26th EUCHEM Conference on Molten Salts and Ionic Liquids

Vienna, July 3-8, 2016

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Institute of Applied Synthetic Chemistry
TU Wien

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July 3 - 8, 2016 Vienna / Austria

DENSITY STUDIES ON ION-ION AND ION-SOLVENT INTERACTIONS OF AQUEOUS SOLUTIONS OF IMIDAZOLIUM CHLORIDE IONIC LIQUIDS [MIm][Cl] AND [BMIm][Cl] AT DIFFERENT TEMPERATURES

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STSM APPLICATION:

- Who: Dr. Renato Tomaš, University of Split (MC member from Croatia, WG2 - Chemical and Physical Properties of ILs; STSM leader; cooperation with M. Bešter-Rogač and A. Tot)
- Where: Chair of Physical Chemistry, Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia, host-professor: Prof. Dr. Marija Bešter-Rogač
- When: from March, 1st to March, 31th 2016

- About University of Split:
- was established in 1974,
- include eleven faculties, one academy of arts, and four university department
- there are about 20000 students enrolled in the University's undergraduate, graduate and postgraduate programs,
- second largest in Croatia; the first is University of Zagreb

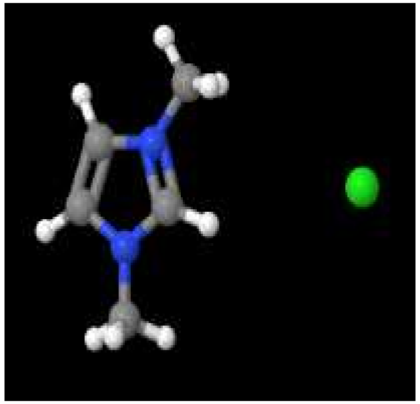
FCT-University of Split

CITY OF SPLIT

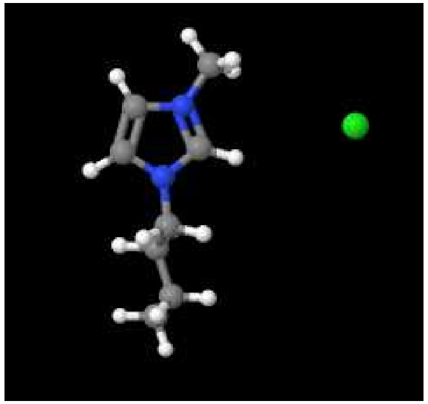
Outline

- Aqueous solutions of imidazolium chloride ionic liquids [**MIm**][**Cl**] and [**BMIm**][**Cl**], were investigated using density experiment at different temperatures.
- From density data, *d* = f (*m*, *T*), values of the apparent molar volumes and also values of the partial molar volumes for investigated ILs and for water are calculated.
- The results obtained in this study will be interpreted in the light of ion-ion and ion solvent interactions.

[**MIm**][**Cl**]



[**BMIm**][**Cl**]



Introduction

a) Volumetric, viscometric, and other thermodynamic data provide valuable information about ion-ion, ion-solvent, and solvent-solvent interactions.

b) Ionic liquids (ILs) as the salts with melting point lower than 100 °C and the remarkable properties such as low toxicity, biodegradability, low vapor pressure, high conductivity anf thermal stability.

c) Imidazolium based ILs contain large imidazolium ring with different hydrophobic alkyl chains whose H-atoms may form hydrogen bonds with water molecules

d) Ions that have strong interactions with water molecules can increase the structuring of water; they are called ***structure-makers***. Other ions are ***structure-breakers***.

e) One of the indicators of IL structure making properties can be the limiting apparent molar expansibility; this parameter we can obtained from the temperature dependence of the limiting partial molar volumes.

Experimental setup

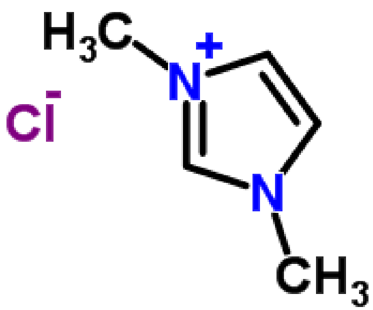
Chemicals used in this experiment:

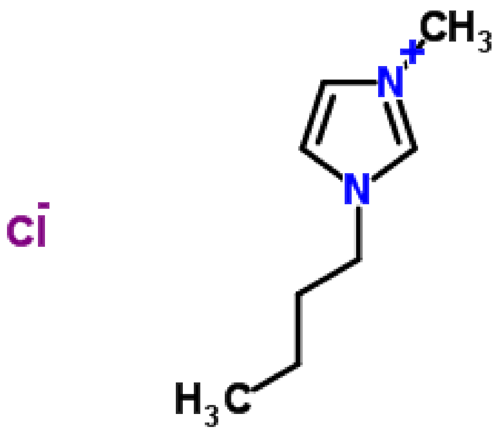
- water (ultra pure)
- ILs from IOLITEC Technologies GmbH, Germany:

*1,3-DIMETHYLIMIDAZOLIUM CHLORIDE (98%); M = 132.59 g mol^{-1}

**1-BUTYL-3-METHYLIMIDAZOLIUM CHLORIDE (99%); M = 174.67 g mol^{-1}

*





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Experimental setup

Stock-solution prepared by mass from DMImCl or MImCl and water.

Real molality ($m \equiv$ mole of ILs *per* kg of water) of stock-solution was:

m(MImCl + water) = 0.09549 mol kg^{-1}

m(BMImCl + water) = 0.10616 mol kg^{-1}

I prepared 8 working-solutions from stock-solution of ILs:

($\sim$0.005 to $\sim$0.075 mol kg^{-1}).

Density of investigated solutions at all working temperatures were determined using **Anton Paar density meter** (DMA 5000) with a reproducibility $\sim 5 \cdot 10^{-6}$ g cm^{-3}

Experimental setup

Molarity (c / mol dm^{-3}) was obtained from the molality and density data:

