J. Chem. Thermodynamics 70 (2014) 122–126

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

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

Unusual trend of viscosities and densities for four ionic liquids containing a tetraalkyl phosphonium cation and the anion bis(2,4,4-trimethylpentyl) phosphinate

Xiangyang Liu [a,c], Waheed Afzal [a,b,d], John M. Prausnitz [a,b,*]

[a] Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720-1462, United States
[b] Lawrence Berkeley National Laboratory, Berkeley, CA, United States
[c] MOE Key Laboratory of Thermo-Fluid Science and Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, PR China
[d] Institute of Chemical Engineering & Technology, University of the Punjab, Lahore 54590, Pakistan

ARTICLE INFO

Article history:
Received 14 July 2013
Received in revised form 25 September 2013
Accepted 27 September 2013
Available online 9 October 2013

Keywords:
Density
Viscosity
Ionic liquid
Tetraalkyl phosphonium

ABSTRACT

Densities and viscosities are reported for three similar ionic liquids, all with anion bis(2,4,4-trimethylpentyl) phosphinate [TMPP]. The hydrocarbon chains attached to the phosphonium cation vary in length; the three cations are tetrabutylphosphonium [P4444], trimethyloctylphosphonium [P8111] and tributylmethylphosphonium [P1444]. Contrary to expectation, neither the densities nor the viscosities show a monotonic trend with the length of the hydrocarbon chains on the cation.

1. Introduction

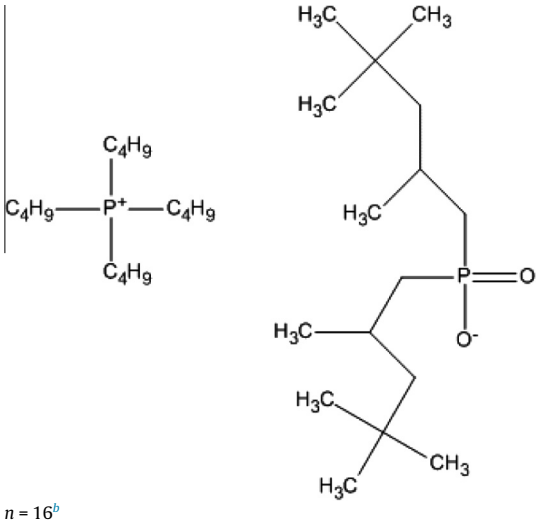
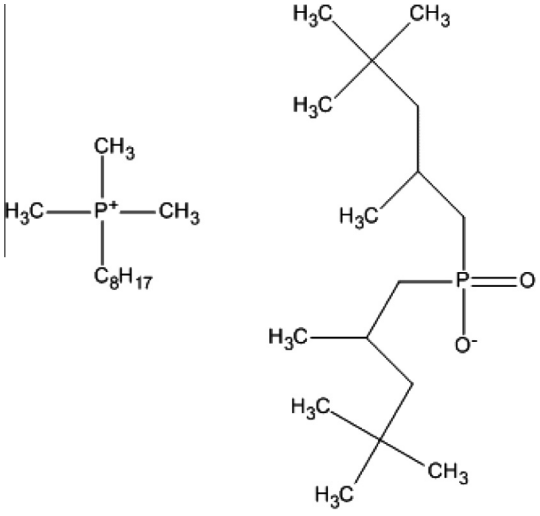
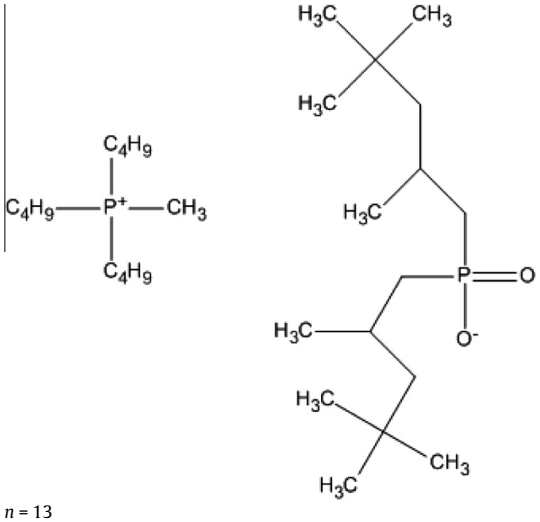
During the last 20 years, ionic liquids have been given much attention because they tend to have good thermal stability, negligible vapor pressure, and nonflammability [1–4]. The effects of cation and anion on physical properties for different classes of ionic liquids have been investigated by several authors, *e.g.* by Fredlake *et al.* [5] who studied the effect of cation and anion on density for 12 imidazolium-based ionic liquids; by Ochedzan-Siodlak *et al.* [6] who studied the effect of cation and anion on density and viscosity for imidazolium-based and pyridinium-based chloroaluminate ionic liquids; by Tsunashima *et al.* who studied the effect of cation on several physical properties including density and viscosity for phosphonium-based and ammonium-based ionic liquids with anions including bis(fluorosulfonyl)amide [7], bis(trifluoromethylsulfonyl)amide [8] and bis(fluorosulfonyl)amide [9]; by Kavitha *et al.* [10] who investigated the influence of alkyl-chain length on density and viscosity for ammonium-based ionic liquids; by Ahosseni *et al.* [11] and Huddleston [12] who studied the effect of cation and anion on viscosity for imidazolium-based ionic liquids; by Rooney [13] who studied densities and viscosities for different kinds of ionic liquids; by Zhang [14] and Yu *et al.* [15] who reviewed the viscosities and densities of ionic liquids; by Vaughan *et al.* [16] who studied density and viscosity for tetra-alkyl phosphonium-based ionic liquids with anions including chloride, bromide, tetrafluoroborate, hexafluorophosphate, dicyanamide and N-fluorobis(trifluoromethylsulfonyl)imide; by Zheng *et al.* [17] who studied the effect of cation symmetry on the morphology and on the densities and viscosities for imidazolium-based ionic liquids. Generally, at fixed temperature, the densities of ionic liquids decrease with rising number of carbon atoms in the alkyl chain on the cation; the viscosities of ionic liquids increase with rising number of carbon atoms in the alkyl chain on the cation. However, Yu *et al.* [15], Vaughan *et al.* [16] and Zheng *et al.* [17] found that at fixed temperature, the viscosities of some ionic liquids decrease with rising number of carbon atoms in the alkyl chain on the cation. Zheng *et al.* [17] found that with the same number of carbons in alkyl chains on the cation, asymmetric ionic liquids have densities and viscosities higher than those of symmetric ionic liquids.

