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Density and viscosity study of pyridinium based ionic liquids as potential absorbents for natural refrigerants: Experimental and modelling

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ABSTRACT

In this work, density and viscosity of two pyridinium based ionic liquids; 1-ethylpyridinium bis(trifluoromethylsulfonyl)imide, $[C_2py][NTf_2]$, and 1-ethylpyridinium triflate, $[C_2py][OTf]$ as well as $[C_2py][OTf] + H_2O$ mixtures have been studied from experimental and theoretical point of view. Density and viscosity were measured, at several temperatures and atmospheric pressure. A linear equation and Vogel–Fulcher–Tammann equation correlated successfully density and viscosity behaviour. Coefficient of thermal expansion of pure ILs and their mixtures with water together with the excess molar volume and viscosity deviation of mixtures were also calculated. Excess molar volumes and viscosity deviations were described using a Redlich–Kister equation. Regarding to theoretical approach, PC-SAFT was used to model volumetric behaviour whereas Hard Sphere theory was used to study viscosity. The obtained results for pure ILs are satisfactory for both models, but for $[C_2py][OTf] + H_2O$ mixtures the deviations are higher.

1. Introduction

Compression refrigeration systems have covered the predominant part of heating and cooling needs over the last decades. However these systems require an intensive use of electrical energy. Thus, energy saving solutions should be considered for the future. In this context, absorption technology could represent a suitable alternative to compression devices since absorption machines are mainly powered by external heat (waste heat, renewable energies as solar, etc.). So, electrical energy consumption is reduced drastically. Besides this advantage, absorption technology suffers from several problems as low efficiencies and also conventional working pairs present several drawbacks. For instance, NH_3/H_2O presents low system performance, necessity of using rectification towers or high driving heat source temperature as main problems. In case of H_2O/LiBr, the low operating pressure, crystallization and corrosion are the main difficulties. Thus, ionic liquids (ILs) have gained attention in both experimental and theoretical research as potential absorbents for heat pumps due to their possibilities of improving the performance of conventional working pairs.

Knowledge about thermophysical properties of refrigerant/absorbent systems is essential to design new absorption cycles, to scale up process equipment and to determine the heat pumps performance. In this work, two important properties, density and viscosity were studied to characterize new potential absorbents based on ILs. High densities would help to minimize the overall size of absorption equipment [1], and thus, the manufacture and the cost will be lower. In addition, density is also important to calculate other properties as dynamic viscosity or the performance of the absorption cycles. Regarding to viscosity, that influences heat and mass transfer, it should be as low as possible in order to reduce pumping power consumption and allow a high heat transfer.

After studying a bunch of ILs, most of them based on imidazolium cation, Khamooshi et al. [2] concluded that H_2O/ionic liquid working pairs have several advantages against the conventional working fluids (NH_3/H_2O and H_2O/LiBr). For example, these compounds could resolve the problems of crystallization, corrosion, toxicity, flammability, etc. Nevertheless, coefficient of

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Abbreviations: IL, ionic liquid; $[C_2py][NTf_2]$, 1-ethylpyridinium bis(trifluoromethylsulfonyl)imide; $[C_2py][OTf]$, 1-ethylpyridinium triflate; DEHP, di(2-ethylhexyl) phthalate; DIDP, diisodecyl phthalate; C100, commercial standard; PC-SAFT, perturbed-chain statistical fluid theory; HS, hard-sphere; VFT, Vogel–Fulcher–Tammann; ARDs, average relative deviations; DMAX, maximum deviations; COP, coefficient of performance.

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List of symbols

M	molecular mass
m	number of segments of PC-SAFT
N	Avogadro constant
R	constant of ideal gas
R_η	roughness factor
s	standard error of estimate
T	absolute temperature
V	specific volume
V_r	reduced specific volume
V_0	close-packed volume
V^E	excess molar volumes
$\bar{V}_i^{E,\infty}$	partial molar volumes at infinite dilution of component i
x	mole fraction
Z	compressibility factor
α_p	isobaric coefficient of thermal expansion
$\Delta\eta$	viscosity deviation
ε	dispersive interaction energy of PC-SAFT
ε^{AiBi}	association energy of PC-SAFT
η	viscosity
η^*_{exp}	reduced viscosity
κ^{AiBi}	effective association volume of PC-SAFT
ρ	density
σ	diameter of segment of PC-SAFT

performance (COP) is lower and the circulation ratio is higher than those obtained for conventional working pairs, due to the ILs high viscosity. Therefore, the cycle must operate with high circulation ratio, provoking the growth of energy requirements. In addition, ILs containing halides or tetrafluoroborate anions may give rise to corrosion problems or to generate HF in presence of water [3]. Thus, new ILs should be explored in order to find those with optimal thermophysical properties. Recently, Królikowska et al. [4,5] have proposed several ILs such as *N*-octylisoquinolinium thiocyanate, 1-butyl-1-methylpiperidinium dicyanamide or 1-butyl-1-methylpyrrolidinium dicyanamide for H_2O as alternative working pairs for the absorption heat pump cycle.

