J. Chem. Thermodynamics 65 (2013) 159–167

Contents lists available at SciVerse ScienceDirect

J. Chem. Thermodynamics

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

Activity coefficients at infinite dilution of organic solutes in the ionic liquid trihexyltetradecylphosphonium bis (trifluoromethylsulfonyl) imide using gas–liquid chromatography at $T = (313.15, 333.15, 353.15$ and $373.15)$ K

Kaniki Tumba [a], Trevor M. Letcher [b], Paramespri Naidoo [a], Deresh Ramjugernath [a,*]

[a] Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, Durban 4041, South Africa
[b] School of Chemistry and Physics, University of KwaZulu-Natal, Durban 4041, South Africa

ARTICLE INFO

Article history:
Received 5 March 2013
Received in revised form 13 May 2013
Accepted 17 May 2013
Available online 25 May 2013

Keywords:
Activity coefficient at infinite dilution
Ionic liquid
Trihexyltetradecylphosphonium bis (trifluoromethylsulfonyl) imide
$[3C_6C_{14}P][BTI]$

ABSTRACT

Activity coefficients at infinite dilution for organic solutes, which include *n*-alkanes, alk-1-enes, alk-1-ynes, cycloalkanes, alkylbenzenes, alcohols and ketones, in the ionic liquid trihexyltetradecylphosphonium bis (trifluoromethylsulfonyl) imide were measured by gas–liquid chromatography using the latter as the stationary phase. This ionic liquid had previously been studied and reported in literature; however due to significant discrepancies in the reported infinite activity coefficient values, there was justification for further study and reporting. The temperature range investigated in this study is significantly wider and at higher temperatures than presented previously in the literature. From the experimental infinite dilution activity coefficient data at the four different temperatures $T = (313.15, 333.15, 353.15$ and $373.15)$ K, partial molar excess enthalpies at infinite dilution were calculated. Values of the selectivity for hexane/benzene and methanol/benzene separations were determined from experimental values of the activity coefficients at infinite dilution and these results were compared to literature values for other ionic liquids, as well as for industrial solvents. The capacities were also determined as it gives an indication of the solvent extraction behavior of the ionic liquid.

1. Introduction

A plethora of potential uses of ionic liquids in the chemical industry in general [1–5], and in separation processes in particular [6–10], have been identified in recent years. Recent work has not only shown the potential suitability of some ionic liquids as separating agents in liquid–liquid extraction and extractive distillation, but also provided insight into the effect of the structure of the ionic liquid on the selectivity and capacity related to separating mixtures [11–15].

The present work is a contribution to the understanding of how the structure of an ionic liquid influences the selectivity and capacity in different separation problems.

Infinite dilution activity coefficients of organic solutes are reported in literature for the ionic liquid trihexyltetradecylphosphonium bis (trifluoromethylsulfonyl) imide, abbreviated as $[3C_6C_{14}P][BTI]$ [16–18]. Banerjee and Khanna [16] presented data at three temperatures, *viz.* (308.15, 318.15, and 328.15) K. Letcher *et al.* [17] undertook measurements of infinite dilution activity coefficients at four temperatures, *viz.* (303.15, 308.15, 313.15, and 318.15) K, while Revelli *et al.* [18] reported infinite dilution activity coefficient values at three temperatures, *viz.* (302.45, 322.35 and 342.45) K. The combined temperature range covered in the literature is between (303.15 and 342. 45) K. A wider temperature range and number of solutes (compared to Refs. [16,17]) are used in this study. Activity coefficient at infinite dilution measurements in $[3C_6C_{14}P][BTI]$ were carried out using gas–liquid chromatography (glc) at $T = (313.15, 333.15, 353.15$ and $373.15)$ K. In addition to *n*-alkanes, alk-1-enes, alk-1-ynes, *n*-alkanols, cycloalkanes and aromatic compounds that were investigated previously, ketones have also been included in this work. Infinite dilution activity coefficient value for three solutes, *viz.* pent-1-yne, non-1-yne, and acetone, which have not previously been reported, are also presented in this study.

