

Measurements of activity coefficient at infinite dilution for organic solutes in tetramethylammonium chloride + ethylene glycol deep eutectic solvent using gas-liquid chromatography

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ABSTRACT

Deep eutectic solvents (DESs) are considered as the new ionic liquids (ILs) analogues that have emerged as potential alternative 'green' solvents, for a diversity of applications. In this study, a type III DES based on ammonium salt was investigated as an alternative solvent to currently employed conventional organic solvents in separation processes. Activity coefficients at infinite dilution, γ_{13}^{∞} for 19 organic solutes in the tetramethylammonium chloride + ethylene glycol DES were measured by the gas-liquid chromatography (GLC) method at four temperatures in the range from (313.15–343.15) K. Experimental measurements were undertaken with an overall uncertainty of $\pm 5.4\%$. The effect of the structure of the solutes on γ_{13}^{∞} was also investigated. For all investigated solutes, Gibbs helmholtz relationship was utilised to derive partial molar excess enthalpy values at infinite dilution ($\Delta H_i^{E,(\infty)}$) from experimental limiting activity coefficient data. From selectivity (S_{ij}^{∞}) and capacity (k_j^{∞}) values at infinite dilution, it was concluded that the investigated DES has the potential to replace a number of industrial solvents for the separation of various industrial mixtures.

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1. Introduction

In the early 1990s, ionic liquids (ILs) emerged as solvents of interest in various research fields in quest for means to adhere to stringent environmental regulations and replace organic solvents known to be toxic and harmful for the environment [1,2]. ILs offer exceptional chemical and physical properties such as high thermochemical stability, extremely low vapour pressure, high solvation capacity, wide liquid range and high thermal conductivity [3]. ILs have shown a considerable promise as alternative solvents in a various number of industrial and laboratory applications such as in extractive distillation, liquid-liquid extraction, gas separation, synthesis and catalysis. In comparison to organic solvents, a number of ILs (i.e imidazolium, pyridinium, etc.) exhibited larger values of selectivities and capacities in separation processes [4]. However, the main challenges with ILs include their high synthesis cost and non-biodegradability [5]. This has hindered their widespread applications in a large-scale of industrial processes. An industrial

solvent is required to be cost-effective and performant.

As part of attempts made to address negative environmental impact and energy costs caused by organic solvents and ILs, DESs have emerged as potential alternative 'green' solvents. Deep eutectic solvents are mixtures generally consisting of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), characterised by a melting temperature significantly lower than that of its individual components [6,7]. DESs share similar properties with ILs (type III DESs) [7]. However, they are largely reported in various industrial applications as promising alternative solvents because they are cheap, biodegradable and very easy to prepare as compared to ILs [7–9]. This has made DESs to be readily available for large-scale industrial applications. However, a good knowledge of their properties and phase equilibria is a fundamental step for the design and optimization of industrial separation processes [10].

Activity coefficients at infinite dilution (IDAC), γ_{13}^{∞} provide a useful indicator or tool for the preselection of solvents to be used in separation processes. Limiting activity data can also be used for the design of such processes. They provide the basic information on the intermolecular interactions between a solvent (DES) and different solutes for better understanding the behaviour of liquid mixtures [11]. Today, developing technologies in separation processes mainly

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focuses on mixtures that are difficult to separate in petrochemical and chemical industries. These technologies are often used to separate close-boiling or azeotropic mixtures by utilising for example extractive distillation or liquid-liquid extraction where ordinary distillation is not practically feasible. In order to screen DESs to be used in these solvent enhanced separation processes, separation performance in terms of selectivity and capacity at infinite dilution have to be determined, through activity coefficients at infinite dilution data.

This paper seeks to evaluate a quaternary ammonium-based DES to be used as an alternative solvent in separation processes. Thermodynamic data (including activity coefficients at infinite dilution) of DESs in binary mixtures are still scarce in the literature. These data are not sufficient to fully define their domains of application in chemical and petrochemical processes. In this study, γ_{13}^{∞} data for different organic solutes including alk-1-anes, alk-1-enes, alk-1-yne, cycloalkanes, alkanols, alkylbenzenes, ketones and heterocyclics in the DES (tetramethylammonium chloride: ethylene glycol) in a 1.0004:2 molar ratio were measured by gas-liquid chromatography (GLC). Measurements were carried out at four different temperatures, $T = (313.15, 323.15, 333.15 \text{ and } 343.15) \text{ K}$.

The main focus of this work was to assess the investigated the DES a potential separation agent for components that have close-boiling points or form azeotropes in the context of industrial processes such as liquid-liquid extraction or extractive distillation. Therefore the values of activity coefficients at infinite dilution were used to determine selectivity and capacity from different separation problems. The calculated values of selectivity and capacity were compared with those available in literature for selected ILs as well as organic solvents.