In our earlier work, we found that the hydrophobic ionic liquid trihexyl (tetradecyl)phosphonium bis(2,4,4-trimethylpentyl) phosphinate [P(14)666][TMPP] shows solubilities for small paraffins and olefins (methane, ethane, ethylene, propane) much larger than those in ordinary ionic liquids [18]. However, [P(14)666][TMPP] has a very high viscosity (1004 cP · s at 25 °C), too high for an

* Corresponding author at: Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720-1462, United States. Tel.: +1 510 642 3592; fax: +1 510 642 4778.
E-mail address: prausnit@cchem.berkeley.edu (J.M. Prausnitz).

0021-9614/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jct.2013.09.037

TABLE 1
Viscosities, densities, molar mass and structure for three ionic liquids.

IL name and molar mass (g/mol)	IL structure and number of carbon atoms in alkyl chains of cation (n)	t/°C	η/cP	ρ/g · cm^{-3}
[P4444][TMPP] 548.9	 $n = 16$[b]	20		0.9198
		25	1740	0.9168
		30	1199	0.9142
		35	844	0.9109
		40	616	0.9078
		45	473	0.9048
		50	358	0.9018
		55	256	0.8988
		60	192	0.8958
		65	153	0.8928
		70	131	0.8898
		75	107	0.8869
		80		0.8839
[T8111][TMPP] 487.7	 $n = 11$	20		0.8938
		25	804	0.8906
		30	560	0.8874
		35	408	0.8843
		40	306	0.8811
		45	227	0.8780
		50	177	0.8749
		55	149	0.8719
		60	110	0.8688
		65	91	0.8657
		70	71	0.8627
		75		0.8594
		80		0.8563
[P1444]TMPP][a] 506.8	 $n = 13$	50	283	0.8956
		55	210	0.8925
		60	162	0.8894
		65	124	0.8863
		70	96	0.8833
		75	78	0.8803
		80	63	0.8772

[a] The melting point is near 45 °C.
[b] n is the total number of carbon atoms in the alkyl chains on the cation.