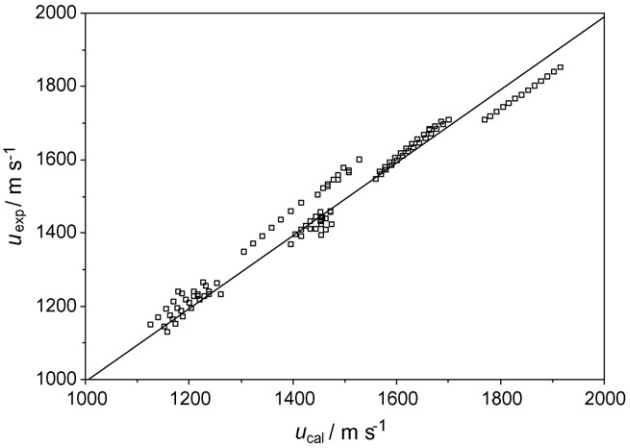

Fig. 2. Linear relationship between experimental and calculated speed of sound using Eq. (1) with $a = 0.6714$ for imidazolium based ionic liquids.

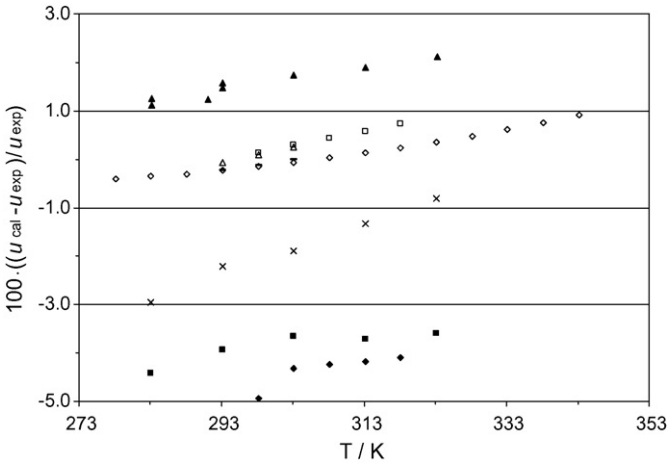

Fig. 3. Relative deviations between the calculated and experimental speed of sound data as a function of temperature, for ionic liquids containing $[C_4mim]^+$ (1-butyl-3-methylimidazolium cation) and different anions: $[PF_6]$: (△) Pereiro and Rodriguez [6]; (□) Zafarani-Moattar and Shekaari [9]; (▲) Azevedo et al. [11]; $[BF_4]$: (■) Azevedo et al. [11]; (♦) Zafarani-Moattar and Shekaari [12]; $[Tf_2N]$: (×) Azevedo et al. [14]; $[MeSO_4]$: (◊) Pereiro et al. [17]; (-) Pereiro and Rodriguez [6].

available in literature [4–20], the overall MPD is 1.96% with a maximum deviation inferior to 5%. From these 40.6% of the estimated speeds of sound were within absolute deviation of 0.00–1.00%, 24.1% were within 1.001–3.00%, 24.1% were within 3.001–4.00%, and only 11.3% were larger than 4.0%. Maximum absolute deviation is 4.93% for $[C_4mim][BF_4]$ (1-butyl-3-methylimidazolium tetrafluoroborate) from Zafarani-Moattar and Shekaari [12] at 298.15 K.

To see the influence of the IL anion on the speed of sound, speed of sound are calculated using $a = 0.6714$ in Eq. (1), for the series of $[C_nmim]^+$ (1-alkyl-3-methylimidazolium cation) with four different anions, $[BF_4]$, $[PF_6]$, $[CF_3SO_3]$ and $[Tf_2N]$ at 298.15 K, and the data are plotted as a function of carbon numbers (n) on the series of $[C_nmim]^+$ in Fig. 4. The results indicate that the speed of sound increases with alkyl chain length of imidazolium cation and this increment is more pronounced in case of ILs containing $[PF_6]$ anions. At 298.15 K, speed of sound for a series of imdazolium based ILs having similar cation, seems to increase with the decrease in molecular volume of anion, showing the trend $[Tf_2N] < [CF_3SO_3] < [PF_6] < [BF_4]$ which is similar to the trend observed in literature for ILs having cations $[C_2mim]^+$ [10,20], $[C_4mim]^+$ [4–12,14], $[C_6mim]^+$ [5–7,10,15], and $[C_8mim]^+$ [5–7,10].

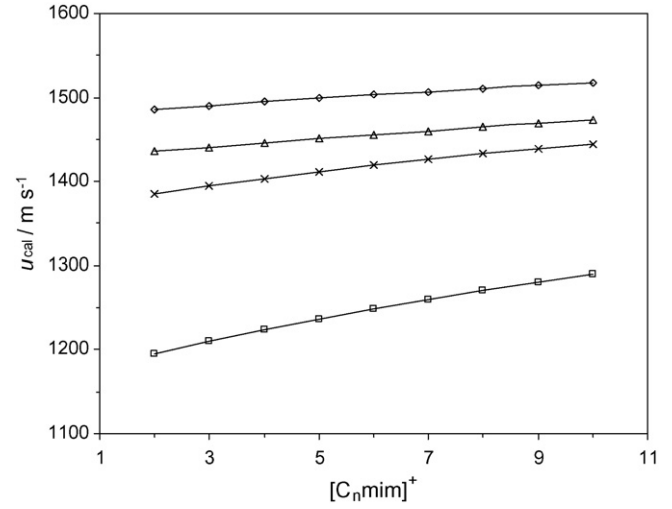

Fig. 4. Speed of sound of ionic liquids as a function of the number of carbons (n), on the series of $[C_nmim]^+$ (1-alkyl-3-methylimidazolium cation) at 298.15 K: (◊) $[C_nmim][BF_4]$; (△) $[C_nmim][PF_6]$; (×) $[C_nmim][CF_3SO_3]$; (□) $[C_nmim][Tf_2N]$.

3. Conclusions

It is here shown that the Auerbach's relation [21] was successfully modified to describe the speeds of sound of imidazolium based ILs. This correlation, using density and surface tension correlations previously proposed by us [1,2] allows the description of speed of sound of imidazolium based ILs, containing PF_6, BF_4, Tf_2N, $MeSO_4$, $EtSO_4$, and CF_3SO_3 as anions, in wide ranges of temperature, 278.15–343.15 K and speed of sound, 1129.0–1851.0 m s^{-1}. For a database of 133 data points for 14 imidazolium based ILs [4–20], the mean percent deviation observed was of only 1.96%. Calculated speeds of sound are thus in good agreement with experimental literature data. The correlations developed here should thus be able to predict the speed of sound of new ionic liquids in wide ranges of temperature.

List of symbols

a, b, c	coefficients of density correlation
Mw	molecular weight
N	Avogadro constant
N_p	number of data points
P	pressure
P_{ch}	parachor
T	temperature
u	speed of sound
V	molecular volume

Greek letters

ρ	density
σ	surface tension

Subscripts

cal	calculated property
exp	experimental property

Acknowledgement

This work was supported by Fundação para a Ciência e a Tecnologia (Project POCI/EQU/58152/2004). R.L. Gardas acknowledges the financial support from Fundação para a Ciência e a Tecnologia through, his Post-Doctoral Fellowship (SFRH/BPD/23246/2005).

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