

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

PHYSICAL AND BIOPHYSICAL CHEMISTRY DIVISION*†

**THERMODYNAMIC AND THERMOPHYSICAL
PROPERTIES OF THE REFERENCE IONIC LIQUID:
1-HEXYL-3-METHYLIMIDAZOLIUM
BIS[(TRIFLUOROMETHYL)SULFONYL]AMIDE
(INCLUDING MIXTURES)
PART 1. EXPERIMENTAL METHODS AND RESULTS
(IUPAC Technical Report)**

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Thermodynamic and thermophysical properties of the reference ionic liquid: 1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]amide (including mixtures)

Part 1. Experimental methods and results

(IUPAC Technical Report)

Abstract: This article summarizes the results of IUPAC Project 2002-005-1-100 (Thermodynamics of ionic liquids, ionic liquid mixtures, and the development of standardized systems). The methods used by the various contributors to measure the thermophysical and phase equilibrium properties of the reference sample of the ionic liquid 1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]amide and its mixtures are summarized along with the uncertainties estimated by the contributors. Some results not previously published are presented. Properties of the pure ionic liquid included thermal properties (triple-point temperature, glass-transition temperature, enthalpy of fusion, heat capacities of condensed states), volumetric properties, speeds of sound, viscosities, electrolytic conductivities, and relative permittivities. Properties for mixtures included gas solubilities, solute activity coefficients at infinite dilution, liquid–liquid equilibrium (LLE) temperatures, and excess volumes. The companion article (Part 2) provides a critical evaluation of the data and recommended values with estimated combined expanded uncertainties.

Keywords: 1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]amide; ionic liquids; experimental measurements; thermodynamic properties; thermophysical properties; transport properties; uncertainties; IUPAC Physical and Biophysical Chemistry Division.

INTRODUCTION

This article is a product of IUPAC Project 2002-005-1-100 (Thermodynamics of ionic liquids, ionic liquid mixtures, and the development of standardized systems) [1], sponsored by the International Union of Pure and Applied Chemistry and the International Association of Chemical Thermodynamics, chaired by Kenneth N. Marsh. Members of the project were Joan F. Brennecke, Michael Frenkel, Andreas Heintz, Joseph W. Magee, Cor J. Peters, Luis Paulo N. Rebelo, and Kenneth R. Seddon.

The project was initiated because of serious disagreements in the published literature for a number of the properties of ionic liquids, especially viscosity and density. It was concluded that these disagreements resulted from a number of factors, including the purities of the ionic liquids, with the prime impurities being water and halide ions, as well as the use of inappropriate measurement methods. Two objectives of the project were: (1) to recommend a reference ionic liquid and make reference-quality measurements on selected thermophysical properties of both the pure ionic liquid and its mixtures, and (2) to establish recommended values for the properties measured and provide recommendations on measurement methods. The first of these objectives was completed, and nearly all of the results of the reference quality measurements have been published in the open literature. The present article summa-

rizes those measurements, giving details of the methods along with the uncertainties estimated by the researchers who reported the particular results.

Many of the initial measurements were made on ionic liquids containing hexafluorophosphate or tetrafluoroborate as the anion, but it was soon realized that these anions hydrolyze in the presence of water to produce hydrogen fluoride, so compounds based on these anions were eliminated from the selection. The initial selection for a reference ionic liquid was 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]amide [$C_4\text{mim}$][NTf₂], but this was eliminated, as it was covered by a patent in the United States. 1-Hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]amide (abbreviated as [$C_6\text{mim}$][NTf₂]) was selected as the reference fluid because it is stable, has a low viscosity compared with that of the ionic liquids based on hexafluorophosphate and tetrafluoroborate anions, has a low water solubility, and is easily prepared and purified. The pure fluid properties measured were the triple-point temperature, glass-transition temperature, enthalpy of fusion, heat capacity (solid, glass, and liquid), density as a function of temperature and pressure, speed of sound, viscosity, electrolytic conductivity, relative permittivity, and decomposition temperature. Mixture properties measured included gas solubility, solute activity coefficient at infinite dilution, excess volume, water solubility, and liquid–liquid equilibrium (LLE) temperatures. The critical evaluation of the data, along with recommended values including their combined expanded uncertainties, are published separately [2].

