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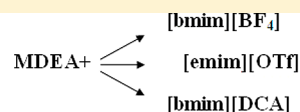
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Density and Viscosity of Aqueous Mixtures of N-Methyldiethanolamines (MDEA) and Ionic Liquids

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ABSTRACT: The density and viscosity of aqueous mixtures of N-methyldiethanolamine (MDEA) and the ionic liquids (ILs) 1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF$_4$]), 1-butyl-3-methylimidazolium dicyanamide ([bmim][DCA]), and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][OTf]) were determined. The measurements were carried out at 1 atm pressure and temperatures ranging from (303.15 to 363.15) K. The concentration of MDEA was fixed at (2.0 and 4.0) M, whereas the IL concentration was varied from (0.5 to 2.0) M. Both densities and viscosities were increased with increasing IL concentration.

MDEA+ → [bmim][BF$_4$]
        → [emim][OTf]
        → [bmim][DCA]

Density and Viscosity

$\rho = \beta \, (T/K - 273.15) + \alpha$ $\qquad$ $ln\eta = Ea/RT + ln\eta_\infty$

Correlation equations of density and viscosity for pure substances and for MDEA and ILs aqueous mixtures as a function of temperature and concentration of MDEA and ILs were also determined. The linear correlation for density had an excellent accuracy with less than 0.98 % deviation for all aqueous mixtures of MDEA and ILs. Meanwhile, the extended Arrhenius equation for viscosity achieved acceptable precision with less than 30 % of deviation from experimental data except for 2.0 M MDEA and 1.5 M [bmim][DCA] mixtures.

■ INTRODUCTION

The emissions of carbon dioxide (CO$_2$) from the combustion of fossil fuels cause more and more environmental problems, especially the greenhouse effect. CO$_2$, the primary greenhouse gas, is one of the main causes for the global warming, which results in a rise of the atmospheric temperature. Alkanolamine solutions using, for example, monoethanolamine (MEA), diethanolamine (DEA), N-methyldiethanolamine (MDEA), and 2-amino-2-methyl-1-propanol (AMP) as solvents are widely used to capture CO$_2$ from gas streams. However, this method has shown some disadvantages such as high energy consumption, serious equipment corrosion, and high amine loss and degradation, which pose environmental problems. Hence, alternative solvents are required, and in this regard, ionic liquids (ILs) show great potential as alternative solvents. IL performance in absorbing CO$_2$ can be severely improved through incorporating an amine function in the structure of the IL.[1]

The unique characteristics of ILs make them interesting as the next generation of solvents for industrial applications. Brennecke and Maginn[2] presented several potential applications of ILs. Gordon,[3] Holbrey and Seddon,[4] Welton,[5] and Zhao et al.[6] reported that ILs are good solvents for a wide range of both organic and inorganic materials, polar and nonpolar. ILs have negligible vapor pressures, which reduces emissions to the environment and working exposure hazards. Other advantageous properties include high electric conductivity, the ability to be recycled, high thermal stability, and nonflammability.

A number of investigations by different groups such as Blanchard et al.,[7] Anthony et al.,[8] Cadena et al.,[9] Camper et al.,[10] Scovazzo et al.,[11] and Ahmady et al.[12] have shown that CO$_2$ is remarkably soluble in conventional ILs. A wide range of literature is available on the absorption of CO$_2$ in ILs.[13,14] The most widely studied class of ILs to date is based on alkylimidazolium cation with tetrafluoroborate and hexaflourophosphate.

Despite all of these works, in industry to date, conventional amines are still preferable because of their lower price, higher CO$_2$ absorption capacity, and lower solution viscosity. The use of mixtures of alkanolamines and ILs can be considered as a possible alternative since it combines the advantages of both systems.

Generally, all tested room-temperature ILs show a very low CO$_2$ loading capacity in comparison to amine-based solvents as in Keskin et al.[15] Hence, researchers attempt to determine other alternatives which have the green properties of ILs and the high productivity of amines as well.

MDEA is one of the commercial amine solutions usable for CO$_2$ absorption, and 1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF$_4$]) is an IL which is water-soluble.[13]

According to Aki et al.,[16] the solubility of CO$_2$ in ILs with anions containing fluoroalkyl groups is high due to a fluoroalkyl group which is "CO$_2$ philic". ILs such as 1-butyl-3-methylimidazolium dicyanamide ([bmim][DCA]), 1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF$_4$]), and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][OTf]) are also reported to be potential solvents for CO$_2$ capture.[12,17]

In recent works, aqueous solutions of MDEA mixed with different types of ILs were used by Feng et al.[18] and Ahmady et al.[1] to absorb carbon dioxide.