In this work, two pyridinium-based ionic liquids were considered, 1-ethylpyridinium bis(trifluoromethylsulfonyl)imide, $[C_2py][NTf_2]$, and 1-ethylpyridinium triflate, $[C_2py][OTf]$. Up to our knowledge, density and viscosity of these pyridinium-based ionic liquids cannot be found in literature. Density and viscosity of $[C_2py][OTf]$ and $[C_2py][NTf_2]$ (dry and hydrated) were measured at several temperatures and correlated with a linear and exponential equation respectively. Only $H_2O + [C_2py][OTf]$ mixtures were experimentally determined since $[C_2py][NTf_2]$ is not miscible in water. It is well known that, ILs containing $[NTf_2]^-$ anion provoke immiscibility in water mixtures [6].

From experimental density data, the isobaric coefficient of thermal expansion, α_p, of $[C_2py][NTf_2]$, $[C_2py][OTf]$ and $H_2O + [C_2py][OTf]$ system was obtained, since it is necessary to dimension the absorption system. Furthermore, excess molar volume and viscosity deviation were also calculated from density and viscosity experimental data and were correlated with Redlich–Kister type equation. From this data, mixture behaviour was studied, providing useful information for the application.

Previously, phase transitions and thermal stability of these ionic liquids had been analysed [7], concluding that no detectable change was observed at temperatures lower than 260 °C. Thus, from point of view of the application, both ILs present a suitable thermal stability.

Furthermore, models with strong physical background have used to study deeply ILs behaviour. Perturbed-chain statistical fluid theory, PC-SAFT, and hard-sphere, HS, were tested to analysed volumetric and viscometric behaviour, respectively, for $[C_2py][NTf_2]$ and $[C_2py][OTf]$ together with $H_2O + [C_2py][OTf]$ mixtures. Up to now, and up to our knowledge, PC-SAFT model was used to correlate and to predict thermophysical properties in H_2O + IL systems by Chen et al. [8], Passos et al. [9], Shahriari et al. [10], Domańska et al. [11] and Paduszyníski et al. [12].

Hard Sphere (HS) theory, developed by Dymond and Assael [13,14] with the aim of modelling transport properties, was used to model viscosity. HS theoretical background should be placed on original Enskog hard sphere theory that had been able to predict transport properties of gases with high accuracy. However, even though many attempts were made to apply Enskog theory to dense fluids, it presented important limitations and results were not fully satisfactory. Hereby, Dymond and Assael introduced some modifications to original HS theory in order to extend its application to dense fluids. Recently Gaciño et al. [15] applied HS theory to 19 ionic liquids. However, as far as we are concerned, HS have not been used to model viscosity of H_2O + IL mixtures.

2. Experimental

ILs studied are commercially available and supplied by Iolitec, being their purity higher than 99% (Table 1). ILs were dried under vacuum of 0.1 Pa during at least 24 h prior to each measurement series. Water content was measured using a coulometric Karl-Fisher titration (Mettler Toledo DL32) before and after each measurements series, and it was found that there was no significant variation of the water quantity in the samples. Water content for dry $[C_2py][NTf_2]$ and $[C_2py][OTf]$ were 232 ppm and 90 ppm, respectively. The hydrophobic $[C_2py][NTf_2]$ was hydrated under atmospheric conditions until mass remained constant. Water content reached 4399 ppm. $[C_2py][OTf]$ was found to be miscible in the temperature range (283.15–353.15 K). To prepare $[C_2py][OTf] + H_2O$ mixtures, water was purified using a Milli-*Q* Plus system.

Solutions were prepared gravimetrically using a digital balance Sartorius CPA225D with an uncertainty of 0.00001 g. The error on the mole fraction composition of the mixtures induced due to balance uncertainty was estimated to be 5.10^{-5}.

Densities, ρ, of the pure compounds and the corresponding binary systems were measured using a vibrating tube densimeter Anton Paar DMA-4500, with automatic viscosity correction. Cell temperature was controlled by a thermostatic bath PolyScience with an uncertainty of ±0.01 K. The densimeter was calibrated using Milli-*Q* quality water and vacuum, according to the method of Lagourette et al. [16]. The uncertainty estimated in density through selected temperature range was of $\pm 0.0001\ \mathrm{g\,cm^{-3}}$.

Viscosity, η, of the pure substances and the corresponding binary mixtures were measured using an Anton Paar AMV 200 rolling ball viscometer according with the following equation:

$$\eta = a(\alpha, T) + \frac{b(\alpha, T)}{\rho_{\mathrm{ball}} - \rho_{\mathrm{liq}}} t \tag{1}$$

where *a* and *b* are calibration parameters, *t*, is the measured time using two magnetic sensors that a gold-coated steel ball needs to roll down in a glass capillary inclined an angle, α, filled with sample, a fixed distance, and ρ_{ball} and ρ_{liq} are the density of the ball and the sample, respectively. Temperature was controlled by a thermostatic bath Polyscience with an uncertainty of ±0.01 K.

To verify reproducibility of these measurements, calibration was performed for four inclination angles. Viscometer range goes from 15° to 90°, nevertheless due to the IL high viscosity selected angles