

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

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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