The synthesis, purification, and purity of the [$C_6\text{mim}$][NTf₂] sample have been described in detail in ref. [3]. Great care was taken to ensure that both the water and halide contents of the distributed reference sample were minimal, as it was realized at the start of the project that most of the discrepancies in the results were due to these impurities. The samples of [$C_6\text{mim}$][NTf₂] (termed the “IUPAC sample”) having a water mass fraction of the order of $1 \cdot 10^{-5}$ and a mole fraction purity greater than 0.995 [3] (determined from ¹H and ¹⁹F NMR spectroscopy) were distributed in sealed Schlenk tubes to the participating laboratories. A fractional melting study by Blokhin et al. with adiabatic calorimetry [4] gave a mole fraction purity of 0.997₆, and a similar study by Shimizu et al. [5] gave a mole fraction purity of 0.998₃. The present article describes the methods used to measure the various pure fluid and mixture properties on the IUPAC sample along with the estimated uncertainties in those measurements. In many cases, the meaning of the accuracy of the values reported, which are quoted in this report as the uncertainty (without the ± sign), is not clear, being quoted as errors, repeatability, accuracy, or uncertainty without qualification. Uncertainties are noted that conform to the *Guidelines to the Expression of Uncertainty in Measurement* (abbreviated as GUM), ISO (International Organization for Standardization), October, 1993 [6] and summarized for reporting experimental thermophysical property data in ref. [7]. Here, we will use the symbols recommended by the GUM with u_c being the combined standard uncertainty and $U = k \cdot u_c$ being the expanded uncertainty with coverage factor $k = 2$, which corresponds to a level of confidence of approximately 95 %. The relative combined uncertainty $u_{c,r} = u_c(y)/|y|$, while $U_r(y) = U(y)/|y|$ is the relative expanded uncertainty (with $k = 2$).

Measurements have been reported on samples other than the IUPAC sample, and those results are included in the critical evaluation [2], but are not discussed here except to comment on the suitability of the techniques.

Due to the hygroscopic nature of [$C_6\text{mim}$][NTf₂], those participating in the project were given instructions on how to minimize contamination with water and were requested to measure and report the water content by Karl Fischer titrations both before and after their measurements.

PURE COMPOUND PROPERTIES

Heat capacities and phase change properties

Heat capacities of both the solid and liquid phase, as well as phase change properties, were measured by adiabatic calorimetry by both Blokhin et al. [4] and Shimizu et al. [5]. Archer [8] made similar studies with differential scanning calorimetry (DSC). Heat capacity measurements at temperatures below

the triple-point temperature present difficulties because of the tendency of the liquid to supercool and to crystallize initially into a metastable form.

Blokhin et al. [4] used a commercial TAU-10 vacuum adiabatic calorimeter and made measurements from (5 to 370) K. Two series of measurements were made with sample masses of about 1.17 g and 0.658 g. The calorimeter performance was tested with reference grade corundum, high-purity copper, and K-1 grade benzoic acid. They concluded that the relative uncertainty in the heat capacity measurements did not exceed 0.4 % in the temperature range (20 to 370) K, 1 % in the range (10 to 20) K, and 2 % at $T < 10$ K. The authors [4] determined the enthalpy of fusion using both a continuous heat method and from fractional melting measurements. The uncertainty in the enthalpy of fusion was estimated to be about 0.06 kJ mol^{-1} , while the triple-point temperature uncertainty was estimated as 0.01 K. No differences were observed between the two samples. Sample 1 (with the higher mass) had a water mass fraction $w(\text{H}_2\text{O}) = 1 \cdot 10^{-4}$, while sample 2 (with the lower mass) had $w(\text{H}_2\text{O}) = 2 \cdot 10^{-4}$.