$$c = \frac{1000\, d\, m}{(1000 + m\, M)}$$

Experimental densities, d

$d = f(c, T)$

~0.005 M ≤ c ≤ ~ 0.1 M
273.15 < T / K < 313.15

Results

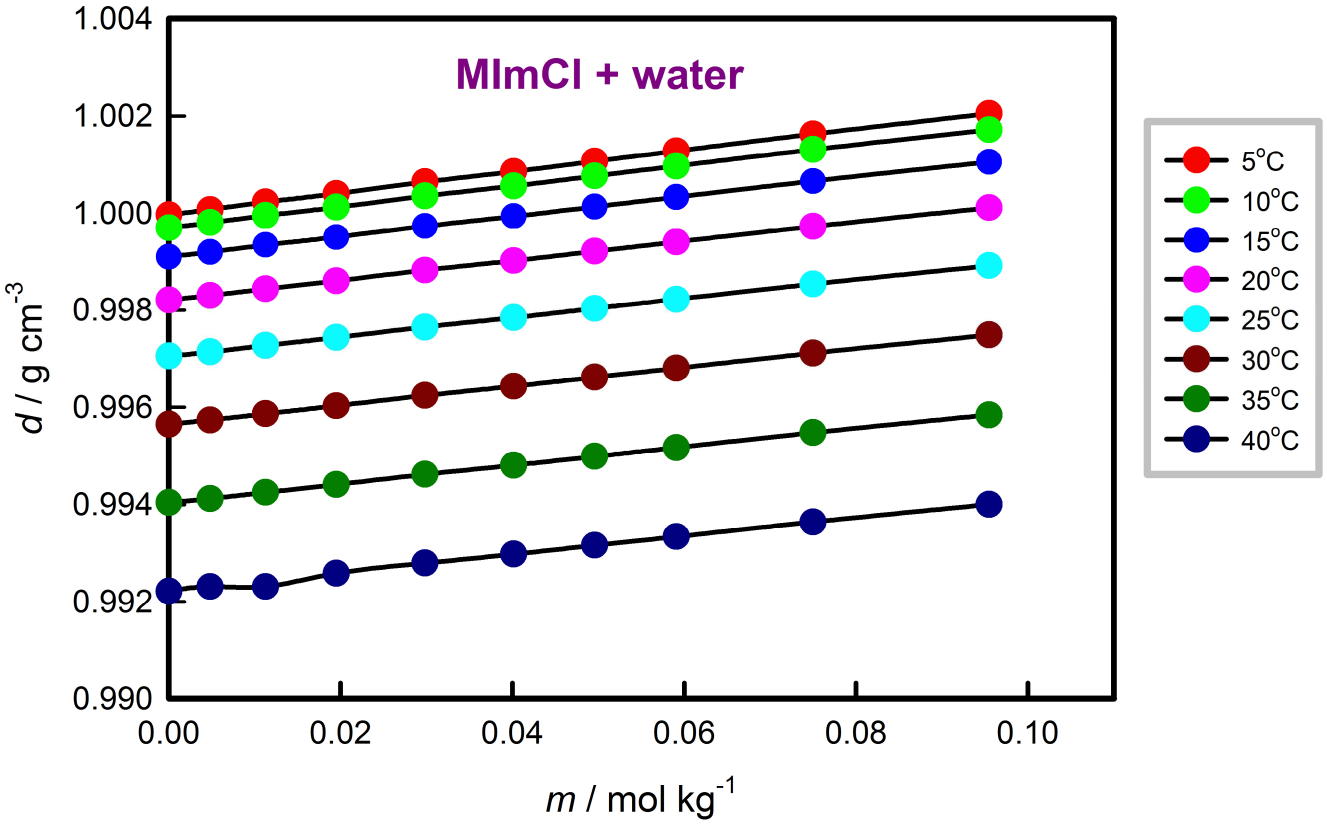

Fig. 1. Densities of (MImCl + water) binary system as a function of molality at various temperatures

Results

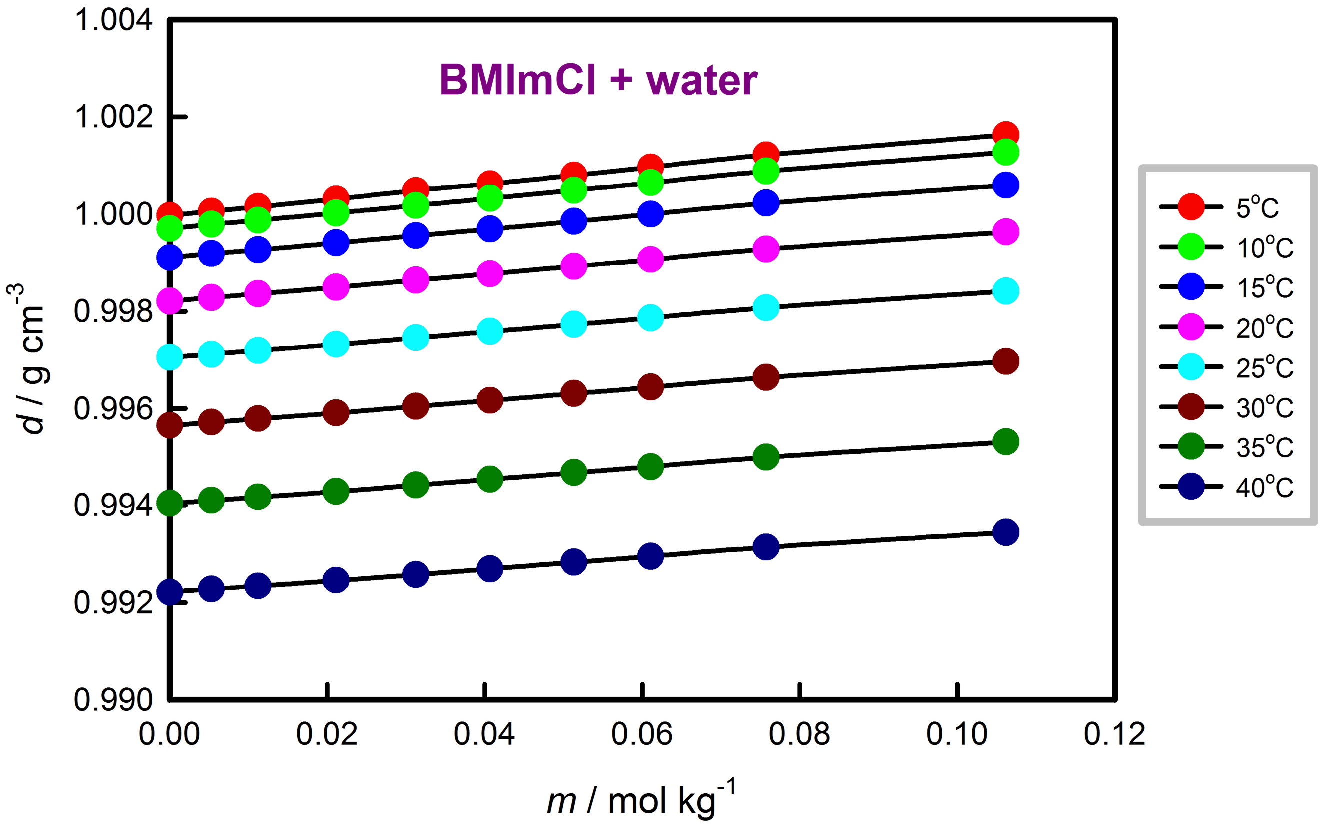

Fig. 2. Densities of (BMImCl + water) binary system as a function of molality at various temperatures