2. Materials and experimental procedure

2.1. Materials

All materials used in this study, including organic solutes, the hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA), were purchased from different suppliers and were used without further purification. Table 1 presents all materials along with their suppliers and purities.

The deep eutectic solvent consisted of tetramethylammonium chloride (HBA) and ethylene glycol (HBD). It was prepared and purified using procedures described by numerous researchers in the literature [6,7,12]. The structure of its components is shown in Fig. 1.

The investigated DES was prepared by mixing tetramethylammonium chloride with ethylene glycol in a 1.0004:2 molar ratio. The uncertainty in mass measurements was $\pm 0.0005 \text{ g}$. The mixture was placed in a tightly sealed beaker and heated at approximately 373.15 K. A magnetic stirrer was used for vigorous mixing. The preparation process was constantly monitored and let to run for at least 4 h until the mixture perfectly formed a clear or colorless homogeneous liquid. The prepared DES was purified by subjecting it to a temperature of 363.15 K in an oven for 8 h to remove traces of impurities and moisture. The solution was kept in an air tight container for storage purpose to prevent exposure to moisture.

2.2. Apparatus and experimental procedure

2.2.1. Refractive index and density measurements

From technological point of view, the knowledge of physical and chemical properties of pure DES is essential. In this study, refractive index and density of prepared DES were measured utilising an

Table 1
Suppliers and quoted purity of materials used in this study.

Compound	Supplier	Purity (Mass fraction)
n-hexane	Merck	≥ 99.0
n-heptane	Sigma-Aldrich	≥ 99.9
cyclopentane	Flucka	≥ 98.5
cyclohexane	ACE	≥ 99.0
hex-1-ene	Sigma-Aldrich	≥ 98.0
hept-1-ene	Flucka	≥ 98.0
hept-1-yne	Sigma-Aldrich	≥ 99.9
oct-1-yne	Sigma-Aldrich	≥ 99.9
ethanol	Sigma-Aldrich	≥ 99.9
methanol	Macron	≥ 99.9
propan-1-ol	Lab scan	≥ 99.5
propan-2-ol	Lab scan	≥ 99.5
benzene	Sigma-Aldrich	≥ 99.9
toluene	Sigma-Aldrich	≥ 99.9
acetone	Sigma-Aldrich	≥ 99.9
butan-2-one	Sigma-Aldrich	≥ 99.7
thiophene	Sigma-Aldrich	≥ 99.9
pyridine	Sigma-Aldrich	≥ 99.9
methyl acetate	Capital lab	≥ 98.0
ethyl acetate	ACE	≥ 99.5
dichloromethane	Sigma-Aldrich	≥ 99.9
helium	Afrox-SA	≥ 99.99
tetramethylammonium chloride	Sigma-Aldrich	≥ 99.0
ethylene glycol	Sigma-Aldrich	≥ 99.9

Atago refractometer model RX-7000 (with an uncertainty of ± 0.0001) and Anton Paar density and sound velocity meter, model DSA 500M (with an uncertainty of $\pm 0.0001 \text{ g/cm}^3$) at $T = 313.15 \text{ K}$. Prior to DES property measurements, both equipments were calibrated by measuring the refractive index and density of ultra-pure water at the temperature of interest. Measured properties of DES are presented in Table 2.

2.2.2. Activity coefficients at infinite dilution measurements

In this study, the experimental procedure used to determine infinite dilution activity coefficients in DES has been previously described [11,13,14]. The columns used were made of 1 m long stainless steel tube (304 grade) with an internal diameter of 4.1 mm. Chromosorb W-HP 80/100 mesh supplied by Sigma-Aldrich was used as a solid support for the desired solvent loading. Dichloromethane was used to dissolve and equally distribute the deposited DES around solid support in a solution. While coating by gentle shaking a mixture, dichloromethane was constantly evaporated using a vacuum pump operated at moderate vacuum pressure of 60 kPa. After evaporation, final masses of chromosorb coated with DES were weighed in a fume cupboard (with a precision of 0.0001 g) and kept in a dessicator to avoid moisture sorption by the DES due to its strong hygroscopic nature. In order to check for adsorption effects, two columns were prepared with different DES loadings, viz 30.02 and 33.11% by mass.

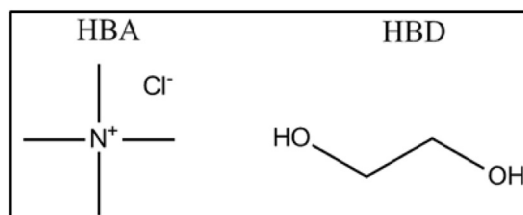


Fig. 1. The structure of the components comprising the Deep Eutectic Solvent (DES): tetramethylammonium chloride (HBA) and ethylene glycol (HBD).

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