The physical properties of ILs and their mixture with alkanolamines are very important for the design of those processes. However, although physical properties have become known lately for many ILs,[12,19−21] these properties still remain scarce for most of them in the open literature.

To the best of our knowledge, there is no any reported density and viscosity data for the aqueous mixtures of MDEA and the ILs [bmim][BF$_4$], [bmim][DCA], and [emim][OTf] in the open literature. These data are very important for the new suggested IL-based solvents for CO_2 absorption.

Thus, in this work the density and viscosity data of the aqueous mixtures of MDEA, [bmim]$^+$[BF$_4$]$^−$, [bmim][DCA], and [emim][OTf] were obtained experimentally. In addition, the density and viscosity as a function of concentration of MDEA, [bmim]$^+$[BF$_4$]$^−$, [bmim]$^+$[DCA]$^−$, and [emim]$^+$[OTf]$^−$ and temperature were correlated.

■ EXPERIMENTAL SECTION

Materials. The carbon dioxide used was from Mox-Linde with a mole fraction purity of 99.9 %. *N*-Methyldiethanolamine (MDEA, ≥ 98.5 wt %), 1-*n*-butyl-3-methylimidazolium tetra-fluoroborate ([bmim][BF$_4$], ≥ 98 wt %), and 1-butyl-3-methyl-imidazolium dicyanamide ([bmim][DCA], ≥ 98 wt %) were purchased from Merck. The 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][OTf]) ≥ 98 wt %) was purchased from Sigma Aldrich. Distilled water used as diluter solvent for all of the experiments. The aqueous MDEA + [bmim][BF$_4$], MDEA + [bmim][DCA], and MDEA + [emim]-[OTf] mixtures were prepared at various concentrations using the dilution method where the concentration of MDEA was fixed at (2.0 and 4.0) M with IL concentration was varied from (0.5 to 2.0) M.

Density Measurements. The DMA 4500 density/specific gravity meter (Anton Paar, Austria), repeatability 1·10^{-4} g·cm^{-3}, and 0.01 K, at atmospheric pressure, and a standard deviation (STD) of 1.4·10^{-6} g·cm^{-3} was used to measure the density. The measurement was carried out in the temperature range of (303.15 to 363.15) K and constant atmospheric pressure.

Viscosity Measurements. A rheometer (R/s plus) was used to measure the viscosity of the pure MDEA, pure IL, and aqueous solution of MDEA + IL. The sample was poured into a CC40 steel cylinder, and a stainless steel rod was immersed in it. Then the steel cylinder was heated by water bath until it reached 303.15 K. Meanwhile the steel rod was connected to a rotator. The duration of each experiment was 100 s, and the viscosity reading was the average of 100 readings taken in each second. The experiment was repeated three times to get the average value for each sample at each experimental temperature. The measurement was carried out at temperatures ranging from (303.15 to 363.15) K and constant atmospheric pressure.

■ RESULTS AND DISCUSSION

Density Measurements. Measurements were repeated three times to ensure reproducibility. Taking into account the sources of error such as calibration, measurement, and purity of materials, the uncertainty of density was estimated to be within ± 0.003 g·cm^{-3}. The densities of pure [bmim][BF$_4$] and [bmim]-[DCA] and the MDEA + water system were measured and compared to literature data to confirm the procedure and reproducibility of the obtained density data. Tables 1, 2, and 3 represent the density of MDEA + water system and pure [bmim][BF$_4$] and [bmim][DCA] in this work and the percentage

Table 1. Density of MDEA + Water Binary System from This Work and a Comparison with Literature

	MDEA mass fraction		density (g·cm^{-3})	
T/K	this work	Zuniga-Moreno et al.[22]	this work	Zuniga-Moreno et al.[22]
313.15	0.234	0.2	1.0041	1.0057
333.15	0.234	0.2	0.9950	0.9959
353.15	0.234	0.2	0.9840	0.9839
363.15	0.234	0.2	0.9769	0.9773
313.15	0.459	0.5	1.0110	1.0335
333.15	0.459	0.5	1.0010	1.0194
353.15	0.459	0.5	0.9899	1.0040
363.15	0.459	0.5	0.9811	0.9959