Shimizu et al. [5] reported the heat capacities in the temperature range $T = 5 \text{ K}$ to $T = 310 \text{ K}$, and included measurements on the liquid, stable crystal, and quenched liquid. Measurements between (79 and 310) K were made in a gold-plated copper vessel with a commercial adiabatic calorimeter (JTA-2000C, Jecc Torisha Co. Ltd) with 16.6966 g of sample. A second sample (5.3619 g) sample was used with a smaller gold-plated copper vessel for measurements from (10 to 300) K. A detailed uncertainty budget was reported with U at 298.15 K of $0.5 \text{ J K}^{-1} \cdot \text{mol}^{-1}$ (corresponding to $U_r = 0.08 \%$). The uncertainties in the enthalpy of fusion and triple-point temperature were not given. The purity of the sample, as reported above, was determined by fractional melting. The water content reported [5], (20 and 29) mg g^{-1} , includes a typographical error in the units, which should be mg kg^{-1} . The mass fraction of water $w(\text{H}_2\text{O}) = 20 \cdot 10^{-6}$ prior to the measurements and $w(\text{H}_2\text{O}) = 29 \cdot 10^{-6}$, after the measurements.

Archer [8] made a study using a commercial DSC on the crystal (both the metastable and stable forms), glass, and liquid phase in the temperature range $150 < (T/\text{K}) < 390$ with sample sizes ranging from (2 to 15) mg. The author [8] estimated that $U_r = 1.2 \%$ at 373 K and $U_r = 2.2 \%$ at 155 K. The fusion temperature was reported with $U = 0.29 \text{ K}$, while for the enthalpy of fusion $U_r = 1.8 \%$.

Crosthwaite et al. [9] and Diedrichs and Gmehling [10] reported heat capacities for a non-IUPAC sample measured also with a commercial DSC. For the liquid, the relative differences from the adiabatic calorimetry results range from (0.5 to 5.5) % high by Archer, (2 to 5) % high by Diedrichs and Gmehling and greater than 7 % low by Crosthwaite et al.

Density of the liquid (near $p = 0.1 \text{ MPa}$)

Densities of the IUPAC sample for the liquid state near pressure $p = 0.1 \text{ MPa}$ were measured by Lachwa et al. [11] from $T = (293 \text{ to } 303) \text{ K}$ using an Anton-Paar DNMA 5000 vibrating-tube densimeter. The overall relative uncertainty in the density was estimated by the authors [11] to be 0.01 % and the temperature uncertainty was 0.01 K. $w(\text{H}_2\text{O})$ was high after completion of the measurements with values as high as $2.4 \cdot 10^{-4}$. Kandil et al. [12] made measurements from $T = (298 \text{ to } 423) \text{ K}$ with an Anton-Paar DMA 512P vibrating-tube densimeter with $U_r = 0.3 \%$. $w(\text{H}_2\text{O})$ at the start was $4.3 \cdot 10^{-5}$ measured by Karl Fischer titration with a Radiometer Analytical Titrator. The mass fraction of water after the measurements was not determined. Widegren and Magee [3] measured the density on a sample with $w(\text{H}_2\text{O}) = 1 \cdot 10^{-5}$ from $T = (258 \text{ to } 373) \text{ K}$ using the vibrating U-tube of a Stabinger viscometer (Anton-Paar model SVM3000) with an estimated $U = 2 \text{ kg m}^{-3}$ at 298 K to give $U_r = 0.15 \%$. They also measured the density from (283 to 343) K with the vibrating tube of an Anton-Paar model DSA5000 sound analyzer. At the completion of these measurements $w(\text{H}_2\text{O})$ was $8.8 \cdot 10^{-4}$, considerably higher than other reported values, due to the difficulty of excluding moisture from entering the instrument. The estimated U was 1.4 kg m^{-3} . Esperança et al. [13] measured the densities from $T = (293 \text{ to } 338) \text{ K}$ with an Anton-Paar DMA 512P vibrating-tube densimeter. Their $w(\text{H}_2\text{O})$ was never more than $2 \cdot 10^{-4}$ at the completion of the measurements, and the uncertainty was estimated at 1.5 kg m^{-3} . Densities measured by Seddon and Driver [14] from $T = (293 \text{ to } 363) \text{ K}$ are reported in Table 1. These

measurement results will not be reported elsewhere. (The results of all other measurements discussed in this report have been published.) Prior to the measurements $w(\text{H}_2\text{O}) = 1.4 \cdot 10^{-5}$, and at the completion $w(\text{H}_2\text{O}) = 2.5 \cdot 10^{-5}$. The density was measured with an Anton–Paar model 4500 and the estimated uncertainty in the measurements was 0.05 kg m^{-3} .

