Fluid Phase Equilibria 303 (2011) 184–190

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

Surface tension of 1-alkyl-3-methylimidazolium based ionic liquids with trifluoromethanesulfonate and tetrafluoroborate anion

Monika Součková, Jaroslav Klomfar, Jaroslav Pátek*

Institute of Thermomechanics, v.v.i., Academy of Sciences of the Czech Republic, Dolejškova 5, CZ 182 00 Prague 8, Czech Republic

ARTICLE INFO

Article history:
Received 18 October 2010
Received in revised form 27 January 2011
Accepted 28 January 2011
Available online 26 February 2011

Keywords:
Ionic liquid
Trifluoromethanesulfonate
Tetrafluoroborate
Surface tension

ABSTRACT

The amount of available accurate experimental data on the surface tension of ionic liquids is still limited; in many cases the data are rare or even absent. In the present study, air–liquid interfacial tension data were determined experimentally for five 1-C_n-3-methylimidazolium based ionic liquids ($n = 2$, 4, and 6), three with trifluoromethanesulfonate and two with tetrafluoroborate anion, at atmospheric pressure in the temperature range from 268 to 356 K. The resultant surface tension data are average values of the measurements repeated many times at each set point temperature. The accuracy of the results, was confirmed by employing the Wilhelmy plate and the du Noüy ring methods in parallel, using the Krüss K100MK2 tensiometer. For the Wilhelmy plate data the combined standard uncertainty is estimated to be about 0.05 mN m^{-1}. The data obtained by du Noüy method show about up to seven times greater scatter than those obtained by the Wilhelmy plate method. To the 50 up to now published surface tension values for the five studied ionic liquids the present study adds further 175 data points. In contrast to that of n-alkanes, the surface tension of 1-alkyl-3-methylimidazolium based ionic liquids decreases and their surface entropy increases with the cation alkyl chain length.

1. Introduction

Owing to their tunable structure and unique chemical and physical properties, ionic liquids find their application in a wide range of fields. For the proper design of any industrial process using ionic liquids, it is necessary to know their thermophysical properties such as the density, viscosity and surface tension. Comprehensive property data are also requisite for the development of correlations and predictive schemes. Only a large body of experimental data obtained by different authors using different methods and samples from different sources provides a base to assess critically the reliability of each individual data set. Despite of efforts of many research groups the amount of available accurate experimental data on physical and chemical properties of ILs is still limited due to the large number of prospective ionic liquids. In many cases, the data are rare or completely nonexistent. This is also the case of the air–liquid interfacial tension of 1-alkyl-3-methylimidazolium based ionic liquids selected for the present study. Three of them have trifluoromethanesulfonate and two tetrafluoroborate anion, while their cation alkyl side-chain length is $n = 2$, 4, and 6 and $n = 2$, and 6, respectively. Usually, only the ionic liquids with an even number of carbon atoms in the alkyl chain are available commercially due to the much higher price of the precursors with an odd number of carbon atoms. Table 1 gives an overview of the literature sources [1–8] for experimental surface tension data for the five ionic liquids selected, together with the corresponding temperature region, sample water content, the measuring method used and the number of data points. The eight available studies provide a total of 50 data points for the surface tension of the five ionic liquids of interest. In the case of [HMIM][CF_3SO_3] no surface tension data are available in the open literature.

The aim of the present study was to obtain new reliable experimental data for the air–liquid interfacial tension of the five above mentioned ionic liquids. Two samples of the [BMIM][CF_3SO_3] were used in the measurements to test the effect of their different origin. The effect was also examined of the use of two Wilhelmy plates with identical nominal geometry in the surface tension measurements.

The new surface tension data together with the data accumulated for various ionic liquids in our previous works and in the works of other authors make it possible to study the relation of the structure of the ionic liquids to the values of their surface tension and surface entropy. Freire et al. [3] studied in this respect 1-butyl-3-methylimidazolium cation with four different anions, the [BMIM] and [OMIM] cation with the [BF_4] anion and the three cations [BMIM], [EMIM], and [OMIM] with hexafluorophosphate anion. Carvalho et al. [9] studied the influence of the cation alkyl said-chain length on the surface tension of eight imidazolium-based ionic liquids with the [NTf_2] anion. The surface tension data from

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* Corresponding author. Tel.: +420 266053163; fax: +420 286584695.
E-mail address: patek@it.cas.cz (J. Pátek).

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doi:10.1016/j.fluid.2011.01.027

Table 1
Literature sources for experimental surface tension data for the ionic liquids of interest with the sample water content given as water mass fraction, w.

