



Gas solubilities in room temperature ionic liquids – Correlation between RTiL-molar mass and Henry's law constant

Jessica Blath^{a,*}, Michael Christ^b, Natalie Deubler^b, Thomas Hirth^{a,b}, Thomas Schiestel^b

^a Institute for Interfacial Engineering, University of Stuttgart, Stuttgart, Germany

^b Fraunhofer Institute for Interfacial Engineering and Biotechnology, Stuttgart, Germany

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ABSTRACT

The solubility of CO₂, CH₄, N₂, and CO was measured in a broad number of ionic liquids using a pressure drop set-up. A successful correlation of the Henry's law constants at 60 °C was made to two empirical models already described in literature (Camper et al. [13] and Moganty and Baltus [25]). Subsequently, a new empirical model was proposed, which describes the Henry's law constant as a function of the molar mass of the ionic liquid, as long as physical interactions between gas and ionic liquid are dominant. Additionally, the entropy and enthalpy of solvation was studied by means of the temperature influence to the Henry's law constant.

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1. Introduction

Ionic liquids are defined as salts with a melting point below 100 °C [1–3]. Unique properties, such as negligible vapor pressure, a broad temperature range of liquidity, and their chemical stability, make them attractive for research activities and offer a high potential for industrial applications.

Ionic liquids can be an alternative for flue gas cleaning and natural gas purification [1,4]. Compared to amine absorber techniques, where mostly monoethanolamine (MEA) is used to scrub CO₂ from flue gas, ionic liquids do not pollute the gas flow due to their non volatility.

In contrast to the amine scrubbing process, no heating step during desorption is necessary to remove the entire CO₂. As a result the energy consumption and therefore energy costs can be dramatically reduced [1]. An alternative application is the supported ionic liquid membrane, where the ionic liquid is immobilized in a porous support by capillary forces. The viscosity of the ionic liquid and the Henry's law constant of gases in the ionic liquid are essential to decide which ionic liquid is suitable for separation processes.

In literature we found five different methods for the experimental determination of Henry's law constant so far. A short summary is given in this section. The first absorption measurements in 2002 were carried out by means of a gravimetric microbalance [5,6]. The main disadvantage of this experimental set-up is the

error produced by the buoyancy. An alternative method is NMR-spectroscopy [7]. But thereby only the absorption capability of gases containing carbon or hydrogen can be measured. Furthermore, an optical method is described [8–10]. Here it is advisable to employ a second method for the low pressure range, since the behavior of the gas–liquid phase varies extremely with pressure. The use of a time lag method is another possibility [11,12]. The RTiL is immobilized in a porous membrane and the solubility is calculated from the time lag of the permeation. The main drawback is the unknown effect of the support and the possible interactions of ionic liquid with the support material.

The pressure drop method is used in most experimental studies in literature [1,13–21]. Here the ionic liquid is brought into contact with a gas in a small chamber with a defined volume at a constant temperature. The pressure drop caused by absorption is monitored and the Henry's law constant can be calculated at the thermodynamic equilibrium.

Besides the experimental investigations, molecular dynamic tools can be used to simulate the absorption capability. These are described by e.g. Kerlé et al., Shi and Maginn, and Shah and Maginn [22–24] who calculated mainly absorption data of imidazolium based ionic liquids with various gases at different temperatures. Though still a more extensive set of data is necessary to improve the prediction of theoretical implementations for new kinds of anion and cation combinations.

In our work we selected a broad range of commercially available ionic liquids with different kinds of cations (imidazolium, pyrrolidinium, piperidinium, pyridinium, sulfonium and phosphonium) and anions (bis(trifluoromethylsulfonyl)imide,

* Corresponding author. Tel.: +49 711970 4133; fax: +49 711970 4200.

E-mail address: jessica.blath@igb.fraunhofer.de (J. Blath).

Nomenclature

δ_{gas}	solubility parameter of the gas [MPa ^{0.5}]
δ_{IL}	solubility parameter of the ionic liquid [MPa ^{0.5}]
$E_{\text{A}}^{\text{vis}}$	activation energy of viscosity [kJ/mol]
f_i°	standard fugacity [bar]
H	Henry's law constant [bar]
Δh	enthalpy of solvation [kJ/mol]
M	molar mass [g/mol]
m	empirical determined constant, slope
n	empirical determined constant, intersection
Δn_{gas}	mol of gas [mol]
η	viscosity [Pa s]
Δp	pressure difference [Pa]
p_{eq}	equilibrium pressure [bar]
p_{ini}	start pressure [bar]
R	ideal gas constant [8.314 J/K/mol]
R^2	coefficient of determination
R_i	ideal separation factor for i
ρ	density [g/ml]
Δs	entropy of solvation [kJ/mol]
T	temperature [K]
u^{vap}	enthalpy of vaporization [kJ/mol]
V_1	volume of the measuring cell [m ³]
v_{IL}	molar volume [ml/mol]
φ_{IL}	volume fraction of the IL
x	mole fraction of gas in ionic liquid [mol _{gas} /mol _{all}]
z_i	charge of anion respectively cation

tetrafluoroborate, tris(pentafluoroethyl)trifluorophosphate, tetracyanoborate). In addition to carbon dioxide, the solubilities of carbon monoxide, nitrogen, and methane were determined. These results were correlated to models already described in literature [13,25]. In addition, the measured Henry's law constants were correlated with the reciprocal molar mass of the ionic liquids.

