

Solubility and diffusivity of 1,1,1,2-tetrafluoroethane in room-temperature ionic liquids

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Abstract

The solubility and diffusivity of 1,1,1,2-tetrafluoroethane (R-134a) in seven room-temperature ionic liquids (RTILs) are presented. Among them, five of the RTILs were prepared for the first time with three new fluorocarbon sulfonate anions, and two were commercially available (1-butyl-3-methylimidazolium hexafluorophosphate was previously studied with R-134a). The gas absorption measurements were made using a gravimetric microbalance. Four isotherms (283.15, 298.15, 323.15, and 348.15 K) were measured at pressures from 0.01 to 0.35 MPa. Two of the newly synthesized ionic liquids, tetradecyl(trihexyl)phosphonium 1,1,2-trifluoro-2-(perfluoroethoxy)ethanesulfonate and tributyl(tetradecyl)phosphonium 1,1,2,3,3,3-hexafluoropropanesulfonate had the strongest interaction (negative deviations from Raoult's Law) with R-134a. Experimental gas solubility data were successfully correlated with the nonrandom two-liquid (NRTL) solution model. The time-dependent absorption data was used to calculate diffusivities that were analyzed using a model based on a modified Stokes–Einstein equation. The derived molecular size for R-134a is 2–3 times larger than the known size. Magnitudes in the observed diffusion coefficients are 10^{-10} to 10^{-11} m² s⁻¹, which are about 10–100 times lower than typical values, found in various organic liquids.

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1. Introduction

The phase behavior of ionic liquids with hydrofluorocarbon gases is necessary to assess the feasibility of their use for separations and as new absorption cooling fluids. Many papers have been published on the solubility and diffusivity of non-fluorocarbon gases in ionic liquids [1–11], but until our work little has been known about the interaction of hydrofluorocarbons and ionic liquids. In our previous work [12], we studied solubilities of hydrofluorocarbons (HFCs), which included trifluoromethane (R-23), difluoromethane (R-32), pentafluoroethane (R-125), 1,1,1,2-tetrafluoroethane (R-134a), 1,1,1-trifluoroethane (R-143a), and 1,1-difluoroethane (R-152a), in 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF₆], and show that R-32 had the highest gas solubility (R-32 > R-152a > R-23 > R-134a > R-125 > R-143a) in the

solvent-rich side. The trend in solubility did not correlate with the HFCs dipole moment as expected; however, the unique H-bonding capability (H–F–H) of HFCs is believed to be involved. In this work, we continue our investigations to understand the gas solubility and diffusivity of R-134a, which is the most commonly used hydrofluorocarbon. R-134a is primarily used in mobile air-conditioning systems. In addition, because R-134a is non-flammable it can be blended with other flammable refrigerants such as R-32, R-143a, and R-152a to produce nonflammable refrigerant mixtures such as R-404A (44 wt.% R-125, 52 wt.% R-143a, 4 wt.% R-134a) and R-407C (23 wt.% R-32, 25 wt.% R-125, and 52 wt.% R-134a). Therefore, we have investigated how R-134a interacts with RTILs.

Two commercially available ionic liquids (1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF₆] and 1-ethyl-3-methylimidazolium bis(pentafluoroethylsulfonyl)imide [emim][BEI]) and five ionic liquids synthesized by DuPont (1-butyl-3-methylimidazolium 1,1,2,3,3,3-hexafluoropropanesulfonate [bmim][HFPS], 1-butyl-3-methylimidazolium 1,1,2-trifluoro-2-(perfluoroethoxy)ethanesulfonate [bmim][TPES], 1-butyl-3-

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methylimidazolium 1,1,2-trifluoro-2-(trifluoromethoxy)ethanesulfonate [bmim][TTES], tetradecyl(trihexyl)phosphonium 1,1,2-trifluoro-2-(perfluoroethoxy)ethanesulfonate [6,6,6,14-P][TPES], and tributyl(tetradecyl) phosphonium 1,1,2,3,3,3-hexafluoropropanesulfonate [4,4,4,14-P][HFPS] were included in this study. Two of the RTILs, [6,6,6,14-P][TPES] and [4,4,4,14-P][HFPS], were prepared for the first time and details of the synthesis are provided. Details for the synthesis of the other three RTILs ([bmim][HFPS], [bmim][TPES], [bmim][TTES]) can be found in our previous work [13]. In addition to our own work, only two literature references are known regarding the interaction (electrical conductivity) of R-134a in an ionic liquid [14,15]. The present study is the first systematic investigation of the solubility and diffusivity of R-134a in RTILs. Similar to our previous work [12,13], we analyze the observed solubility data with the NRTL solution model and correlate the diffusivity behavior with a simple semi-theoretical model.

