Determination of activity coefficients at infinite dilution of water and organic solutes (polar and non-polar) in the Ammoeng 100 ionic liquid at T = (308.15, 313.5, 323.15, and 333.15) K

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ABSTRACT

Activity coefficients at infinite dilution (γ_{13}^∞) have been determined for 27 solutes, *viz.* water and organic compounds (*n*-alkanes, cycloalkanes, 1-alkenes, 1-alkynes, aromatics, alcohols, and ketones) in the ionic liquid Ammoeng 100, by gas–liquid chromatography at four different temperatures, T = (308.15, 313.15, 323.15, and 333.15) K. Columns with different phase loadings (20 to 24)% of the ionic liquid in the stationary phase were employed to obtain γ_{13}^∞ values at each temperature investigated. Partial molar excess enthalpies at infinite dilution ($\Delta H_1^{E,\infty}$) were calculated for the solutes from the temperature dependency relationship of the $\ln(\gamma_{13}^\infty)$ values for the temperature range in this study. The uncertainties in the determinations of the γ_{13}^∞ and $\Delta H_1^{E,\infty}$ values are 6% and 10%, respectively. Selectivity values at infinite dilution (S_{ij}^∞), have been computed from the γ_{13}^∞ values to assess the potential candidacy of the Ammoeng 100 ionic liquid for the separation of alkane/alcohol mixtures. The results from this study have been compared to those available for several ionic liquids from previous investigations.

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1. Introduction

The study of ammonium ionic liquids (ILs) as stationary phases in gas–liquid chromatography (g.l.c.) goes back about 25 years [1], however, the screening of ammonium ILs as potential solvents in solvent-enhanced separations via g.l.c. has only been investigated recently. These include studies on butyl(trimethyl)ammonium bis(trifluoromethylsulfonyl)imide [2], hexyl(trimethyl)ammonium bis(trifluoromethylsulfonyl)imide [3] and work done previously by our laboratory on methyl(trioctyl)ammonium bis(trifluoromethylsulfonyl)imide [4].

The considerable advantages offered by utilizing ionic liquids, as opposed to conventional molecular solvents [5] (NMP, sulfolane, glycols, *etc.*), in solvent-enhanced processes such as liquid–liquid extraction and extractive distillation have been widely documented [6–8]. These advantages have their origin principally in the negligible vapour pressures of ILs at process operating conditions (favouring solvent recycling and containment), unique solvation chemistry for separation (offered by a host of possible solvent–solute interactions), large *liquidus* range (as opposed to conventional inorganic salts) and tuneability of physicochemical properties (due to numerous combinations of cation–anion pairings). The screening of potential candidates as solvents for extractive distillation can be most conveniently achieved by obtaining activity coefficients at infinite dilution (γ_{13}^∞) of the solutes to be separated in the solvent of interest. For this purpose, gas–liquid chromatography offers an expedient, cost-effective, and reliable route to obtain these invaluable thermodynamic parameters. Of the contemporary methods employed for γ_{13}^∞ determinations in ILs, gas–liquid chromatography is by far the most popular [9–11].

The lack of investigations on phosphonium, and especially ammonium-based ILs for separation processes is quite self-evident in the scarcity of data available for these classes of ionic liquids when compared to imidazolium or pyridinium ILs [9,12]. To facilitate an elucidation of the correlation between structure and function for ammonium and phosphonium ILs, it is necessary for the database of physicochemical properties on these ILs to be extended considerably. Studies thus far on tetralkyl ammonium and phosphonium ILs have shown that these types of ILs with long hydrocarbon side chains such as trihexyl(tetradecyl)-based phosphonium ILs [13–16] and methyl(trioctyl)-based ammonium ILs [4,17] are less effective for application in industrially-relevant separations (aliphatic/aromatic) than their shorter-chained counterparts [2,3,18,19]. A similar trend is observed for imidazolium ILs through a comparison of γ_{13}^∞ results for 1-ethyl-3-methylimidazolium thiocyanate [20] with that of 1-hexyl-3-methylimidazolium thiocyanate [21].

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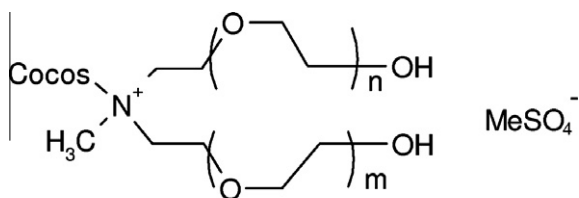 *E-mail address:* ramjuger@ukzn.ac.za (D. Ramjugernath).

FIGURE 1. Structure of the ionic liquid, Ammoeng 100.

TABLE 1
Physical properties of Ammoeng 100.

T/K	Density/(g · cm^{-3})	Refractive index
303.15	1.081815	1.47066
313.15	1.075406	1.46810
323.15	1.069040	1.46516
333.15	1.062715	1.46225
343.15	1.056430	1.45926

Consequently, designing an ammonium or phosphonium IL with a hydrophobic side chain capable of being useful for industrially relevant separations is a challenging task indeed.

