Fluid Phase Equilibria 362 (2014) 300–306

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

CO_2 absorption properties, densities, viscosities, and electrical conductivities of ethylimidazolium and 1-ethyl-3-methylimidazolium ionic liquids

Takashi Makino[a,*], Mitsuhiro Kanakubo[a,*], Yoshio Masuda[a], Tatsuya Umecky[b], Akira Suzuki[a,c]

[a] National Institute of Advanced Industrial Science and Technology, 4-2-1 Nigatake, Miyagino, Miyagi, Sendai 983-8551, Japan
[b] Department of Chemistry and Applied Chemistry, Graduate School of Science and Engineering, Saga University, 1 Honjo-machi, Saga 840-8502, Japan
[c] New Industry Creation Hatchery Center, Tohoku University, 6-6-10 Aramaki-aza-aoba, Aoba, Miyagi, Sendai 980-8579, Japan

ARTICLE INFO

Article history:
Received 15 July 2013
Received in revised form 12 October 2013
Accepted 16 October 2013
Available online 6 November 2013

Keywords:
Ionic liquid
CO_2
Solubility
Volumetric property
Transport property

ABSTRACT

We have focused on a protic ionic liquid, ethylimidazolium bis(trifluoromethanesulfonyl)amide ([eimH][Tf_2N]), and the analogous aprotic ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([emim][Tf_2N]). Densities, viscosities, and electrical conductivities of the two ionic liquids have been measured over the temperature range $T = (273.15–363.15)$ K at atmospheric pressure. The densities of [eimH][Tf_2N] and [emim][Tf_2N] decrease with increasing temperature. The protic ionic liquid has the higher density (the smaller molar volume) than the aprotic one. The transport properties of the two ionic liquids show ordinary temperature dependencies. [eimH][Tf_2N] has the higher viscosities (smaller electrical conductivities) than [emim][Tf_2N]. Empirical Walden products indicate that [eimH][Tf_2N] shows smaller conductivities than [emim][Tf_2N] at certain viscosities. To investigate CO_2 absorption properties of the ionic liquids, binary phase equilibria in CO_2 + ionic liquid systems have been investigated under high pressures up to 6 MPa at $T = (298.15, 313.15, 333.15)$ K. The solubilities of CO_2 in [eimH][Tf_2N] and [emim][Tf_2N] show typical pressure dependencies in both mole fraction and molarity scales as physical absorbents. The mole fraction of CO_2 in [eimH][Tf_2N] is slightly smaller than that in [emim][Tf_2N] under the conditions investigated, while the molarity of CO_2 in [eimH][Tf_2N] is comparable to that in [emim][Tf_2N]. The molar volumes in ionic liquid phase almost linearly decrease with the mole fraction of CO_2 in the present systems. The partial molar volume of CO_2 in [eimH][Tf_2N] at infinite dilution is almost same as that in [emim][Tf_2N].

1. Introduction

Room temperature ionic liquids (ILs) are salts, which commonly consist of a large asymmetric cation and organic or inorganic anion. Their physical and chemical properties can be controlled by the chemical modifications of the cation and anion. ILs generally have the melting points at or below ambient temperature, extremely low vapor pressures, non-flammability, high thermal and chemical stability as liquids over an extended temperature range, wide electrochemical window, high solubility of certain specific gases, and so on. Because of these favorable characteristics, ILs have attracted considerable attention, for example, as solvents, catalysts, electrolytes, lubricants, and absorbents. On the other hand, ILs have some unfavorable issues for industrial applications, one of them is high production cost. Protic ILs (PILs), a subclass of ILs, have an advantage over aprotic ILs (AILs) in the cost of manufacturing, because PILs are easily synthesized by neutralization of an acid with a base. PILs have proton-donor and acceptor sites in the cation and anion, which can form an extended intermolecular network [1–3]. As indicated in the recent spectroscopic study [4], the cation and anion in PILs interact more strongly than in AILs.

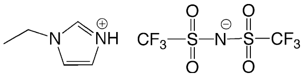
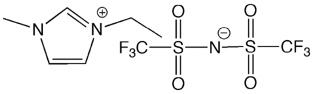
Here, in order to investigate the difference of the physicochemical properties between the protic and aprotic ILs in terms of intermolecular interactions, we have focused on a PIL, ethylimidazolium bis(trifluoromethanesulfonyl)amide ([eimH][Tf_2N]) and the analogous AIL, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([emim][Tf_2N]), of which the latter is one of the most widely used AILs. Their chemical structures are presented in Table 1. The difference in molecular structure between [eimH][Tf_2N] and [emim][Tf_2N] is the presence or absence of the methyl group on the cation. Therefore, the comparisons in the physicochemical properties primarily provide information about the protic or aprotic natures in ILs. In the present

---

* Corresponding author. Tel.: +81 22 237 5257; fax: +81 22 232 7002.
E-mail addresses: makino.t@aist.go.jp (T. Makino), m-kanakubo@aist.go.jp (M. Kanakubo).

0378-3812/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.fluid.2013.10.031

Table 1
Chemicals used in the present study.