The main reason, however, for repeating the infinite dilution measurements for the ionic liquid trihexyltetradecylphosphonium bis (trifluoromethyl) imide is the discrepancy in the infinite dilution values reported in the literature for most of the solutes. The discrepancies in the reported infinite dilution activity coefficient values are generally much larger than the reported uncertainties in the measurements. This justified the need to undertake more

* Corresponding author. Tel.: +27 31 2603128; fax: +27 31 2601118.
E-mail address: ramjuger@ukzn.ac.za (D. Ramjugernath).

0021-9614/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jct.2013.05.030

TABLE 1
Suppliers and purities of the chemicals used in this study.

Compound	CAS number	Supplier[a]	Mass fraction purity
n-Pentane	109-66-0	1	>0.98
n-Hexane	110-54-3	1	>0.98
n-Octane	111-65-9	1	>0.98
n-Nonane	111-84-2	1	>0.98
Pent-1-ene	109-67-1	1	>0.98
Hex-1-ene	592-41-6	1	>0.98
Hept-1-ene	592-76-7	1	>0.98
Pent-1-ene	627-19-0	1	>0.98
Hex-1-yne	693-02-7	1	>0.98
Hept-1-yne	628-21-7	1	>0.98
Oct-1-yne	629-05-0	1	>0.98
Non-1-yne	3452-09-3	1	>0.98
Cyclopentane	287-92-3	1	>0.98
Cyclohexane	110-82-7	1	>0.98
Cycloheptane	291-64-5	1	>0.98
Cyclooctane	292-64-8	1	>0.98
Methanol	67-56-1	1	>0.98
Propan-1-ol	71-3-8	1	>0.98
Benzene	71-43-2	1	>0.98
Toluene	108-88-3	1	>0.98
Acetone	67-64-1	1	>0.98
Butan-2-one	78-93-3	1	>0.98
Trihexyltetradecylphosphonium bis (trifluoromethylsulfonyl) imide	460092-03-9	2	>0.98

[a] 1 = Capital Lab Supplies (South Africa); 2 = Cytec Industries (France).

TABLE 2
The vapor pressure values, P_1^*, molar volumes, V_1^*, and virial coefficients B_{11} and B_{12} used in the calculation of infinite dilution activity coefficients, γ_{13}^{∞} at temperatures T = (313.15, 333.15, 353.15 and 373.15) K.