Table 2. Density of Pure [bmim][BF$_4$] from This Work and a Comparison with Literature

	density (g·cm^{-3})		
T/K	this work	Harris et al.[23]	% deviation
303.15	1.1913	1.19775	0.53
313.15	1.1823	1.19068	0.70
333.15	1.1667	1.17670	0.42
353.15	1.1549	1.16292	0.84
363.15	1.1394	1.15611	1.44

Table 3. Density of Pure [bmim][DCA] from This Work and a Comparison with Literature

	density (g·cm^{-3})		
T/K	this work	Carvalho et al.[24]	% deviation
303.15	1.0551	1.0599	0.45
313.15	1.0493	1.0537	0.41
333.15	1.0371	1.0413	0.40
353.15	1.0242	1.0290	0.46
363.15	1.0193	1.0227	0.33

deviation with the density data reported in the literature.[22−24] The percentage differences show good consistency between the generated data in this study and the data from literature.

The overall results indicate that the mixtures of MDEA + [bmim][BF$_4$], MDEA + [bmim][DCA], and MDEA + [emim]-[OTf] demonstrate temperature-dependent behavior. The densities of aqueous MDEA + [bmim][BF$_4$], MDEA + [bmim]-[DCA], and MDEA + [emim][OTf] mixtures measured in this work are shown in Tables 4, 5, and 6, respectively. It is obvious that the pure + [emim][OTf], [bmim][BF$_4$], and [bmim][DCA] exhibit the highest density followed by pure MDEA and aqueous MDEA + [emim][OTf], MDEA + [bmim][BF$_4$], and MDEA + [bmim][DCA] mixtures. Water in aqueous MDEA + [emim]-[OTf], MDEA + [bmim][BF$_4$], and MDEA + [bmim][DCA] mixtures acts as diluents and therefore lowers the density of overall mixture.[25] As shown in Tables 4, 5, and 6, the density decreases with an increasing amount of the organic solvents and MDEA at fixed temperature and decreases with increasing temperature at fixed composition. The densities measured are generally decreasing linearly with increasing temperature.[26]

Correlation of Density as a Function of Temperature, Concentration of MDEA, and Concentrations of [bmim]-[BF$_4$], [bmim][DCA], and [emim][triflate]. The density (ρ) as a function of temperature is expressed by the following equation:

$$\rho = \beta(T/K - 273.15) + \alpha(\text{g·cm}^{-3}) \tag{1}$$

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Table 4. Experimental Results of Density for Aqueous MDEA and [bmim][BF$_4$]^a

				density (g·cm^{-3})			
	sample concentration mass fraction		303.15 K	313.15 K	333.15 K	353.15 K	363.15 K
1	MDEA	0.234	1.0117	1.0041	0.9950	0.9840	0.9769
2	MDEA	0.233	1.0209	1.0157	1.0051	0.9919	0.9842
	[bmim][BF$_4$]	0.111					
3	MDEA	0.231	1.0305	1.0250	1.0140	1.0007	0.9901
	[bmim][BF$_4$]	0.219					
4	MDEA	0.229	1.0414	1.0350	1.0229	1.0067	0.9949
	[bmim][BF$_4$]	0.326					
5	MDEA	0.227	1.0489	1.0435	1.0328	1.0163	1.0020
	[bmim][BF$_4$]	0.431					
6	MDEA	0.459	1.0183	1.0110	1.0010	0.9899	0.9811
7	MDEA	0.464	1.0272	1.0223	1.0091	0.9947	0.9855
	[bmim][BF$_4$]	0.110					
8	MDEA	0.459	1.0395	1.0335	1.0220	1.0043	0.9934
	[bmim][BF$_4$]	0.217					
9	MDEA	0.454	1.0498	1.0445	1.0331	1.0166	1.0022
	[bmim][BF$_4$]	0.323					
10	pure MDEA		1.0347	1.0271	1.0130	0.9976	0.9875
11	pure [bmim][BF$_4$]		1.1913	1.1823	1.1667	1.1549	1.1394

^{a}The uncertainty for mass fraction is ± 0.002, and the uncertainty of measured density at corresponding temperature was estimated to be ± 0.003 g·cm^{-3} and ± 0.01 K, respectively.