Ammoeng ionic liquids are a class of ILs that have garnered interest for commercialisation due their surfactant properties [22]. These ILs have a truly amphiphilic structure containing both hydrophobic (long alkyl side chain) and hydrophilic (hydroxyl) groups and are consequently quite an interesting class of ILs to study from a solubility point of view. There has been one phase equilibrium study to date on an Ammoeng IL as conducted by Pereiro and Rodriguez [23] in the application of Ammoeng 102 for the separation of a heptane/toluene mixture at T = 298.15 K. The results obtained in this study did not indicate that Ammoeng 102 would be a suitable solvent for an efficient separation of aliphatic/aromatic mixtures. The Ammoeng IL studied in this investigation is Ammoeng 100, as shown in figure 1. There have been no phase equilibrium data or physicochemical properties that have been published to date for this ionic liquid and the results represent an important contribution to the pool of data on ammonium ILs for separation process design.

2. Experimental

2.1. Materials

The Ammoeng 100 ionic liquid was supplied by Solvent Innovation (Germany) with a certified minimum mass fraction purity of 0.98. The ionic liquid was purified further through the use of vacuum evaporation coupled with ultrasonic heating at T = 343.15 K for 6 h to remove any volatile impurities present. The measured density (Anton Paar DMA 5000) and refractive index (Atago RX-7000α) values of the purified Ammoeng 100 IL for the temperature range T = (303.15 to 343.15) K are listed in table 1.

The organic solutes were obtained from Aldrich and Fluka, with mass fraction purities greater than 0.98. Purification of the solutes was not necessary since the g.l.c. technique performs the separation of any impurities during the run on the column. The support material used for the solvent phase was Chromosorb W-HP (80/100 mesh), supplied by Supelco (USA). The Chromosorb material was also subjected to vacuum purification with heating to remove any adsorbed moisture. Dry ultrahigh purity helium (99.999%) was used as the carrier gas for the measurements.

2.2. Apparatus and procedure

The details on the preparation of the packed g.l.c. columns for γ_{13}^∞ determinations, as used in this work have been described elsewhere [4,13,15,18]. The columns used were 304 grade stainless steel with a length of 1.0 m and an internal diameter of 3 mm. The columns were prepared for use by washing with hot soapy water, rinsing with cold water, and finally drying with acetone. In the preparation of the stationary phase, the purified Ammoeng 100 was added to a pre-weighed amount of the Chromosorb W-HP support material. Dichloromethane was then added to the mixture as the slurry solvent to allow for the uniform coating of the ionic liquid phase onto the inert support material. The dichloromethane was removed during the coating procedure by rotary evaporation with a moderate rotation speed. The original masses of the ionic liquid and the Chromosorb weighed separately and that of the combined ionic liquid and Chromosorb in the prepared stationary phase were found to be in agreement to within 0.005 g. The accurate determination of the phase loading of the solvent in the stationary phase is an area of significant uncertainty in the determination of physicochemical properties by g.l.c. [18,24,25]. Consequently, verification of the stationary phase loading was achieved by comparing the results obtained gravimetrically with those obtained with Soxhlet extraction of a sample of the IL stationary phase with dichloromethane as the solvent [25]. The results from the Soxhlet extraction were in excellent agreement with those obtained gravimetrically, with the difference between the two methods being less than 0.1%. Prior to any runs, the newly prepared column was conditioned by passing dry helium gas through the column at a high flow rate for about 2 h to remove any traces of volatile materials left in the packing and to pre-saturate the packing with the carrier gas.

At each temperature studied, two stainless columns with different phase loadings between 20% and 25% were used to investigate the effects of interfacial adsorption of the solute at the interfaces of the support and the solvent liquid phase, another area of significant uncertainty for γ_{13}^∞ determinations by g.l.c. [25]. The two IL column loadings used in this study were 20% (1.2 mmol) and 24% (1.7 mmol), based on mass percent of ionic liquid in the stationary phase. These loading sizes were deemed to be large enough to avoid residual adsorption effects of the solute on the support material. This was confirmed by the acquisition of symmetrical peak shapes and reproducible retention times for multiple runs of the solutes investigated in this study for different injection volumes. In terms of the contribution of interfacial adsorption of the solute on the liquid solvent, close agreement between the γ_{13}^∞ values for different phase loadings (±3%) would serve as an indication that this was insignificant [26].

All the measurements in this study were performed with a Shimadzu GC-2014 gas chromatograph, equipped with a thermal conductivity detector, an auto-sampler and an auto-injector. The flow-rate of the dry helium carrier gas was obtained through the use of a calibrated soap bubble flow meter positioned at the outlet of the detector. The flow rates were corrected for water vapour pressure at the temperature of the run and were allowed to stabilize for at least 15 min prior to carrying out any series of runs for the solutes. Injection volumes ranged from (0.1 to 0.3) · 10^{-3} cm^3 and were considered small enough to comply with the condition of infinite dilution. The solute retention times were obtained in triplicate to ensure reproducibility and stability of the system during the runs. Dry air was injected into the column before and after each run for a class of solutes to obtain the retention time corresponding to the component not retained. The accuracy of the column temperature measurement and control was better than ±0.01 K. The validation of the g.l.c. technique and equipment used in this study was performed by determining infinite dilution activ-