J. Chem. Thermodynamics 48 (2012) 267–275

Contents lists available at SciVerse ScienceDirect

J. Chem. Thermodynamics

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

Temperature dependence of the surface tension and 0.1 MPa density for 1-C_n-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate with $n = 2$, 4, and 6

Monika Součková, Jaroslav Klomfar, Jaroslav Pátek *

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

ARTICLE INFO

Article history:
Received 16 September 2011
Received in revised form 19 December 2011
Accepted 27 December 2011
Available online 5 January 2012

Keywords:
Ionic liquid
Tris(pentafluoroethyl)trifluorophosphate
Density
Surface tension
1-Alkyl-3-methylimidazolium
Group contribution method
QSPR

ABSTRACT

Experimental air–liquid interfacial tension data and density data are presented for three 1-C_n-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphates (FAP), $[C_nMIM][(C_2F_5)_3PF_3]$, with $n = 2$, 4, and 6, measured at atmospheric pressure in the temperature range from 267 K to 360 K using the Krűss K100MK2 tensiometer. The accuracy of the surface tension measurements was checked by employing the Wilhelmy plate and the du Noüy ring methods in parallel. The combined standard uncertainty associated with the Wilhelmy plate method is estimated to be $\pm 0.1\ \text{mN} \cdot \text{m}^{-1}$. The density data were obtained using buoyancy method with an estimated standard uncertainty less then $\pm 0.4\ \text{kg} \cdot \text{m}^{-3}$ $(3 \cdot 10^{-4}\varrho)$. The chloride anions decrease the density of the tris(pentafluoroethyl)trifluorophosphates of interest up to six times more effectively than they decrease the density of the imidazolium based tetrafluoroborates. A QSPR analysis of the surface tension of imidazolium based ionic liquids with BF_4, TFA, DCA, FAP, NTf_2, and PF_6 anions indicates, that the FAP ionic liquids fit well into the analyzed group of imidazolium based ionic liquids while those having hexafluorophosphate anion show anomalously high deviations of the experimental surface tension from the values predicted by the QSPR model.

1. Introduction

The air- and hydrolytic stability of ionic liquids (ILs) is a property crucial for most applications. That is why the development of new ionic liquids proceeded towards creation of ever more air- and water-stable ILs. For that reason, 1-alkyl-3-methylimidazolium hexafluorophosphates attracted in the past a considerable general interest of both academic and industrial researchers. Recently, the development has advanced to a new type of air- and water-stable 1-alkyl-3-methylimidazolium based ionic liquids with the tris(perfluoroalkyl)trifluorophosphate anions, also known as FAP anions. The new class of the ILs was developed by Merck KGaA of Darmstadt, Germany [1], as a replacement for ILs containing $[PF_6]$ anion. In the present paper, we follow the common practice of using the general abbreviation FAP for the special case of tris(pentafluoroethyl)trifluorophosphate anion as the more correct abbreviation FEP is used much less often. Systematic studies on thermophysical properties of the new ionic liquids as density, heat capacity, and viscosity, necessary for their applications are highly desirable. Property data for ionic liquids with a new anion also will contribute to the development of correlations and predictive schemes. Literature data on the density and the surface tension for ionic liquids with tris(pentafluoroethyl)trifluorophosphate anion are scarce. Liu *et al.* [2] reported 12 experimental density and 12 surface tension values for [EMIM][FAP] at temperatures from 283.15 K to 338.15 K. Li *et al.* [3] reported 11 values of the 0.1 MPa density for [HMIM][FAP] at temperatures from 293.15 K to 343.15 K. One value of the [HMIM][FAP] density and surface tension at 293.15 K is reported by Yao *et al.* [4].

In view of the above facts, the present study is aimed to measure the density and the surface tension at atmospheric pressure in the temperature range from 267 K to 360 K for three 1-C_n-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphates, $[C_nMIM][(C_2F_5)_3PF_3]$, with $n = 2$, 4, and 6. The study is a continuation of our previous similar studies for 1-alkyl-3-methylimidazolium-based ionic liquids with tetrafluoroborate, trifluoromethanesulfonate, and dicyanamide anions [5–9]. The second aim of the present work was to study models capable of describing the density and the surface tension of different ionic liquids based on variables characterizing their structure. A group contribution model has been developed for predicting the density at the atmospheric pressure for the mixtures of ionic liquids of interest with imidazolium-based chlorides. Base on this model, effect of the chloride anions in the FAP-ionic liquids density measurements were assessed quantitatively. Based on the obtained experimental surface tension data and the data from our previous studies, suitable variables, and

---

* Corresponding author. Tel.: +420 266053153; fax: +420 286584695.
E-mail address: patek@it.cas.cz (J. Pátek).

0021-9614/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jct.2011.12.033

TABLE 1
Basic information on the samples used in the present study: their CAS numbers, supplier, stated mass fraction purities, and their respective mass fraction water content.

	[EMIM][FAP][a]	[BMIM][FAP][b]	[HMIM][FAP][c]
CAS number	377739-43-0	917762-91-5	713512-19-7
Supplier	Merck[d]	Merck[d]	Merck[d]
Minimum mass fraction purity	0.99	0.99	0.99
Water content (mass fraction)	$26 \cdot 10^{-6}$	$26 \cdot 10^{-6}$	$35 \cdot 10^{-6}$
Maximum halides content (mass fraction)	$100 \cdot 10^{-6}$	$100 \cdot 10^{-6}$	$100 \cdot 10^{-6}$

[a] 1-Ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate.
[b] 1-Butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate.
[c] 1-Hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate.
[d] Merck KGaA, Darmstadt, Germany.

regressors were selected making it possible to develop QSPR models describing the surface tension of various imidazolium-based ILs.