Table 5. Experimental Results of Density for Aqueous MDEA and [bmim][DCA]^a

				density (g·cm^{-3})			
	sample concentration mass fraction		303.15 K	313.15 K	333.15 K	353.15 K	363.15 K
1	MDEA	0.235	1.0142	1.0094	0.9993	0.9852	0.9662
	[bmim][DCA]	0.101					
2	MDEA	0.239	1.0153	1.0101	0.9991	0.9861	0.9684
	[bmim][DCA]	0.202					
3	MDEA	0.234	1.0181	1.0132	1.0011	0.9881	0.9723
	[bmim][DCA]	0.302					
4	MDEA	0.233	1.0202	1.0152	1.0021	0.9891	0.9823
	[bmim][DCA]	0.402					
6	MDEA	0.466	1.0224	1.0173	1.0061	0.9921	0.9731
	[bmim][DCA]	0.100					
7	MDEA	0.465	1.0242	1.0181	1.0062	0.9934	0.9733
	[bmim][DCA]	0.200					
8	MDEA	0.469	1.0321	1.0271	1.0143	1.0001	0.9834
	[bmim][DCA]	0.298					
9	pure [bmim][DCA]		1.0551	1.0493	1.0371	1.0242	1.0193

^{a}The uncertainty for mass fraction is ± 0.002, and the uncertainty of measured density at corresponding temperature was estimated to be ± 0.003 g·cm^{-3} and ± 0.01 K, respectively.

Equation 1 was used to correlate the experimental densities, and it was found that the influence of temperature from (303.15 to 353.15) K on densities can be fitted by eq 1. The characteristic parameters α and β were determined from the y-intercept and slope of plotting a linear graph of density versus temperature at different concentrations. The α and β parameters for aqueous MDEA + [bmim][BF$_4$], MDEA + [bmim][DCA], and MDEA + [emim][OTf] mixtures can be represented by eqs 2 to 7. Meanwhile, the α and β parameters for pure MDEA, pure [bmim][BF$_4$], [bmim][DCA], and [emim][OTf] from this work and pure [bmim][BF$_4$] from literature are presented in Table 7. The α and β parameters for pure [bmim][BF$_4$] of this work slightly deviate from literature. The temperature range used for both correlations is different where this will cause the deviation of α and β parameters.

The equations for the aqueous mixture of MDEA + [bmim][BF$_4$] can be written as follows:

$$\beta \cdot 10^{-4} = (-0.4667[MDEA] + 0.2666)([bmim][BF_4])^3$$
$$+ (1.1143[MDEA] + 0.1428)([bmim][BF_4])^2$$
$$+ (-0.8119[MDEA] - 0.4524)([bmim][BF_4])$$
$$+ 0.6471[MDEA] + 5.0114 \qquad (2)$$

$$\alpha = (-0.01411[MDEA] + 0.0191)([bmim][BF_4])^3$$
$$+ (0.0109[MDEA] + 0.0542)([bmim][BF_4])^2$$
$$+ (-0.0271[MDEA] + 0.0405)([bmim][BF_4])$$
$$+ 0.0109[MDEA] + 1.0168 \qquad (3)$$

Table 6. Experimental Results of Density for Aqueous MDEA and [emim][OTf][a]

	sample concentration mass fraction		density (g·cm^{-3})				
			303.15 K	313.15 K	333.15 K	353.15 K	363.15 K
1	MDEA	0.231	1.0307	1.0247	1.0145	1.0018	0.9935
	[emim][OTf]	0.139					
2	MDEA	0.226	1.0544	1.0489	1.0379	1.0243	1.0161
	[emim][OTf]	0.273					
3	MDEA	0.221	1.0797	1.0746	1.0617	1.0410	1.0292
	[emim][OTf]	0.401					
4	MDEA	0.216	1.1048	1.0981	1.0841	1.0693	1.0595
	[emim][OTf]	0.522					
6	MDEA	0.457	1.0426	1.0371	1.0254	1.0118	1.0040
	[emim][OTf]	0.138					
7	MDEA	0.447	1.0656	1.0584	1.0466	1.0336	1.0244
	[emim][OTf]	0.270					
8	MDEA	0.438	1.0893	1.0823	1.0689	1.0548	1.0457
	[emim][OTf]	0.397					
9	pure [emim][OTf]		1.3818	1.3717	1.3509	1.3387	1.3260

[a]The uncertainty for mass fraction is ± 0.002, and the uncertainty of measured density at the corresponding temperature was estimated to be ± 0.003 g·cm^{-3} and ± 0.01 K, respectively.

