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Determination of activity coefficients at infinite dilution of organic solutes in the ionic liquid, tributylmethylphosphonium methylsulphate by gas–liquid chromatography

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Abstract

Activity coefficients at infinite dilution, γ_i^{∞} , have been determined for organic solutes in the phosphonium-based ionic liquid, tributylmethylphosphonium methylsulphate at T = 308.15 K, 318.15 K and 328.15 K. The experimental activity coefficient data presented are the first to be reported for this ionic liquid, through the use of the technique of steady-state gas–liquid chromatography. The organic solutes that were investigated were normal alkanes (pentane, hexane, heptane and octane), alkenes (1-hexene, 1-heptene and 1-octene), alkynes (1-hexyne, 1-heptyne and 1-octyne), cycloalkanes (cyclopentane, cyclohexane and cycloheptane) and benzene. The partial molar excess enthalpies at infinite dilution, $H_i^{E,\infty}$, were also determined for the solutes from the temperature dependency of the γ_i^{∞} values.

The γ_i^{∞} data obtained for tributylmethylphosphonium methylsulphate in this investigation have been compared to those obtained for other ionic liquids available in literature; most notably that of trihexyl(tetradecyl)-phosphonium tris(pentafluoroethyl) trifluorophosphate. This comparison allows for an assessment of the potential for the use of different ionic liquids as solvents in industrial solvent-enhanced separation processes such as extractive distillation.

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1. Introduction

Considerable interest from the global scientific community has centred around the diverse potential applications of ionic liquids, which is evident in the plethora of conferences and workshops [1,2] and published literature [3–5] disseminating information about these versatile fluids. Ionic liquids can be "designed" and structurally modified for efficacy in specific applications, which allows for an almost infinite number (around 10^{18} [6]) of ionic liquid structures, due to an abundance of potential cation–anion couplings.

With the advent of increasing concerns over the necessity of cleaner chemical process technologies, the "greenness" of ionic liquids indeed favours their incorporation into industrial processes such as solvent-enhanced separations in the form of

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liquid–liquid extraction and extractive distillation, where many concerns over the detrimental impact of conventional organic solvents, which are volatile, flammable and not easily recyclable, have surfaced. All of the above-mentioned considerations have assisted in endearing ionic liquids to many research laboratories. However, to extend ionic liquids from the realm of mere theoretical interest to practical or industrial applicability, there is a dire need for a database of reliable phase equilibrium data and physico-chemical properties of these remarkable solvents to be established with much haste.

The determination of activity coefficients at infinite dilution, γ_i^{∞} , of organic solutes in ionic liquid solvents offers an invaluable means for the effective assessment of ionic liquids for potential application in solvent-enhanced separation processes for organic liquid mixtures [7].

The use of the steady-state gas–liquid chromatographic technique for the determination of γ_i^{∞} values has been employed by many researchers as it offers a relatively inexpensive, rapid and reliable means for γ_i^{∞} determination [8]. Ionic liquids

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are particularly suitable for the determination of γ_i^{∞} by this method because of their negligible vapour pressures, which makes them ideal stationary phases for gas-liquid chromatography. Forays by contemporary researchers into the determination of activity coefficients at infinite dilution, γ_i^{∞} , have been traditionally limited to ionic liquids based on the imidazolium [9–14] and pyridinium [12,15] cations. In light of the above, the investigation of trihexyl(tetradecyl)-phosphonium tris(pentafluoroethyl)trifluorophosphate by this group [16] represented a significant departure from the norm, which proved very fruitful in light of the highly unexpected results that were obtained. Consequently, as part of an ongoing investigation of tetraalkyl phosphonium-based ionic liquids, γ_i^{∞} values have been determined at T = 308.15 K, 318.15 K and 328.15 K for normal alkanes (pentane, hexane, heptane and octane), alkenes (1-hexene, 1-heptene and 1-octene), alkynes (1-hexyne, 1-heptyne and 1-octyne), cycloalkanes (cyclopentane, cyclohexane and cycloheptane) and benzene in the ionic liquid, tributylmethylphosphonium methylsulphate. This represents the first set of activity coefficient data that has been measured for this phosphonium-based ionic liquid, whose structure is shown below:



Values for the partial molar excess enthalpies at infinite dilution, $H_i^{\text{E},\infty}$, were also determined for the solutes from the temperature dependency of the γ_i^{∞} . For the assessment of the feasibility of the use of the ionic liquid solvent in extractive distillation, the experimental γ_i^{∞} values are used to compute the values for the selectivity, S_{ij}^{∞} , of the ionic liquid solvent [7] for the separation of different mixture types, i.e. alkane–aromatic, cycloalkane–aromatic and alkane–alkene.