2. Experimental

2.1. Samples and synthesis

R-134a was obtained from DuPont Fluoroproducts with a minimum purity of 99.9%. A molecular sieve trap was installed to remove any trace amounts of water from the gas. Table 1 provides the chemical name, CAS registry number, source, abbreviation, structure, and the molecular weight of the seven RTILs that were tested. The samples obtained from Fluka Chemika have stated purities of >97%. The samples synthesized by DuPont have purities >98% based on elemental analysis. The cation salts were obtained from Cytek Specialty Chemicals. DuPont synthesized the anion salts, and the molecular structure was verified by nuclear magnetic resonance (NMR) and the thermal stability by thermogravimetric analysis (TGA). ^{19}F NMR and ^1H NMR spectra were recorded on a Bruker model DRX-400 spectrometer at 376.8937 and 400.550 MHz, respectively, using trichloromethane (CFCl_3) as an internal standard and deuterated chloroform (CDCl_3) as a lock solvent. A TA Instruments Q500 TGA was used to measure the change in mass of the ionic liquid as a function of temperature and atmosphere (air and nitrogen). Details for the synthesis of [6,6,6,14-P][TPES] and [4,4,4,14-P][HFPS] include:

2.1.1. Preparation of tetradecyl(trihexyl)phosphonium 1,1,2-trifluoro-2-(perfluoroethoxy)ethanesulfonate [6,6,6,14-P][TPES]

To a 500 mL round bottom flask was added acetone (spectroscopic grade, EMD, 50 mL) and ionic liquid tetradecyl(tri-*n*-hexyl)phosphonium chloride ([6,6,6,14-P][Cl], Cyphos[®] IL 101, CAS# 258864-54-9, 33.7 g). The mixture was magnetically stirred until it was one phase. In a separate 1 L flask, potassium 1,1,2-trifluoro-2-(perfluoroethoxy)ethanesulfonate (TPES-K, 21.6 g) was dissolved in acetone (400 mL). These solutions were combined and stirred under positive N_2 pressure at 299.15 K for 12 h producing a white precipitate of KCl. The precipitate was removed by suction filtration and the acetone was removed in vacuo on a rotovap to produce the crude product

as a cloudy oil (48 g). Chloroform was added (100 mL) and the solution was washed once with deionized water (50 mL). It was then dried over magnesium sulfate and reduced in vacuo first on a rotovap and then on a vacuum line (8 Pa, 297.15 K) for 8 h to yield the final product as a slightly yellow oil (28 g, 56 mass% yield).

^{19}F NMR (DMSO- d_6) δ [ppm]: -86.1 (s, 3F); -88.4 , -90.3 (subsplit ABq, $J_{\text{FF}} = 147$ Hz, 2F); -121.4 , -122.4 (subsplit ABq, $J_{\text{FF}} = 258$ Hz, 2F); -143.0 (dm, $J_{\text{FH}} = 53$ Hz, 1F).

^1H NMR (DMSO- d_6) δ [ppm]: 0.9 (m, 12H); 1.2 (m, 16H); 1.3 (m, 16H); 1.4 (m, 8H); 1.5 (m, 8H); 2.2 (m, 8H); 6.3 (dm, 1H, $J_{\text{FH}} = 54$ Hz).

Water mass percent by Karl-Fischer titration as synthesized was 0.11%.

Anal. calc. for $\text{C}_{36}\text{H}_{69}\text{F}_8\text{O}_4\text{PS}$: C, 55.4; H, 8.9; N, 0.0. Found: C, 55.2; H, 8.2; N, 0.1.

The following mass percent losses were observed:

- TGA (air): 10% loss at 584.15 K, 50% loss at 612.15 K.
- TGA(N_2): 10% loss at 588.15 K, 50% loss at 616.15 K.

2.1.2. Preparation of tributyl(tetradecyl) phosphonium 1,1,2,3,3,3-hexafluoropropanesulfonate [4,4,4,14-P][HFPS]

To a 4 L round bottom flask was added the ionic liquid tetradecyl(tri-*n*-butyl)phosphonium chloride ([4,4,4,14-P][Cl], Cyphos[®] IL 167, CAS # 81741-28-8, 345 g) and deionized water (1000 mL). The mixture was magnetically stirred until it was one phase. In a separate 2 L flask, potassium 1,1,2,3,3,3-hexafluoropropanesulfonate (HFPS-K, 214.2 g) was dissolved in deionized water (1100 mL). These solutions were combined and stirred under positive N_2 pressure at 299.15 K for 1 h producing a milky white oil.

The oil slowly solidified (439 g) and was removed by suction filtration and then dissolved in chloroform (300 mL). The remaining aqueous layer (pH 2) was extracted once with chloroform (100 mL). The chloroform layers were combined and washed with an aqueous sodium carbonate solution (50 mL) to remove any acidic impurity. They were then dried over magnesium sulfate, suction filtered, and reduced in vacuo first on a rotovap and then on a vacuum line (4 Pa, 373.15 K) for 16 h to yield the final product as a white solid (380 g, 76 mass% yield).

^{19}F NMR (DMSO- d_6) δ [ppm]: -73.7 (s, 3F); -114.6 , -120.9 (ABq, $J = 258$ Hz, 2F); -210.5 (m, 1F, $J_{\text{HF}} = 41.5$ Hz).

^1H NMR (DMSO- d_6) δ [ppm]: 0.8 (t, 3H, $J = 7.0$ Hz); 0.9 (t, 9H, $J = 7.0$ Hz); 1.3 (br s, 20H); 1.4 (m, 16H); 2.2 (m, 8H); 5.9 (m, 1H, $J_{\text{HF}} = 42$ Hz).

Water mass percent by Karl-Fischer titration as synthesized was 0.09%.

Anal. calc. for $\text{C}_{29}\text{H}_{57}\text{F}_6\text{O}_3\text{PS}$: C, 55.2; H, 9.1; N, 0.0. Found: C, 55.1; H, 8.8; N, 0.0.

The following mass percent losses were observed:

- TGA (air): 10% loss at 646.15 K, 50% loss at 694.15 K.
- TGA (N_2): 10% loss at 656.15 K, 50% loss at 709.15 K.

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