Chemical	Source	Purity (mol%)	Analysis method
 $[eimH][Tf_2N]$[a]	Synthesized	>99	NMR and elemental analysis[e]
 $[emim][Tf_2N]$[b]	Synthesized	>99	NMR
N-Ethylimidazole	Aldrich	99	Not available
Bis(trifluoromethanesulfonyl)amide	Kanto Kagaku Co., Ltd.	>99	Not available
Methanol	Wako Pure Chemical Co.	>99.8	Gas chromatography
[emim][Br][c]	Kanto Kagaku Co., Ltd.	99	Not available
$Li[Tf_2N]$[d]	Kanto Kagaku Co., Ltd.	99	Not available
CO_2	Iwatani Industrial Gases Co.	99.99	Gas chromatography

[a] Ethylimidazolium bis(trifluoromethanesulfonyl)amide.
[b] 1-Ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide.
[c] 1-Ethyl-3-methylimidazolium bromide.
[d] Lithium bis(trifluoromethanesulfonyl)amide.
[e] Calcd: C, 22.28; H, 2.40; N, 11.14. Found: C, 22.54; H, 2.42; N, 10.93.

study, the densities, viscosities, and electrical conductivities of $[eimH][Tf_2N]$ and $[emim][Tf_2N]$ have been measured over the temperature range $T = (273.15–363.15)$ K at atmospheric pressure, and the CO_2 solubilities have been determined under high pressures up to 6 MPa at $T = (298.15, 313.15, 333.15)$ K. These properties of $[eimH][Tf_2N]$ were compared with those of $[emim][Tf_2N]$ to discuss the effect of intermolecular interactions.

2. Experimental

2.1. Materials

Chemicals used in the present study are summarized in Table 1. $[eimH][Tf_2N]$ was synthesized by neutralization of *N*-ethylimidazole (eim, purity: >99 mol%) and bis(trifluoromethanelsulfonyl)amine (HTf_2N, purity: >99 mol%). eim was slowly added to a methanol (purity: >99.5 mol%) solution of HTf_2N with stirring in an ice bath. The mixture was stirred at room temperature for 12 h, and the IL phase was separated and washed with deionized water three times. Methanol and water were removed from the IL mixture by evacuation at 313 K for a week, and then yellowish colored $[eimH][Tf_2N]$ was obtained. $[emim][Tf_2N]$ was prepared from 1-ethyl-3-methylimidazolium bromide ([emim][Br]) by anion exchange from $[Br]^-$ to $[Tf_2N]^-$. A mixture of aqueous solutions of [emim][Br] and lithium bis(trifluoromethanesulfonyl)amide ($Li[Tf_2N]$) was stirred for 12 h at room temperature, and then the organic phase was separated and washed with deionized water. The halogen content of aqueous solution in contact with $[emim][Tf_2N]$ was less than the detection limit of $AgNO_3$ testing. The purities were checked with NMR (Varian 300 NMR spectrometer, $[eimH][Tf_2N]$ and $[emim][Tf_2N]$) and elemental analysis ($[eimH][Tf_2N]$), and identified as >99 mol%. Any excess water in the sample was further removed by evacuation at 313 ($[eimH][Tf_2N]$) or 343 K ($[emim][Tf_2N]$) for ~100 ($[eimH][Tf_2N]$) or ~30 h ($[emim][Tf_2N]$) just prior to measurements. Dried ILs were transferred to a closed cell or other instruments by using an air-tight syringe under dry nitrogen or argon. The Karl Fischer titration (KEM, MKC-510) revealed that the water contents of $[eimH][Tf_2N]$ and $[emim][Tf_2N]$ were 112 and 30×10^{-6} mass fractions, respectively.

2.2. Measurement of density, viscosity, and electrical conductivity

The instruments and experimental equipments were the same as previously described elsewhere [5,6]. The densities were measured using a vibrating tube densimeter (Anton Paar, DMA 5000M). The built-in viscosity correction for this instrument was employed as previously confirmed by the references with known viscosities [7–9]. The instrumental constants were calibrated using dry air and distilled water, which was purified by a Millipore Simpli Lab Purification Pack. The viscosities were determined with a rotating-cylinder viscometer (Anton Paar, Stabinger SVM 3000). The reliability and validity of the viscosities were confirmed by measuring the reference samples supplied by Cannon Instrument Company as described in the previous studies [5,6]. The impedance measurement was performed with an impedance analyzer (Bio Logic, SP-150). The solution resistance (R_{sol}) was obtained from the Nyquist plot by fitting the measured impedances to the feasible electric circuit. A syringe-type cell with a pair of platinum electrodes was employed. The cell constant was $35.4\ \mathrm{m^{-1}}$ at 298.15 K and the correction for thermal expansion was made at different temperatures [5,6]. The sample temperature was kept within ±0.01 K at most in all the measurements. The instrumental accuracy for the densities is less than $\pm 0.05\ \mathrm{kg\,m^{-3}}$, whereas the expanded uncertainty for the densities is ±0.1% because of the sample impurities. The expanded uncertainties for the viscosities and electrical conductivities are less than ±2%.

2.3. Measurement of volume expansion

The experimental apparatus and procedures are the same as reported in our previous work [10]. IL was introduced in the sapphire tube cell; then, the cell was attached to the experimental apparatus. The apparatus was first evacuated and purged by CO_2 several times. The IL was pressurized up to a certain pressure with CO_2. The IL and gas phases were mixed with a magnetic bar, which was moved vertically from outside of the cell. When the pressure change was smaller than $0.0001\ \mathrm{MPa\,h^{-1}}$, we assumed that the two-phase (CO_2 + IL phases) equilibrium was established. The height of the IL phase was measured visually using the cathetometer to obtain the volume of liquid phase. The calibration curve between the height and volume had preliminarily been made at each temperature. The volume expansion $\Delta V^L\left(T, p_{CO_2}\right)$ at a certain condition was determined as

$$\Delta V^L(T, p_{CO_2}) = \frac{V^L(T, p_{CO_2}) - V^L(T, p^0)}{V^L(T, p^0)} \qquad (1)$$

where $\Delta V^L\left(T, p_{CO_2}\right)$ stands for the volume of IL phase at a temperature T and pressure p. $V^L(T,p_0)$ is the volume of IL phase at normal