Table 1 Densities and viscosities near pressure $p = 0.1 \text{ MPa}$ measured by Driver and Seddon [14] for the IUPAC sample $[\text{C}_6\text{mim}][\text{NTf}_2]$.

T/K	$\rho/\text{kg m}^{-3}$	T/K	$\eta/\text{mPa s}$
293.15	1376.5	298.15	80.7
303.15	1367.4	308.05	51.6
313.15	1358.3	318.05	34.2
323.15	1349.3	328.15	24.3
333.15	1340.2	338.15	17.9
343.15	1331.2	348.05	13.7
353.14	1322.3	358.15	10.6
363.14	1313.3	368.05	8.33

Density of the liquid at high pressures

Densities of the liquid IUPAC sample were determined by Kandil et al. [12] from $T = (298 \text{ to } 423) \text{ K}$ and $p = (0.1 \text{ to } 40) \text{ MPa}$ and Esperança et al. [13] from $T = (293 \text{ to } 338) \text{ K}$ and $p = (0.1 \text{ to } 65) \text{ MPa}$ using the same method as described above with the same uncertainty. Measurements on a non-IUPAC sample were published previously by Gomes de Azevedo et al. [15] from $T = (298 \text{ to } 333) \text{ K}$ and $p = (0.1 \text{ to } 60) \text{ MPa}$. Although the initial water content of this sample was low, $w(\text{H}_2\text{O}) = 7.5 \cdot 10^{-3}$, the density results are 0.3 % lower than those using the IUPAC sample.

Vapor pressure

The vapor pressure of the IUPAC sample was measured by Zaitsau et al. [16] with a Knudsen effusion method from $T = (446 \text{ to } 494) \text{ K}$. The measured pressures ranged from $p = (0.007 \text{ to } 0.17) \text{ Pa}$. Uncertainty estimates were not provided by the authors.

Viscosity of the liquid

Viscosities were measured by Kandil et al. [12] from $T = (298 \text{ to } 423) \text{ K}$ and pressures from $(0.1 \text{ to } 40) \text{ MPa}$ with a vibrating-wire viscometer. This technique involved the measurement of the fundamental resonance frequency of a vibrating wire clamped at both ends and immersed in the liquid. This is an absolute method, but in practice the wire diameter was determined by calibration with the reference fluid methylbenzene. One sample had $w(\text{H}_2\text{O}) = 4.3 \cdot 10^{-5}$ before and $4.1 \cdot 10^{-4}$ after the measurements, and the other sample had $7 \cdot 10^{-6}$ before and $1.17 \cdot 10^{-4}$ after. The estimated $U_r = 2 \%$. Only the results with the lower water mass fraction were considered in the analysis.

Widgren and Magee [3] made measurements from $T = (258 \text{ to } 373) \text{ K}$ with a Stabinger viscometer (Anton–Paar model SVM3000) and with a Ubbelohde capillary viscometer (Schott–Geräte GmbH, size II) at $(293.15 \text{ and } 298.15) \text{ K}$ both at $p = 0.1 \text{ MPa}$. The Stabinger viscometer consisted of a rotating concentric cylinders device that is fully automatic and gives a direct readout of the viscosity. The temperature uncertainty was estimated as 0.05 K and the estimated $U_r = 2 \%$ in the temperature range $(293.15 \text{ to } 373.15) \text{ K}$ and increased to $U_r = 5 \%$ at $T < 298 \text{ K}$. They estimated $U_r = 1 \%$ for the Ubbelohde viscometer measurements.

Santos et al. [17] made measurements from $T = (298.15 \text{ to } 343.15) \text{ K}$ with an Ostwald viscometer (Cannon type C size #71) with an uncertainty in temperature of 0.01 K and uncertainty in viscosity of better than 0.5 %. Table 1 lists previously unpublished experimental values from Seddon and Driver [14] from $T = (298 \text{ to } 368) \text{ K}$ measured with a rotating cone and plate viscometer (Brookfield LVDV-II) with a reported uncertainty of 1 %. $w(\text{H}_2\text{O})$ was $1.19 \cdot 10^{-4}$ before and $1.96 \cdot 10^{-4}$ after the measurements.