Results

From the experimental densities the **apparent molar volumes** were calculated using the next equation:

$$V_\phi = \frac{1000(d_0 - d)}{m d d_0} + \frac{M_2}{d}$$

The **partial molar volume** of water (V_1), and ILs (V_2), can be calculated using next equations (program in Excel):

$$V_1 = \frac{M_1}{d_0} - \frac{M_1 m^{3/2}}{2000}\left(\frac{\partial V_\phi}{\partial \sqrt{m}}\right)_{p,T,n_2} \qquad V_2 = \frac{\sqrt{m}}{2}\left(\frac{\partial V\phi}{\partial \sqrt{m}}\right)_{p,T,n_1} + V\phi$$

Results

The **limiting apparent molar volume** (V_ϕ^0) of investigated ILs in water at different temperatures were estimated using the Masson equation:

$$V_\phi = V_\phi^0 + S_V c^{1/2}$$

V_ϕ^0 is equal to the partial molar volume at infinite dilution ($c \longrightarrow 0$)

S_V is the experimental slope

Results

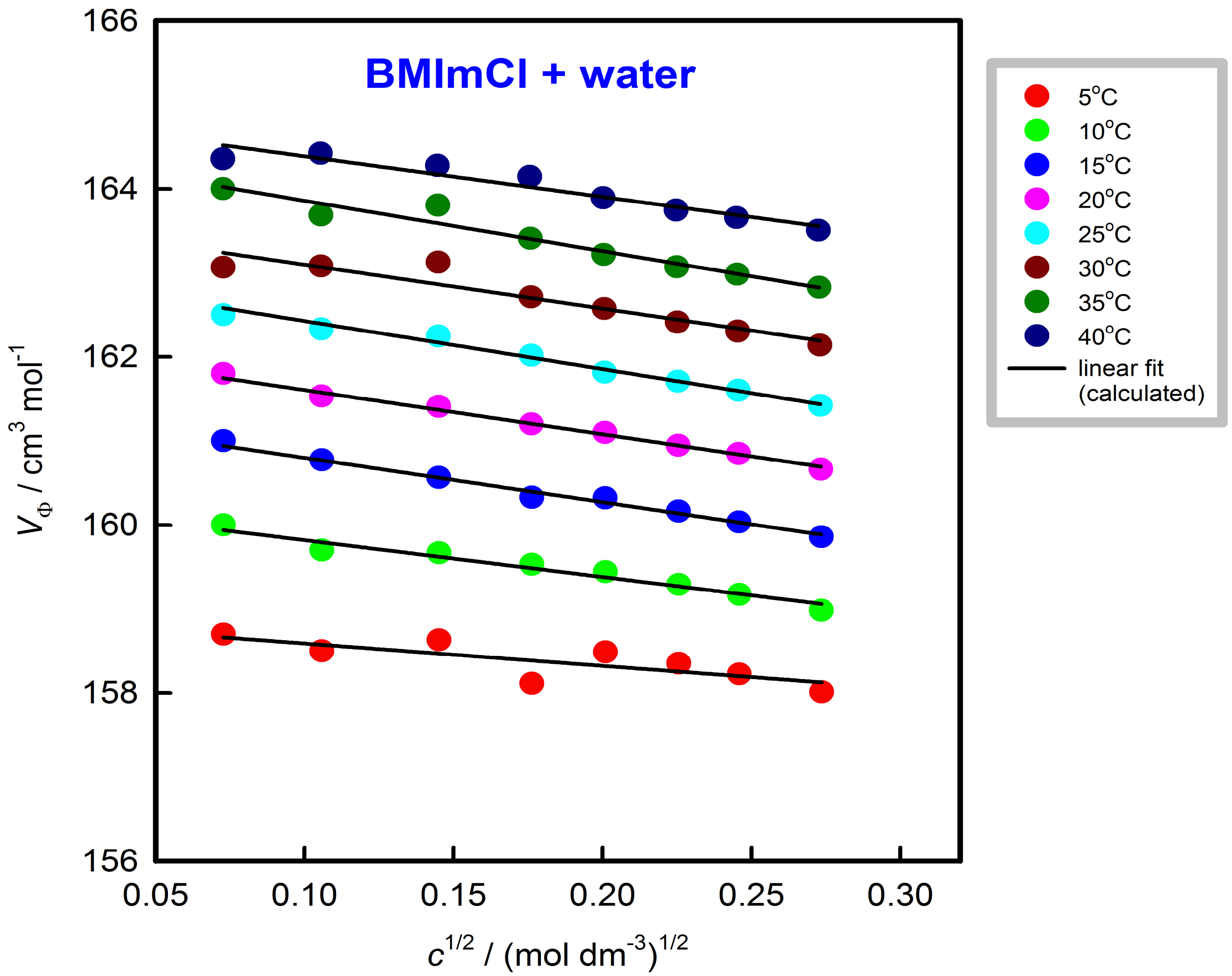

Fig. 3. Apparent molar volume vs. $c^{1/2}$ (Masson equation) for (BMImCl + water) system at different temperatures as an example