2. Experimental section

2.1. Materials

Table 1 lists the main primary characteristics of the samples studied, including their CAS numbers, their supplier, manufacturer stated minimum mass fraction purities, the initial water mass fraction in the samples as measured in our laboratory with a coulometric Karl Fischer titrator Mettler Toledo C30 and the upper-bound to the chloride ion mass fraction as stated by manufacturer. The samples were used without further purification except drying.

2.2. Surface tension and density measurements

In the present study, both the surface tension and the density measurements were performed using the Krűss K100MK2 tensiometer equipped with a microbalance having a resolution of 10 μg. For the surface tension measurements, the Wilhelmy plate method and the du Noüy ring method were used in parallel while the density was measured by the buoyancy method. The essential details of the apparatus and the experimental procedures have been described elsewhere [5,6]. Here, we only recall the details relevant to the resultant data accuracy.

The sample vessel of the apparatus is placed in a vessel thermostated externally by the Lauda ECO RE1050 G thermostat, which gives a bath temperature stability of ±0.01 K. In this way, the sample temperature stability of the order of magnitude of 0.01 K is achieved. The sample temperature is measured with a platinum resistance thermometer immersed into the sample with a manufacturer's stated standard uncertainty of 0.02 K.

In the evaluation of the surface tension force acting on the wetting line of the Wilhelmy plate from the equivalent mass value given by the microbalance, the local value $9.81007\ \mathrm{m \cdot s^{-2}}$ of the earth's gravitational acceleration, g, was used for the Institute of Thermomechanics, Prague, Czech Republic. The wetting length, l, of the used Wilhelmy plate given by the manufacturer is 40.234 mm. Both g and l is known with high accuracy, so that the combined uncertainty evaluated from the quadratic sum of uncertainties in all directly measured quantities that enter the working equation of the method is dominated by the uncertainty in the mass, m, equivalent to the surface force measured by the microbalance ($\sigma = mg/l$). This uncertainty seems to arise from the disturbances produced by the natural convection generated by small temperature gradients persisting at the liquid surface. Their effect seems to be well reproducible at a given temperature but it changes irregularly with changing temperature. Thus, the uncertainty in the microbalance data cannot be calculated from a model. Therefore, we employed the top-down approach to estimate the surface tension uncertainty using water and methanol as the reference fluids at temperatures from 279 K to 333 K. The root-mean-square deviation of our surface tension data for water from the IAPWS correlation [10] is $0.03\ \mathrm{mN \cdot m^{-1}}$. The overall standard deviation of our surface tension data for methanol, which follows from the comparison with the most reliable data obtained by the capillary rise method is estimated to be of $\pm 0.1\ \mathrm{mN \cdot m^{-1}}$ [11]. The somewhat less accurate results obtained for methanol, most probably, are to be attributed to the effect of evaporation of the more volatile methanol after the sample vessel is open for the Wilhelmy plate can be immersed into the sample. We have accepted the value of $\pm 0.1\ \mathrm{mN \cdot m^{-1}}$ as the upper bound for the uncertainty in the surface tension values obtained with the present apparatus. In general, the data obtained by the du Noüy ring method show greater scatter than those obtained by the Wilhelmy plate method. So the standard uncertainty associated with the present du Noüy ring measurements is estimated to be of $\pm 0.25\ \mathrm{mN \cdot m^{-1}}$.

The relative variant of the method of hydrostatic weighting evaluates the ratio of the densities ϱ and ϱ_{cal} of the measured and the calibration liquid, respectively, from the ratio B/B_{cal} of the buoyancy forces acting on a sinker immersed in the two fluids at a given temperature. In the present measurements toluene was used as a calibration standard (HPCL grade, 0.999 mass fraction purity), supplied by Penta Chrudim, Czech Republic. The needed toluene density data were calculated from the equation of McLinden and Splett [12]. Similarly, as in the case of the surface tension, the uncertainty in the obtained density was estimated by measuring on water as a reference fluid. A water sample of pro-analysis grade supplied by Carl Roth GmbH + Co. was used to this purpose. The maximum deviation of the obtained density values from the IAPWS95 formulation [13] was less then $0.05\ \mathrm{kg \cdot m^{-3}}$. The standard uncertainty associated with the present buoyancy density measurements is estimated to be of $3 \cdot 10^{-4}\varrho$ [15].

The experimental uncertainty of the buoyancy density measurements may somewhat differ for individual ionic liquids owing to their different viscosity, thermal conductivity, and isobaric heat capacity, which affect the action of natural convection. In the present measurements, the temperature of the sinker was adjusted before the measurement to be equal to the temperature of the liquid sample. Thus, the potential effect of the transient natural convection induced by the initial difference between temperatures of the sinker and of the liquid sample was suppressed. The repeatability of the present surface tension, density and temperature measurements expressed in terms of the experimental standard deviation of the values obtained within one experimental run is typically $0.05\ \mathrm{mN \cdot m^{-1}}$, 0.02 K, and $0.2\ \mathrm{kg \cdot m^{-3}}$ respectively.

3. Results and discussion

3.1. Density

The present study provides 54 new experimental data points on the density–temperature relation at pressure of 0.1 MPa for the