T/K	P_1^*/kPa	$V_1^*/\text{cm}^3 \cdot \text{mol}^{-1}$	$B_{11}/\text{cm}^3 \cdot \text{mol}^{-1}$	$B_{12}/\text{cm}^3 \cdot \text{mol}^{-1}$
		n-Pentane		
	115.14	116.34	−1030.52	47.31
333.15	313.15	120.70	−882.32	48.37
353.15	368.89	125.73	−765.29	49.30
373.15	595.59	131.68	−671.03	50.13
		n-Hexane		
313.15	37.15	134.63	−1654.91	54.11
333.15	76.12	138.86	−1396.50	55.29
353.15	142.36	143.59	−1196.36	56.32
373.15	246.91	148.98	−1038.01	57.24
		n-Octane		
313.15	4.15	166.37	−3601.38	66.28
333.15	10.50	170.57	−2961.96	67.64
353.15	23.36	175.15	−2479.37	68.83
373.15	46.89	180.18	−2107.15	69.88
		n-Nonane		
313.15	1.41	182.15	−5070.63	72.47
333.15	3.98	186.43	−4126.76	73.90
353.15	9.71	191.06	−3420.47	75.16
373.15	21.05	196.10	−2880.45	76.28
		Pent-1-ene		
313.15	140.6	115.66	−989.75	47.25
333.15	257.79	120.11	−848.03	48.28
353.15	439.23	125.28	−736.03	49.12
373.15	704.84	131.43	−645.69	49.99
		Hex-1-ene		
313.15	44.90	128.19	−1536.41	52.24
333.15	90.49	132.26	−1297.34	53.37
353.15	166.48	136.84	−1112.02	54.36
373.15	284.61	142.05	−965.28	55.24
		Hept-1-ene		
313.15	14.93	142.45	−2302.18	57.70
333.15	33.22	146.43	−1917.57	58.93
353.15	66.45	150.82	−1623.85	60.01
373.15	121.85	155.72	−1394.62	60.96
		Pent-1-yne		
313.15	100.73	105.91	−1070.09	43.98
333.15	194.06	109.34	−912.57	45.05
353.15	343.27	113.22	−789.00	45.96
373.15	566.29	117.68	−690.03	46.78
		Hex-1-yne		
313.15	32.54	121.85	−1760.38	49.23
333.15	69.15	125.07	−1476.53	50.40
353.15	133.64	128.61	−1258.28	51.43
373.15	238.86	132.56	−1086.82	52.34
		Hept-1-yne		
313.15	11.69	129.03	−2319.21	54.07
333.15	27.30	132.49	−1926.25	55.30
353.15	55.79	136.29	−1627.04	56.39
373.15	102.69	140.50	−1394.22	57.35
		Oct-1-yne		
313.15	3.87	151.74	−3809.60	60.20
333.15	9.95	155.16	−3115.52	61.55
353.15	22.40	158.74	−2594.25	62.74
373.15	45.50	162.68	−2194.20	63.80
		Non-1-yne		
313.15	1.49	168.27	−5140.18	67.66
333.15	4.02	172.01	−4170.95	69.09
353.15	9.57	176.02	−3447.40	70.35
373.15	20.58	180.37	−2895.50	71.46
		Cyclopentane		
313.15	73.95	96.37	−1097.60	41.30
333.15	142.35	99.26	−933.10	42.36
353.15	252.07	102.49	−804.63	43.29
373.15	416.62	106.14	−702.19	44.12
		Cyclohexane		

careful measurements for this ionic liquid. The study of Revelli *et al.* [19] presents a similar case as in this manuscript, where the ionic liquid studied and presented in their paper had been previously measured and reported in the literature. The discrepancies in values presented in the literature, however, are as high as 30%. This justified their re-measurement of infinite dilution activity coefficient of the ionic liquid and reporting in a paper. Revelli *et al.* [19,20] also provide details on the complexity of the understanding of retention in gas chromatography and the influence that poor understanding of this phenomenon can have on reported infinite dilution activity coefficient data.

The knowledge of infinite dilution activity coefficients is important in chemical engineering [21] as it allows for the synthesis, design and optimization of separation processes, and the development of predictive thermodynamic models [22,23]. Moreover, by means of an appropriate excess Gibbs energy model and infinite dilution activity coefficient data, one can calculate VLE data over the entire concentration range both rapidly and at a reduced cost when compared to direct VLE measurements [23].

2. Experimental

2.1. Materials

The solutes were purchased from Capital Lab Supplies in South Africa, with a supplier stated mass fraction purity greater than 0.98. Gas chromatographic (GC) analysis of the solutes confirmed the stated purities. No further purification was undertaken since the GC technique by nature separates any impurities. The ionic liquid trihexyltetradecylphosphonium bis (trifluoromethylsulfonyl) imide (figure 1), used as a stationary phase, was supplied by Cytec Industries, France with a certified purity of greater than 0.98 mass fraction. Before use, it was heated under vacuum at 20 kPa and T = 343.15 K for 6 h to remove any traces of impurities. The density of the purified sample measured using a vibrating tube densitometer was $(1068.87 \pm 4.28)\ \text{kg} \cdot \text{m}^{-3}$ at T = 293.15 K. The solid