Results

Table 1. Masson's equation fitting parameters for the ([MIm][Cl] + water) and ([BMIm][Cl] + water) solutions in the temperature range from (278.15 to 313.15 K) with the deviations of their fit (σ)

T / K	([MIm][Cl] + water)		
	V_{Φ}^{0} / cm^{3}mol^{-1}	S_V / cm^3 kg$^{1/2}$ mol$^{-3/2}$	σ
278.15	109.68	2.60	0.031
283.15	110.66	1.78	0.031
288.15	111.47	1.29	0.030
293.15	112.26	0.43	0.010
298.15	112.98	0.23	0.030
303.15	113.27	0.56	0.015
308.15	113.57	1.08	0.021
313.15	114.05	0.79	0.032
	([BMIm][Cl] + water)		
278.15	158.86	–2.67	0.030
283.15	160.26	–4.38	0.005
288.15	161.32	–5.25	0.002
293.15	162.13	–5.27	0.002
298.15	163.00	–5.72	0.003
303.15	163.62	–5.24	0.017
308.15	164.45	–5.99	0.013
313.15	164.86	–4.79	0.009

COST is supported by the
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Horizon 2020

Results

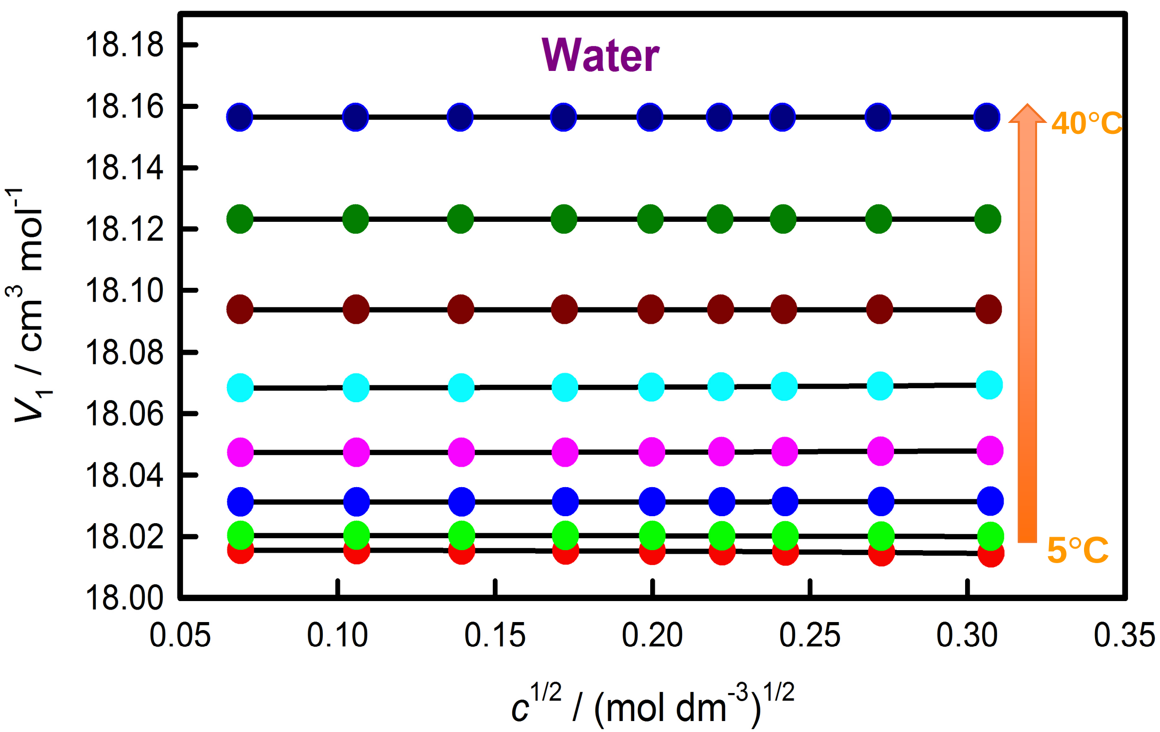

Fig. 4. Partial molar volume of water in (MImCl + water) binary system at different temperatures