Electrolytic conductivity (near $p = 0.1 \text{ MPa}$)

The electrolytic conductivity was measured by Kandil et al. [12] from $T = (278 \text{ to } 323) \text{ K}$ with an LKB Model 5312 A flow cell. The resistance was measured at frequencies f from (0.5 to 10) kHz, and the results were extrapolated to $f \rightarrow \infty$. U_r for the reported electrolytic conductivities was 2 %. Temperature uncertainty was 0.01 K. Water content was not determined.

Widegren et al. [18] measured electrolytic conductivities from $T = (288 \text{ to } 323) \text{ K}$ with a small-volume commercial conductivity cell with a cell constant of $(99.89 \pm 0.7) \text{ m}^{-1}$. The measured resistance was extrapolated to $f \rightarrow \infty$. Measurements were made as a function of water content. The lowest water content was $w(\text{H}_2\text{O}) = 8.8 \cdot 10^{-6}$ before and after the measurements. The estimated $U_r = 2 \%$. Measurements were repeated in ref. [3] with the same technique and same relative expanded uncertainty. The two results agreed within 2 %.

Speed of sound (near $p = 0.1 \text{ MPa}$)

Widegren and Magee [3] measured the speed of sound from $T = (283 \text{ to } 343) \text{ K}$ using an Anton–Paar model DSA5000 sound analyzer. U was estimated to be 1.7 m s^{-1} . With this apparatus, it was difficult to exclude water, and the final $w(\text{H}_2\text{O})$ was high at $8.7 \cdot 10^{-4}$ for the first series of measurements and $5.1 \cdot 10^{-4}$ for the second series.

Relative permittivity (near $p = 0.1 \text{ MPa}$)

Hunger et al. [19] determined relative permittivity ϵ from $T = (278 \text{ to } 338) \text{ K}$ by dielectric relaxation spectroscopy applied to high-frequency dielectric spectra in the range from $f = (0.3 \text{ to } 89) \text{ GHz}$. The dielectric spectra were recorded with a vector network analyzer in a range $f = (0.3 \text{ to } 20) \text{ GHz}$ and with two waveguide interferometers in the ranges $f = (27 \text{ to } 39) \text{ GHz}$ and $f = (60 \text{ to } 89) \text{ GHz}$. Samples were stored in either a desiccator or a glove box, and measurements were made under a dry nitrogen atmosphere. $w(\text{H}_2\text{O})$ was $4.5 \cdot 10^{-5}$ before and $1.65 \cdot 10^{-4}$ after the measurements. Values of relative permittivity ϵ were obtained by fitting a Cole–Cole model for the dominant low-frequency process and a Debye model for the higher-frequency process [18]. The estimated uncertainty for ϵ is 1, which corresponds to relative uncertainties from (7 to 9) %. The magnitude of the uncertainty is due primarily to long relaxation times and to inaccessible lower frequencies stemming from the relatively large electrolytic conductivity of the sample.

Effect of water on the properties of $[\text{C}_6\text{mim}][\text{NTf}_2]$

The effect of water on the density, viscosity, speed of sound, and electrolytic conductivity was studied by Widegren and Magee [3], while the effect of water on the electrolytic conductivity was studied by Widegren et al. [18]. Viscosity and electrical conductivity changed significantly with variation of the water content. The analysis in Part 2 indicates that most of the discrepancies in the measurements, particularly on non-IUPAC samples, are the result of the presence of water.

Other pure component properties

Crosthwaite et al. [9] measured the decomposition temperature with a Mettler–Toledo TGA/SDTA 851e/SF/1100 °C thermal gravimetric analyzer under a nitrogen atmosphere. They determined both the onset temperature T_{onset} (the intersection of the plot of the baseline mass and the tangent of the mass-temperature curve as decomposition occurred) and T_{start} (the temperature where decomposition is first detected in the apparatus). The reported $T_{\text{onset}} = 700$ K and $T_{\text{start}} = 620$ K.