Author(s)	Year	T (K)	$w \times 10^6$	Methods	No. of data
1-Ethyl-3-methylimidazolium trifluoromethanesulfonate [EMIM][CF_3SO_3]					
Martino et al. [1]	2006	295.15	n/a	Capillary rise	1
Kilaru et al. [2]	2007	296.28–353.56	9060	du Noüy ring	13
This work	2010	268.29–356.09	105	Wilhelmy plate	17
		268.36–356.28	105	du Noüy ring	18
1-Butyl-3-methylimidazolium trifluoromethanesulfonate [BMIM][CF_3SO_3]					
Freire et al. [3]	2007	293.20–343.20	181	du Noüy ring	6
This work (Merck)	2010	293.40–355.89	28	Wilhelmy plate	13
		293.45–356.00	28	du Noüy ring	12
This work (Solvionic)	2010	292.18–352.45	28	Wilhelmy plate	13
		292.24–352.70	28	du Noüy ring	12
1-Hexyl-3-methylimidazolium trifluoromethanesulfonate [HMIM][CF_3SO_3]					
This work	2010	293.98–355.44	98	Wilhelmy plate	13
		294.03–355.44	98	du Noüy ring	13
1-Ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF_4]					
Zhou et al. [4]	2005	298.15	300	Pendant drop	1
Martino et al. [1]	2006	297.15	n/a	Capillary rise	1
Rilo et al. [5]	2009	298.15	220	Drop volume	1
This work	2010	288.06–355.99	164	Wilhelmy plate	14
		288.05–355.91	164	du Noüy ring	14
1-Hexyl-3-methylimidazolium tetrafluoroborate [HMIM][BF_4]					
Ghatee and Zolghadr [6]	2008	298–393	n/a	Capillary rise	20
Muhammad et al. [7]	2008	298.15–338.15	324	Spinning drop	5
Yi et al. [8]	2008	298.15	n/a	n/a	1
Rilo et al. [5]	2009	298.15	273	Drop volume	1
This work	2010	268.58–356.17	51	Wilhelmy plate	18
		268.58–356.17	51	du Noüy ring	18

this and our previous studies [10,11] for 15 ionic liquids with 5 different cations and 5 different anions are analyzed here in the same respect together with the data of the above mentioned authors. The total number of 21 ionic liquids studied, prevents fallacious conclusions that may occur when this number is substantially limited [12].

2. Experimental

In the present study, the surface tension measurements were performed by the Wilhelmy plate method and by the du Noüy ring method using the Krüss K100MK2 tensiometer equipped with a microbalance having a resolution of 10 μg. The essential details of the apparatus and procedure, are given elsewhere [11]. The sample vessel of the apparatus is placed in a vessel, which is thermostated externally by a Julabo MB-5 thermostat providing bath temperature stability of ±0.02 K. At temperatures below 298 K, in addition, external immersion cooler LAUDA ETK 30 is employed. In this way, the sample temperature stability of the order of magnitude of 0.01 K was achieved. The sample temperature is measured with a platinum resistance thermometer immersed into the sample.

The apparatus and the Wilhelmy plate measurements procedure were tested by measurements on water and methanol. The overall standard uncertainty of the resultant surface tension values is estimated to be 0.05 mN m^{-1}. The repeatability of the present surface tension and temperature measurements expressed in terms of the experimental standard deviation of the values obtained within one experimental run is typically 0.05 mN m^{-1} and 0.05 K, respectively. We used two different Wilhelmy plates in the measurements, to test possible differences in data provided by Wilhelmy plates of identical specified wetting length, that might arise from different wettability of their surface.

Contrary to the plate method, the ring method requires a correction amounting up to 10–15% of the obtained raw value of the surface tension. In the present study, the most recent correction was used derived on the basis of the rigorous theory by Hugh and Mason [13]. For the densities of ionic liquids necessary to evaluate the correction the values given in Ref. [14] were used.

Table 2 gives the suppliers of the samples used in the present measurements, minimum mass fraction purities of the samples as specified by suppliers and the water content expressed by the water mass fraction as measured in our laboratory with the coulometric Karl Fischer titrator Mettler Toledo C30 just before the measurements. The samples were used without further purification except drying. Two samples of 1-butyl-3-methylimidazolium trifluoromethanesulfonate were studied, obtained from different suppliers (Merck KGaA and Solvionic SA).

The measurements were performed in 4 h periods, one period a day. After each 4 h measurement period, the samples were dried by intensive stirring and evaporation under vacuum at temperature 353 K for 4 h and than kept under vacuum overnight. The mass fraction water content of (30–100) × 10^{-6} was usually achieved.

The measurements were taken at the only one temperature during each 4 h measurement period. At relative air-moisture of 40–50%, the water mass fraction in the samples increased from its initial value up to (600–900) × 10^{-6} during 2 h of measurements. Nevertheless, no change in the surface tension value that could be attributed to the increased mass fraction of the gases or moisture absorbed from air, was observed during particular one-day measurements. These results are consistent with those obtained in Refs. [3,11]. At low water mass fractions, in general, below a certain value

Table 2
The suppliers of the ionic liquid samples used in the present study, their stated mass fraction purities, and water mass fraction, w.

Ionic liquid	Supplier	Mass fraction purity	$w \times 10^6$
[EMIM][CF_3SO_3]	Iolitec[a]	0.990	105
[BMIM][CF_3SO_3]	Merck[b]	0.990	28
	Solvionic[c]	0.995	28
[HMIM][CF_3SO_3]	Iolitec[a]	0.990	98
[EMIM][BF_4]	Solvent-Innovation[d]	0.998	164
[HMIM][BF_4]	Solvionic[c]	0.990	51

[a] Ionic Liquids Technologies GmbH, Heilbronn, Germany.
[b] Merck KGaA, Darmstadt, Germany.
[c] Solvionic SA, Toulouse, France.
[d] Solvent-Innovation GmbH, Cologne, Germany.