VOLUMETRIC PROPERTIES OF SOLUTIONS OF 1-METHYLIMIDAZOLIUM ACETATE IN *N*,*N*-DIMETHYLACETAMIDE, *N*,*N*-DIMETHYLFORMAMIDE, AND DIMETHYL SULFOXIDE

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INTRODUCTION:

Ionic liquids (ILs) are molten salts with melting points lower than 100°C. They usually consist of pair of organic cation and anorganic anion. ILs exhibit unique properties such as nonvolatility, high thermal stability, and high ionic conductivity [1,2].

The aim of this work is to present measurements of density for 1-methylimidazolium acetate, [Mim][Ac] IL solutions in *N*,*N*-dimethylacetamide (DMA), *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) at different molalities and different temperatures. (from 278.15 to 313.15 K).

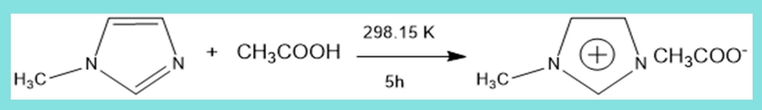
From experimental values of densities as function on molality and temperature in 3 different solvents, the values of apparent molar volume, standard partial molar volumes, apparent molar volume at infinite dilution, Masson's interaction coefficient, limiting apparent molar expansibilities, and Heppler's coefficient was calculated.

EXPERIMENTAL:

Solutions of IL in DMA, DMF and DMSO were prepared by mass. Density measurements were carried out using fully automated DMA 4500M Anton Paar apparatus with a measurement accuracy of ±0.00005 g cm-3. The thermal control and stability over the entire investigated temperature range is estimated to be >0.01 K. Before each series of measurements, calibration of the instrument was carried out at the atmospheric pressure (p = 101.3 kPa) using triple-distilled water in the investigated temperature range.

SYNTHESIS OF [Mim][Ac] :

[Mim][Ac] was obtained from 1-methylimidazole and acetic acid following the literture method [3]:



Scheme 1. Molecular structure and synthesis of [Mim][Ac]

[Mim][Ac] was dried under vacuum at 60 oC for at least 48 h before use; the water content was determined by Karl Fisher titration; the structure of [Mim][Ac] was identified by FTIR spectroscopy.

CALCULATIONS:

Molality to molarity:

$$c = \frac{1000 \cdot m \cdot d}{(1000 + m \cdot M_{IL})}$$

Apparent molar volume:

$$V_\Phi = \frac{1000(d_0 - d)}{m d d_0} + \frac{M_{IL}}{d}$$

Masson's equation:

$$V_\Phi = V_\Phi^0 + S_V \cdot \sqrt{c}$$

Partial molar volume of solvent, 0:

$$\overline{V_1} = \frac{M_0}{d_0} - \frac{M_0 \cdot m^{3/2}}{2000}\left(\frac{\partial V_\Phi}{\partial \sqrt{m}}\right)_{T,p,n}$$

Partial molar volume of solute, IL:

$$\overline{V_2} = \frac{\sqrt{m}}{2}\left(\frac{\partial V_\Phi}{\partial \sqrt{m}}\right)_{T,p,n_0} + V_\Phi$$

Temperature dependence (second-order polynomial function):

$$V_\Phi^0 = a + b \cdot T + c \cdot T^2$$

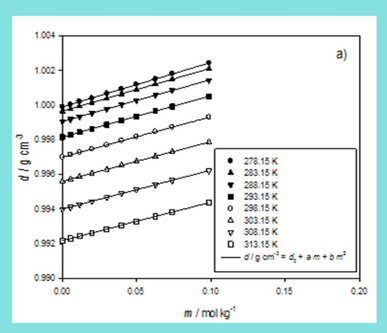
Limiting molar expansibility:

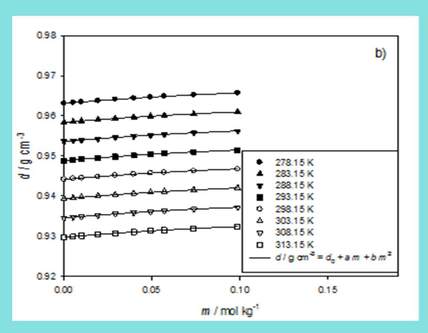
$$E_\Phi^0 = \left(\frac{\partial V_\Phi^0}{\partial T}\right)_p = b + 2 \cdot c \cdot T$$

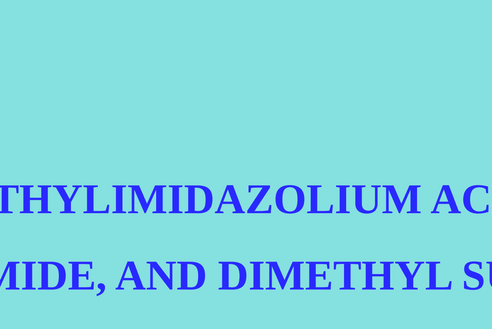
Heppler's coefficient:

$$\left(\frac{\partial E_\Phi^0}{\partial T}\right)_p = \left(\frac{\partial^2 V_\Phi^0}{\partial T^2}\right)_p = 2 \cdot c$$

RESULTS:







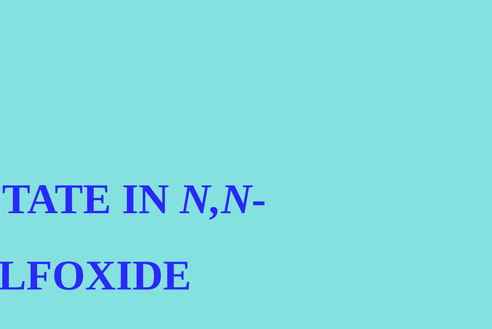
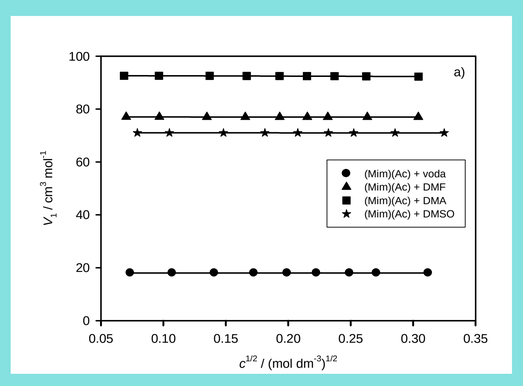


Figure 1. Experimental densities as functions on molality and temperature for [Mim][Ac] ionic liquid in a) water medium, b) DMF, c) DMA and d) DMSO



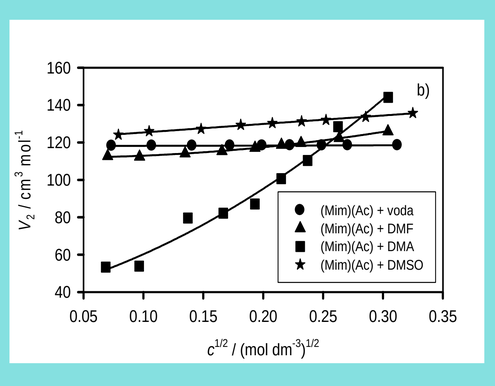


Figure 2. Concentration dependence a) partial molar volume of solvents V_1, and b) partial molar volume of [Mim][Ac], V_2, in investigated solvents at T = 293.15 K