MIXTURE PROPERTIES

Vapor–liquid equilibrium (VLE) with carbon dioxide (gas solubility)

Various techniques have been used to measure the solubility of gases in liquids. Some techniques involve high-pressure measurements (up to 20 MPa), while for others the maximum pressure was ≈ 0.1 MPa. The solubility of carbon dioxide in the IUPAC sample was determined by Kumelan et al. [20] from (293.15 to 413.2) K, where the maximum pressure reached was 10 MPa. The measurements were based on a synthetic method using a view cell where the pressure required to dissolve an accurately known amount of carbon dioxide in an accurately known amount of $[\text{C}_6\text{mim}][\text{NTf}_2]$ was measured. The uncertainty in temperature was 0.1 K, the relative uncertainty in pressure was 5 % at low pressure and 0.6 % at the highest pressure, while the average uncertainty in the amount of carbon dioxide dissolved was $0.0084 \text{ mol kg}^{-1}$. The water mass fraction determined by Karl Fischer titration was less than $5 \cdot 10^{-4}$ both before and after the measurements.

Costa Gomes [21] made low-pressure measurements from (283 and 343) K at $p \approx 0.1$ MPa. The technique involved contacting a gas at a known pressure with a known mass of the ionic liquid in a closed system. The typical volume of the ionic liquid was (2 to 5) cm^3 . $w(\text{H}_2\text{O})$ before the measurements was less than $2.0 \cdot 10^{-5}$ and $w(\text{Br}^-)$ was less than $1.0 \cdot 10^{-5}$. At equilibrium, the measurement of the pressure above the liquid was used to calculate the solubility. The total relative uncertainty of the solubility was estimated by the author [21] to be 5 % for the carbon dioxide measurements.

Muldoon et al. [22] used two techniques. At pressures < 1.3 MPa, an intelligent gravimetric analyzer (IGA) (Hiden Analytical Ltd, UK) microbalance was used. Approximately 75 mg of the ionic liquid was loaded into the quartz cell of the microbalance, and the solubility of CO_2 was determined at the applied CO_2 pressure from the mass uptake at equilibrium. Relative uncertainties were estimated to be near 0.6 %. For their measurements, the water mass fraction was typically $< 2 \cdot 10^{-4}$. They claimed that this amount of water did not affect the CO_2 solubility. At high pressure (up to 15 MPa) measurements were made in a sapphire sample cell. Typically, 1.5 g of ionic liquid and a known amount of CO_2 were added, and the amount of gas dissolved was obtained by calculating the difference in the amount of gas delivered to the sample chamber and the gas present in the vapor phase, as calculated with an equation of state for CO_2 .

Shiflett and Yokozeki [23] measured CO_2 solubility from $T = (282 \text{ to } 348)$ K and p to 2 MPa also with a Hiden IGA microbalance in the static mode and a sample of about 65 mg. $w(\text{H}_2\text{O})$ was $< 2 \cdot 10^{-5}$ prior to the measurements. The uncertainties in temperature and pressure were estimated to be 0.1 K and 0.8 kPa, respectively. The uncertainty in the mole fraction solubility of CO_2 was estimated to be less than 0.006. At higher pressures, a vapor–liquid–liquid apparatus consisting of a glass tube with inside diameter 3.94 mm and length 100 mm was used. Known masses of ionic liquid and CO_2 were transferred to the cell, and the height of the liquid and the pressure of CO_2 at equilibrium were measured at a known temperature. The uncertainties in T and mole fraction of CO_2 were 0.2 K and 0.004, respectively. The authors also reported the existence of a region of vapor–liquid–liquid equilibrium for $(\text{CO}_2 + [\text{C}_6\text{mim}][\text{NTf}_2])$ at x_{CO_2} near 0.8.

VLE studies with other compounds

Other VLE studies involving the IUPAC sample have been reported in the literature. Costa Gomes [21], using the technique described above, measured the solubility of hydrogen and propane from $T = (283 \text{ to } 343) \text{ K}$ at $p \approx 0.1 \text{ MPa}$. Hydrogen was about 0.02 times as soluble as CO_2 , while propane was about half as soluble. Kumelan et al. [24] measured the solubility of hydrogen from $T = (293 \text{ to } 413) \text{ K}$ and p from near (2 to 10) MPa, using the technique described above. Studies on non-IUPAC samples of $[\text{C}_6\text{mim}][\text{NTf}_2]$ are listed in Part 2.

Activity coefficients of solutes at infinite dilution

Activity coefficients at infinite dilution γ^∞ for methanol, butan-1-ol, and hexan-1-ol in the IUPAC sample were measured by Heintz et al. [25] using a gas chromatography technique at $T = (298 \text{ to } 396) \text{ K}$. The relative uncertainties in the γ^∞ values were estimated to be 3 %.