Results

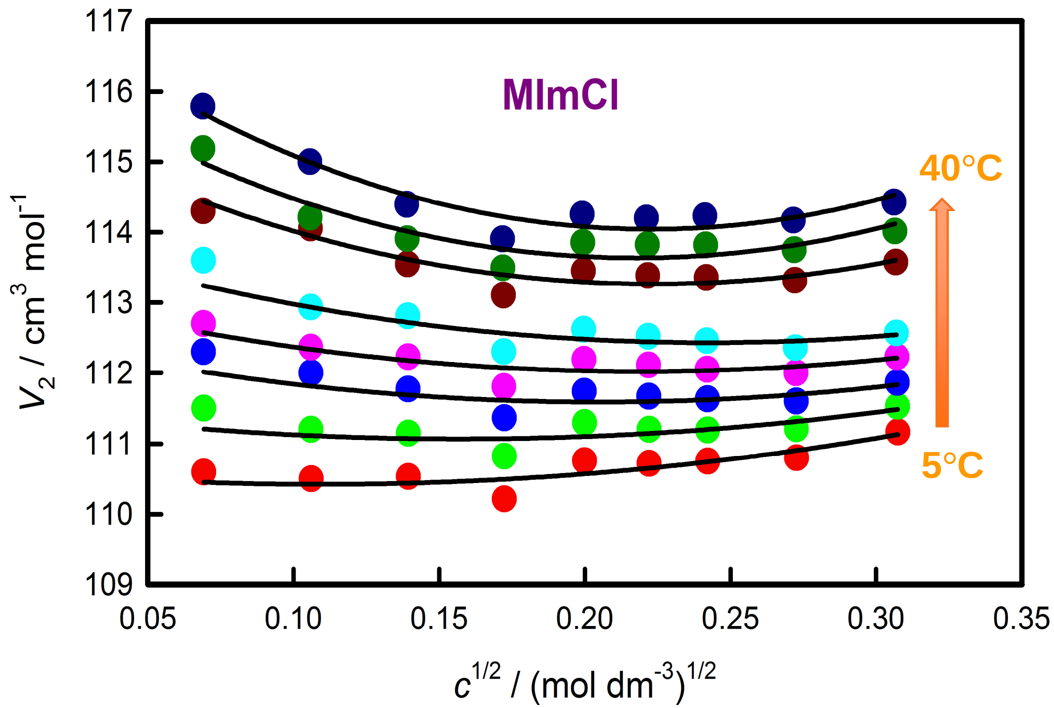

Fig. 5. Partial molar volume of MIMCl in (MImCl + water) binary system at different temperatures