Table 7. Summaries of α and β Parameters for Pure MDEA and ILs

pure substance	characteristic parameter	
	$-\beta/(10^4 \text{ g·cm}^{-3}\text{·°C})$	$\alpha/(\text{g·cm}^{-3})$
MDEA	7.6	1.057
[bmim][DCA]	6.1	1.073
[emim][OTf]	8.8	1.408
[bmim][BF$_4$], this work	7.3	1.212
[bmim][BF$_4$], Sanchez et al.[32]	7.1	1.414

The equations for the aqueous mixture of MDEA + [bmim]-[DCA] can be written as follows:

$$-\beta \cdot 10^4 = (-0.3767[\text{MDEA}] + 0.3733)([\text{bmim}][\text{DCA}])^3$$
$$+ (0.9829[\text{MDEA}] - 0.2714)([\text{bmim}][\text{DCA}])^2$$
$$+ (-0.7066[\text{MDEA}] - 0.4605)([\text{bmim}][\text{DCA}])$$
$$+ (0.3289[\text{MDEA}] + 5.624) \qquad (4)$$

$$\alpha = (-0.0051[\text{MDEA}] + 0.0038)([\text{bmim}][\text{DCA}])^3$$
$$+ (0.0195[\text{MDEA}] - 0.0134)([\text{bmim}][\text{DCA}])^2$$
$$+ (-0.0196[\text{MDEA}] + 0.0137)([\text{bmim}][\text{DCA}])$$
$$+ (0.0104[\text{MDEA}] + 1.0179) \qquad (5)$$

The equations for the aqueous mixture of MDEA + [emim]-[OTf] can be written as follows:

$$-\beta \cdot 10^4 = (1.2[\text{MDEA}] - 4.933)([\text{emim}][\text{OTf}])^3$$
$$+ (-2.628[\text{MDEA}] + 13.11)([\text{emim}][\text{OTf}])^2$$
$$+ (1.157[\text{MDEA}] - 7.496)([\text{emim}][\text{OTf}])$$
$$+ (0.326[\text{MDEA}] + 5.796) \qquad (6)$$

$$\alpha = (-0.006[\text{MDEA}] + 0.003)([\text{emim}][\text{OTf}])^3$$
$$+ (0.018[\text{MDEA}] + 0.005)([\text{emim}])[\text{OTf}]^2$$
$$+ (-0.0159[\text{MDEA}] + 0.0349)([\text{emim}][\text{OTf}])$$
$$+ (0.010[\text{MDEA}] + 1.017) \qquad (7)$$

After getting both α and β parameters, density is calculated by using eq 1, and the results are compared with experimental density in this work. For IL [bmim][DCA], the percentage of deviation of calculated density from experimental value is less than 0.21 %, while the percentage deviation for IL [emim][OTf] is less than 0.98 %.

Table 8 shows the percentage deviation by comparing the experimental data with the calculated data at 303 K. The percentage deviation from Table 8 is less than 0.1 %. For the other temperature range, the highest percentage deviation is 0.26 %.

These results have proved that the correlation equations are well-fitted to the ILs in this work within the temperature range investigated.

Viscosity Measurements. The viscosity of pure MDEA, [bmim][BF$_4$], and [bmim][DCA] were measured and compared to literature data to confirm the procedure and reproducibility of obtained viscosity data. Tables 9, 10, and 11 represent the viscosity of pure MDEA, [bmim][BF$_4$], and [bmim][DCA] in this work and the percentage deviation with the density data reported in the literature.[23,24,27] The percentage differences show good consistency between the generated data in this study and the data from literature.