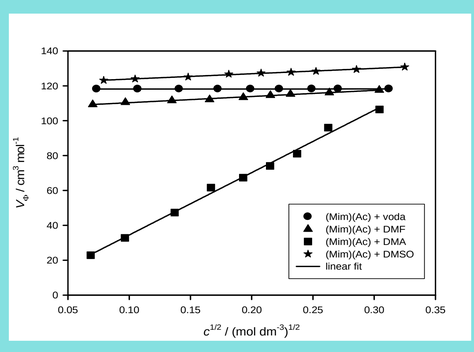


Figure 3. Masson's graph for [Mim][Ac] in different solvents at T = 293.15 K

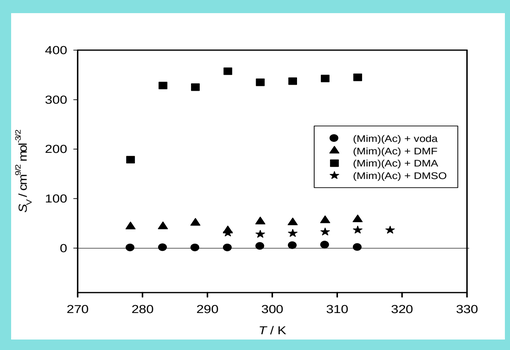


Figure 4. Temperature dependence of Masson's interaction coefficient for investigated systems

Table 1. Parameters of Masson's equation for investigated systems

T / K	V_Φ^0 / cm³ mol⁻¹	S_V / cm$^{9/2}$ mol$^{-3/2}$	R^2
	[Mim][Ac] + DMF		
278.15	104.11 ± 0.22	43.3 ± 1.3	0.9931
283.15	104.87 ± 0.21	43.5 ± 1.1	0.9955
288.15	103.21 ± 0.19	50.6 ± 1.0	0.9974
293.15	106.80 ± 0.24	35.3 ± 1.1	0.9921
298.15	103.72 ± 0.30	53.4 ± 1.5	0.9945
303.15	104.52 ± 0.33	51.6 ± 1.6	0.9928
308.15	103.77 ± 0.30	55.8 ± 1.5	0.9949
313.15	103.70 ± 0.34	57.6 ± 1.7	0.9939
	[Mim][Ac] + DMA		
278.15	46.77 ± 0.76	178.7 ± 3.8	0.9967
283.15	1.46 ± 0.74	328.5 ± 3.7	0.9991
288.15	1.83 ± 0.65	325.2 ± 8.2	0.9949
293.15	1.27 ± 0.87	357.5 ± 9.8	0.9947
298.15	2.09 ± 0.76	335.1 ± 8.8	0.9952
303.15	2.04 ± 0.79	337.3 ± 9.0	0.9950
308.15	0.79 ± 0.13	342.7 ± 6.7	0.9975
313.15	0.67 ± 0.13	345.0 ± 6.9	0.9972
	[Mim][Ac] + DMSO		
293.15	120.79 ± 0.18	30.6 ± 0.8	0.9944
298.15	121.46 ± 0.13	28.1 ± 0.6	0.9968
303.15	121.30 ± 0.18	29.9 ± 0.9	0.9942
308.15	120.24 ± 0.19	32.8 ± 0.8	0.9950
313.15	119.85 ± 0.22	36.5 ± 1.0	0.9941
318.15	120.02 ± 0.23	36.3 ± 1.1	0.9935

Table 2. Limiting apparent molar expansibilities and Heppler's coefficients for investigated systems

	E_Φ^0 / cm³ mol⁻¹ K⁻¹ za [Mim][Ac] + water								
T / K	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15	$\left(\frac{\partial E_\Phi^0}{\partial T}\right)_p$
	0.085	0.087	0.089	0.092	0.093	0.095	0.097	0.099	0.0004
	cm³ mol⁻¹ K⁻¹ za [Mim][Ac] + DMF								
T / K	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15	
	0.070	0.040	0.010	-0.020	-0.050	-0.079	-0.109	-0.140	-0.0060
	cm³ mol⁻¹ K⁻¹ za [Mim][Ac] + DMA								
T / K	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15	
	0.140	0.104	0.007	0.003	-0.004	-0.040	-0.076	-0.112	-0.0072
	cm³ mol⁻¹ K⁻¹ za [Mim][Ac] + DMSO								
T / K	293.15	298.15	303.15	308.15	313.15	318.15	-	-	
	0.031	0.007	-0.017	-0.041	-0.065	-0.089	-	-	-0.0048

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[3] W. Qian, Y. Xu, H. Zhu, C. Yu, *J. Chem. Thermodynamics* 2012, *49*, 87-94.