2. Experimental

2.1. Chemicals

The ionic liquid, tributylmethylphosphonium methylsulphate, was purchased from Solvent Innovation with a purity of greater than 98% (NMR) and water content of less than 33.0 ppm. The ionic liquid was purified by subjecting the liquid to a low-pressure vacuum (10^{-4} Torr) for 6 h with heating at 353.15 K, to remove any traces of volatile contaminants including water. The organic solutes were used without any further purification due to the nature of the chromatographic process, where small amounts of impurities are separated from the major component and have negligible effect on the retention times of the major peaks.

2.2. Procedure

Packed columns, as opposed to open tubular columns, were used as the ionic liquids do not form stable films on the inner wall of capillary tubes [8]. The columns used were those of grade 304 stainless steel of 1 m length and with an internal diameter of 4.7 mm. The columns were washed, dried and coiled prior to use. The latter was incorporated into the procedure to prevent any crushing of the delicate stationary phase material if the column were to be firstly packed and then coiled.

The inert support material used was Chromosorb W-HP (80/100) mesh. The Chromosorb W-HP was firstly subjected to a stream of dry helium gas in column to remove any "fines" or broken particles due to the handling, storage and transportation of the material and as a means of pre-saturation. The purified ionic liquid was then carefully weighed and then dissolved in freshly distilled dichloromethane and then quantitatively transferred to a pre-weighed amount of the stationary phase in a round-bottomed flask. The mixture was then gently shaken and subjected to vacuum-assisted rotary evaporation, with slow rotation, to remove the solvent. A heated stream of helium gas was passed through the stationary phase for the final drying of the phase. This also ensured a pre-saturation of the stationary phase with the carrier gas to improve its packing characteristics in the coiled column. The coiled column was then packed with the stationary phase with the assistance of a slight vacuum on the injector end of the column.

The phase loadings were determined gravimetrically and the accuracy of the determination was confirmed through a comparison with results obtained from a Soxhlet extraction of a sample of the stationary phase. Three columns were prepared with varying loads of 20–25%, as described above, to ensure that the activity coefficient values were not dependent upon phase loading. The custom built gas-liquid chromatographic apparatus primarily consisted of a packed injection port, column housing for a 1/4 in. column and a thermal conductivity detector, all of which were maintained at the temperature of the investigation. A drying tube was attached to the carrier gas line to negate the uptake of moisture from the carrier gas, which was also preheated prior to entry into the column. The reference and column flows through the thermal conductivity detector were measured through the use of soap flow bubble meters and were controlled through the use of precision needle valves. The retention time for an unretained component was obtained. The chromatograms were recorded on a Kipp and Zonen chart recorder, from where the retention times were determined. The retention time of an unretained component was obtained by obtaining the retention time of dried air and that for the organic solutes by injecting amounts varying from 0.1–0.5 µL. The integrity of the ionic liquid phase with regard to moisture content was tested by obtaining the retention time of a standard solute in the form of *n*-hexane over frequent time intervals, i.e. every hour. Reproducibility of the retention time (with all other conditions fixed) allows for a confirmation that the stationary phase was not compromised in its chromatographic behaviour due to an increased or significant water content.

Further details on the general procedure for γ_i^{∞} determination can be found elsewhere [17]. Due to the long retention times and resulting broad peaks of the alkynes at the lower temperatures, γ_i^{∞} values were not recorded for these compounds. As opposed to previous investigations [16], the γ_i^{∞} values for alcohols were not determined also due to the extremely long retention times and corresponding broad peaks for these solutes. Download English Version:

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