Liquid–liquid equilibria (LLE) with water

The solubility of water in the IUPAC sample of $[\text{C}_6\text{mim}][\text{NTf}_2]$ was studied by Widegren and Magee [3] using coulometric Karl Fischer titration. The sample consisted of 3.2 cm^3 of ionic liquid and 0.2 cm^3 of water contained in a glass vial with a magnetic stirrer and sealed with a septum cap. At 298.15 K $w(\text{H}_2\text{O})$ was constant within $2 \cdot 10^{-4}$ over a period of 3 days, and at 293.15 K $w(\text{H}_2\text{O})$ showed no observable change after 2 months. The uncertainty in $w(\text{H}_2\text{O})$ was estimated to be $4 \cdot 10^{-4}$.

Chapeaux et al. [26] also reported (at $T = 296.6 \text{ K}$) the mass fraction solubility of the IUPAC sample in water determined by coulometric Karl Fischer titration. The estimated uncertainty in $w(\text{H}_2\text{O})$ was $1 \cdot 10^{-4}$. They also determined the mass fraction solubility of $[\text{C}_6\text{mim}][\text{NTf}_2]$ in water using a UV–vis spectroscopic method with an uncertainty $w(\text{IL}) = 1 \cdot 10^{-4}$.

Liquid–liquid equilibria

LLE temperatures for the IUPAC sample of $[\text{C}_6\text{mim}][\text{NTf}_2]$ + butan-1-ol, + pentan-1-ol, + hexan-1-ol, and + octan-1-ol were reported by Lachwa et al. [11] at $p = 0.1 \text{ MPa}$. The estimated uncertainty in $w([\text{C}_6\text{mim}][\text{NTf}_2])$ was $1 \cdot 10^{-5}$, while the uncertainty in the visually determined LLE temperature was 0.2 K . At mass fractions close to the upper critical solution temperature (UCST), they also measured LLE at pressures up to 50 MPa for butan-1-ol, pentan-1-ol, and hexan-1-ol using two methods. At $p < 5 \text{ MPa}$ they used a light-scattering technique in samples contained over mercury, which acted as the pressure transmission medium. For these measurements, the uncertainties in transition temperature and pressure were 0.2 K and 0.01 MPa , respectively. At higher pressures, they used a stainless steel cell ($V \approx 0.5 \text{ cm}^3$) closed at both ends with sapphire windows. Pressure was transmitted through a long 1.56-mm -diameter stainless steel tube filled with the solution (buffer) followed by the alcohol under study. Temperature and pressure uncertainties were 0.01 K and 0.1 MPa , respectively. Wertz et al. [27] also reported LLE for the system (IUPAC sample + hexan-1-ol) at 0.1 MPa . The transition was determined by light scattering. Samples were prepared gravimetrically with an uncertainty in $w([\text{C}_6\text{mim}][\text{NTf}_2]) = 1.5 \cdot 10^{-3}$ and an uncertainty in temperature of 0.1 K .

Other mixture properties

Excess volumes were determined by Lachwa et al. [11] at $p = 0.1 \text{ MPa}$ on the IUPAC sample of $[\text{C}_6\text{mim}][\text{NTf}_2]$ + ethanol, + propan-1-ol, + butan-1-ol, + and pentan-1-ol at $T = (293.15, 298.15, \text{ and } 303.15) \text{ K}$. Measurements were made with an Anton–Paar DMA 500 vibrating-tube densimeter.

Samples were prepared by mass. The estimated relative uncertainties in the mass fraction and the density were 0.02 and 0.01 %, respectively.

CONCLUSIONS

The techniques used to measure the thermodynamic, transport, and phase equilibria properties of the IUPAC sample of [C₆mim][NTf₂] and its mixtures are summarized. Also included is a summary of the uncertainties associated with the measurements, as reported by the researchers who completed the particular experimental study. Often the meaning of the uncertainty statements provided is unclear, with values quoted as errors, repeatability, accuracy, or uncertainty without qualification. Heat capacities measured with DSC are in only fair agreement with values measured by adiabatic calorimetry. For the majority of other measurements where different techniques were used, the agreement is generally within the expected uncertainties for the measurement methods.

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