2. Experimental methods and material

The ionic liquids were purchased by either IoLiTec (Ionic Liquids Technologies GmbH, Heilbronn, Germany) or Merck (Merck KGaA, Darmstadt, Germany). The purity of the purchased RTiLs, as well as

the molar weight, and the density are listed in Table 1. The ionic liquids were used as received. The gases were supplied from Air Liquide (AIR LIQUIDE Deutschland GmbH Düsseldorf, Germany) or Westfalen AG (Westfalen AG, Münster, Germany). Further information is summarized in Table 2.

The water content of the ionic liquid was determined with Karl Fischer titration. Therefore, a C20 Compact KF Coulometer (Mettler-Toledo GmbH, Gießen, Germany) was used. The data is listed in Table 1, too.

The experimental set-up is based on the system described in Camper et al. [13]. In Fig. 1 the isochoric pressure drop installation is presented. The bellow-seal valves 1 and 2 (SS-6BG-MM, Swagelok, Reutlingen-Altenburg, Germany) connect the measuring cell (22.76 ml ± 1.4%) with the reference cell (59.82 ml ± 1.5%) and the reference cell with the vacuum pump (MP 054 ZP, Ilmvac GmbH, Ilmenau, Germany) respectively the gas bottles. The digital piezoelectric pressure transducer (PR 35X-V-10, Omega Newport Electronics GmbH, Deckenpfronn, Germany) records the pressure every 2 s. A magnetic stir bar inside the measuring cell ensures a faster settling of the thermodynamic equilibrium within a short period of time. The reference and measuring cell are made of stainless steel. In addition, the measuring cell was enameled to avoid any corrosion. All connecting tubes are made of stainless steel with an inner diameter of 2 mm. The reference and the measuring cell are placed inside an electrical drying oven (TR60, Nabertherm GmbH, Lilienthal/Bremen, Germany) to guarantee a constant temperature in the measuring system. In addition, all tubes and connections are thermally insulated. Furthermore, the gases are additionally dried by means of moisture traps (Molecular Sieve 5 A, MT-D, Agilent Technologies Waldbronn, Germany).

Prior to a pressure drop measurement, the set-up including the RTiL is evacuated at examination temperature for at least 1 h under stirring. Thereby, the absolute pressure in the system is lower than 7 mbar. Then valve 1 is closed and the reference cell is filled with the desired gas via valve 2, where it is heated up for 15 min to adapt to measuring conditions. Afterwards, valve 1 is opened and the measurement is started immediately. The thermodynamic equilibrium is reached between 2 h and 18 h depending on both the gas, and the ionic liquid as well as its quantity. The amount of RTiL was between 1.5 and 3.5 ml per batch. The set-up was operated from 30 °C to 230 °C. Due to the discussion about decomposition temperature of some ionic liquids [26], most measurements were performed at 60 °C. All absorption experiments were repeated three times to obtain reliable data.

Table 1

The properties of the applied room temperature ionic liquids – with molar weight M , density ρ , and purity.

Ionic liquid	Abbreviation	Supplier	M (g/mol)	ρ (g/ml)	Purity (%)	Water (ppm)
1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfanyl)imide	[EMIM] [NTf ₂]	Iolitec	391.31	1.52	99	1955
1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfanyl)imide	[HMIM] [NTf ₂]	Iolitec	447.42	1.37	99	664
1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfanyl)imide	[BM-Pyrrolid.] [NTf ₂]	Iolitec	422.388	1.401	99	91
n-Hexylpyridinium bis(trifluoromethylsulfanyl)imide	[H-Pyrid.] [NTf ₂]	Merck	444.42	1.39	>98	865
Triethylsulfonium bis(trifluoromethylsulfanyl)imide	[S ₂₂₂] [NTf ₂]	Iolitec	399.371	1.465	>99	1837
1-Methyl-1-propylpiperidinium bis(trifluoromethylsulfanyl)imide	[MP-Piperid.] [NTf ₂]	Iolitec	422.388	1.41	99	982
1-Ethyl-3-methylimidazolium trifluoromethanesulfonate	[EMIM] [CF ₃ SO ₃]	Iolitec	260.113	1.368	99	1197
1-Ethyl-3-methylimidazolium tetrafluoroborate	[EMIM] [BF ₄]	Iolitec	197.97	1.34	>98	7604
1-Butyl-3-methylimidazolium tetrafluoroborate	[BMIM] [BF ₄]	Iolitec	226.016	1.203	99	1126
1-Ethyl-3-methylimidazolium tetracyanoborate	[BMIM] [B(CN) ₄]	Merck	254.14	1.0183	>98	8659
1-Hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate	[HMIM] [FAP]	Merck	612.26	1.56	99	268
Trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate	[P ₆₆₆₁₄] [FAP]	Merck	928.828	1.18	99	111

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