Results

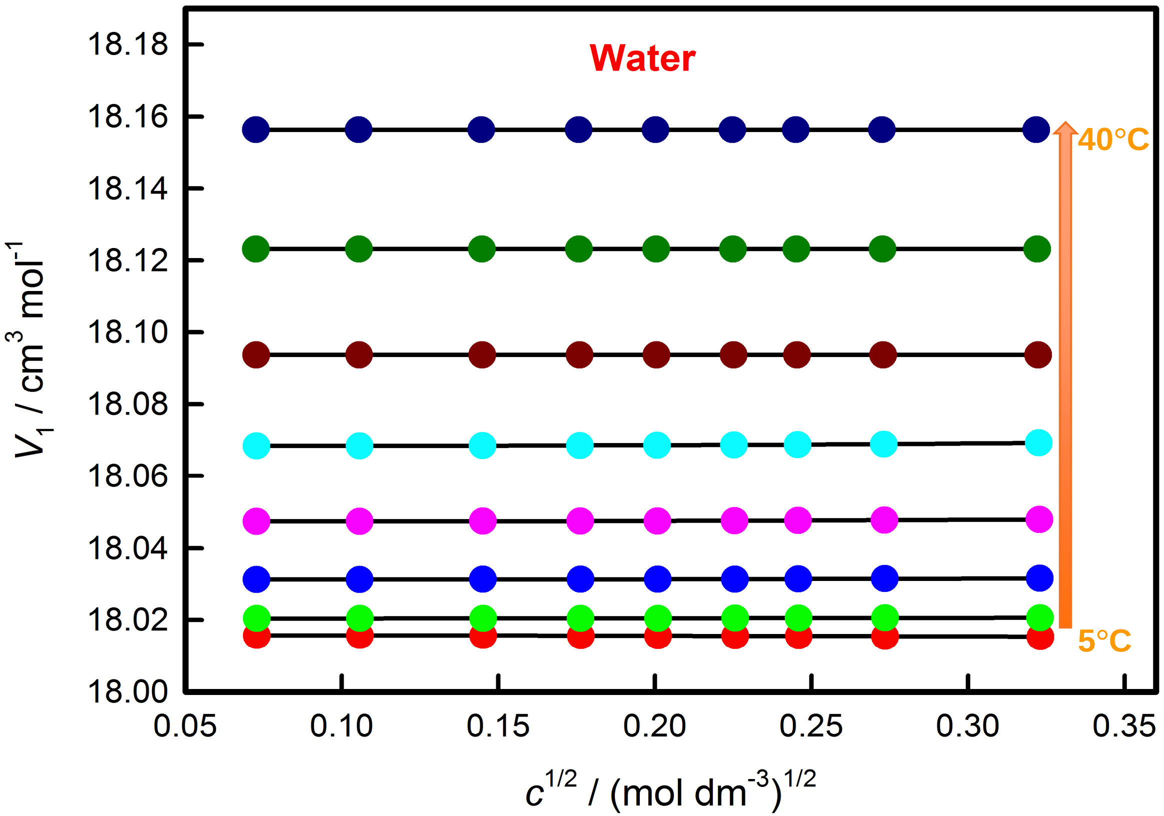

Fig. 6. Partial molar volume of water in (BMImCl + water) binary system at different temperatures

Results

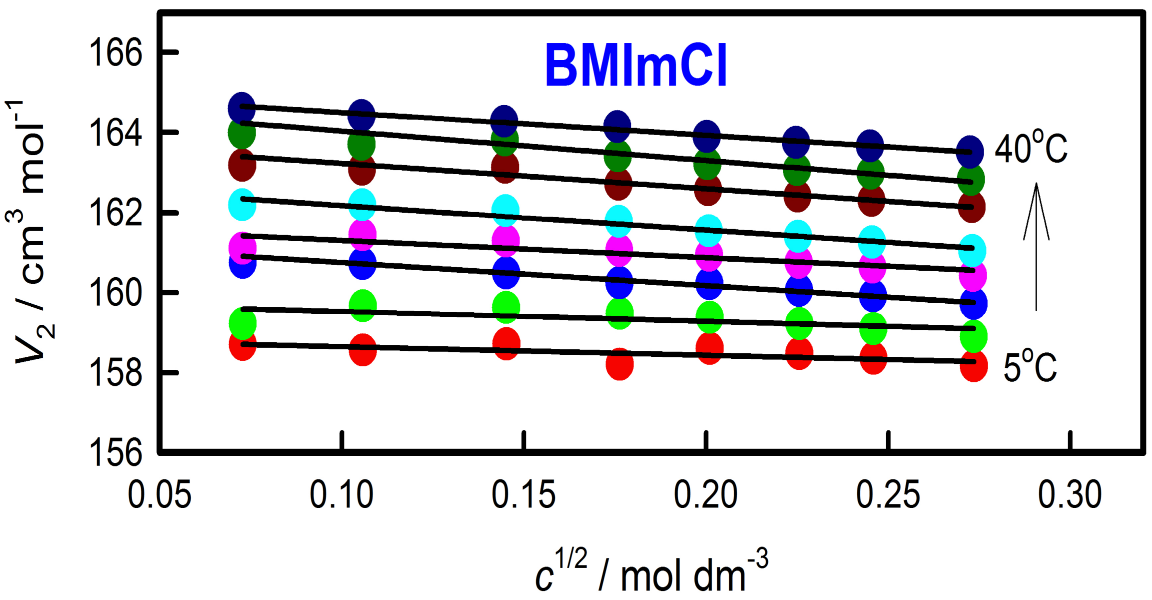

Fig. 7. Partial molar volume of BMImCl in (BMImCl + water) binary system at different temperatures

Results

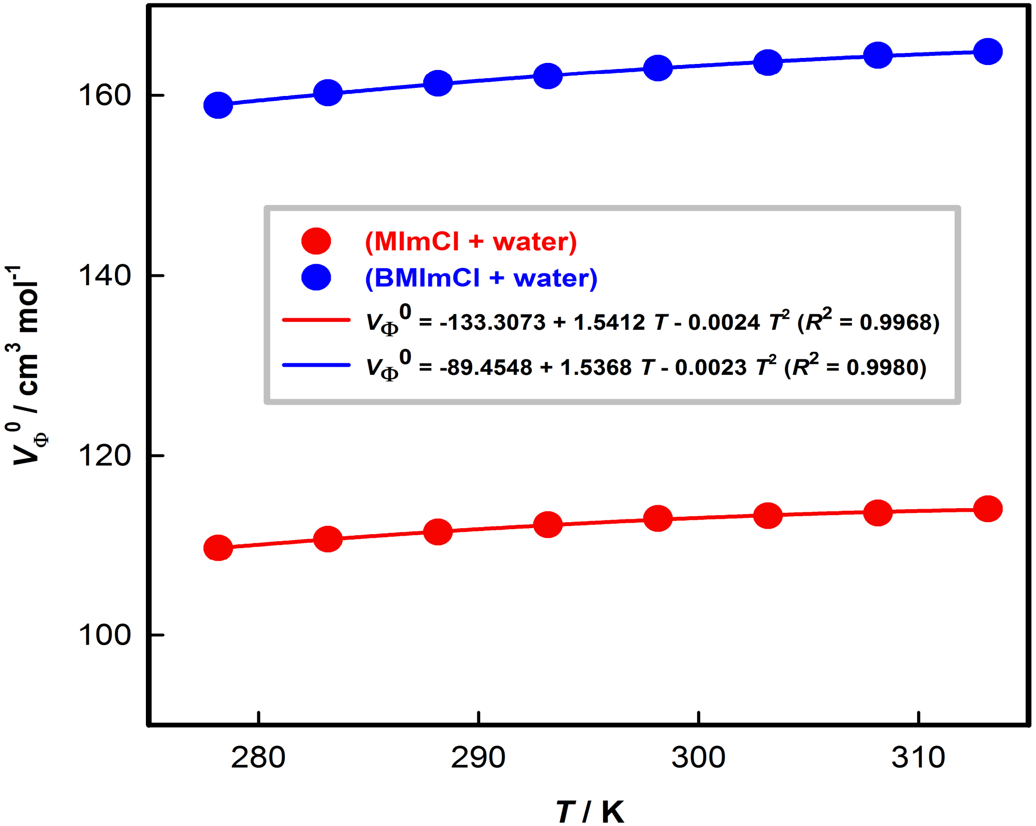

Fig. 8. Temperature dependence of the apparent molar volumes at infinite dilution

Results

From temperature dependencies for $V_{\Phi}{}^{0}$, we were obtained the **limiting apparent molar expansibility, $E_{\Phi}{}^{0}$**, using the following equation:

$$E_{\phi}^{0} = \left(\frac{\partial V_{\phi}^{0}}{\partial T} \right)_{p} = a_1 + 2a_2 T$$

Table 2. Limiting apparent molar expansibilities at different temperature

	MImCl + water							
***T* / K**	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15
$E_{\Phi}{}^{0}$ / cm^3 mol^{-1} K^{-1}	0.206	0.182	0.158	0.134	0.110	0.086	0.062	0.038
	BMImCl + water							
***T* / K**	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15
$E_{\Phi}{}^{0}$ / cm^3 mol^{-1} K^{-1}	0.257	0.234	0.211	0.188	0.165	0.142	0.119	0.096

$$\left(\frac{\partial E_{\phi}^{0}}{\partial T} \right)_{p} = \left(\frac{\partial^2 V_{\phi}^{0}}{\partial T^2} \right)_{p} = 2a_2$$

Heppler's coefficient → for both systems are negative

Conclusions

A. For investigated systems density decreases with increase of the temperature and increase of ILs molality.
B. Partial molar volume for BMImCl decrease with increase concentration at all temperatures.
C. Partial molar volume for MImCl up to about 25°C increase with increase concentration; over the 25°C we have a reverse trend.
D. Partial molar volume for water in both systems do not show significant changes.
E. V_{Φ}^{0} (BMImCl) > V_{Φ}^{0} (MImCl) and increase with increase temperature: this indicates the presence of strong solute-solvent interaction;
S_{V} (BMImCl) > S_{V} (MImCl): strong solute-solute interaction for BMImCl
F. Values for E_{Φ}^{0} are positive in the whole temperature range and indicates structure making properties of studied system (see also B. and C.).