Tables 12, 13, and 14 represent the viscosities data of aqueous MDEA + [bmim][BF$_4$], MDEA + [bmim][DCA], and MDEA + [emim][OTf] mixtures. The viscosities for aqueous MDEA + [bmim][BF$_4$], aqueous MDEA + [bmim][DCA], and aqueous MDEA + [emim][OTf] mixtures increase with increasing concentration of pure [bmim][BF$_4$], [bmim][DCA], and [emim][OTf] at a fixed temperature. This aspect can be described by hydrogen bonding existing in pure IL and between IL with solvent as well. When organic solvents are mixed with ILs, interactions will occur between the solute molecules and the imidazolium ring of the IL. The reduction of the hydrogen

Table 8. Comparison of Density as a Function of Temperature Using Correlation and Data of the Experiment for the Aqueous Mixture of MDEA + $[bmim][BF_4]$ at 303 K^a

		sample concentration mass fraction	density (g·cm^{-3})		
			exptl	calcd	% deviation
1	MDEA	0.234	1.0117	1.0126	0.09
2	MDEA	0.233	1.0209	1.0214	0.05
	$[bmim][BF_4]$	0.111			
3	MDEA	0.231	1.0305	1.0304	0.01
	$[bmim][BF_4]$	0.219			
4	MDEA	0.229	1.0414	1.0413	0.01
	$[bmim][BF_4]$	0.326			
5	MDEA	0.227	1.0489	1.0486	0.03
	$[bmim][BF_4]$	0.431			
6	MDEA	0.459	1.0183	1.019	0.07
7	MDEA	0.464	1.0272	1.0281	0.09
	$[bmim][BF_4]$	0.110			
8	MDEA	0.459	1.0395	1.0401	0.06
	$[bmim][BF_4]$	0.217			
9	MDEA	0.454	1.0498	1.0823	0.03
	$[bmim][BF_4]$	0.323			

^{a}The uncertainty for mass fraction is ± 0.002, and the uncertainty of measured density at the corresponding temperature was estimated to be ± 0.003 g·cm^{-3} and ± 0.01 K, respectively.

Table 9. Viscosity of Pure MDEA from This Work and a Comparison with Literature

	viscosity (mPa·s)		
T/K	this work	Bernal-Garcia et al.[27]	% deviation
313.15	37.682	34.617	8.13
333.15	15.256	14.377	5.76
353.15	6.756	7.082	4.60
363.15	4.539	5.277	13.98

Table 10. Viscosity of Pure $[bmim][BF_4]$ from This Work and a Comparison with Literature

	viscosity (mPa·s)		
T/K	this work	Harris et al.[23]	% deviation
313.15	46.961	51.3	8.45
333.15	23.799	24.5	2.86
353.15	13.936	13.9	0.25

Table 11. Viscosity of Pure $[bmim][DCA]$ from This Work and a Comparison with Literature

	viscosity (mPa·s)		
T/K	this work	Carvalho et al.[24]	% deviation
303.15	23.916	26.286	9.01
313.15	17.116	18.495	8.05
333.15	10.490	10.653	1.53
353.15	6.773	6.9228	2.16
363.15	5.523	5.7700	4.28

bonding force between the imidazolium ring and the anion in IL leads to a decrease in viscosity of the mixture.[28,29] Furthermore, the liquid viscosity of aqueous MDEA + $[bmim][BF_4]$, aqueous MDEA + $[bmim][DCA]$, and aqueous MDEA + $[emim][OTf]$ decreases linearly with increasing in temperature, and the mixture of aqueous MDEA + $[bmim][BF_4]$, aqueous MDEA +

$[bmim][DCA]$, and aqueous MDEA + $[emim][OTf]$ demonstrates temperature-dependent behavior as well.

The addition of distilled water during the IL mixture preparation reduced to a large extent the aqueous mixture viscosities due to the water low viscosity. Seddon et al.[30] represent that water is accommodated in the IL structure in the salt-rich region, possibly by forming hydrogen bonds with both the anion and the cation. The dramatic decrease of the viscosity is due to the presence of the water molecules which reduces the electrostatic attractions between the ions. Therefore, the overall cohesive energy of the system is decreased, and consequently viscosity is decreased as well.[30,31] Furthermore, the increase in temperature will also cause the viscosity to decrease exponentially for both pure substances and mixtures. It is obvious that the decreasing trend of viscosity for pure MDEA is greater than pure IL and followed by aqueous mixtures. Thus, temperature has greatest impact on pure MDEA.[26] A different trend was observed for pure $[emim][OTf]$ data which could be seen from Table 10. By taking temperature at 333.15 K as a reference point, the viscosity of pure $[emim][OTf]$ is lower than pure MDEA at earlier stages. But when the temperature is increased from (333.15 to 363.15) K, the viscosity of pure $[emim][OTf]$ becomes higher than pure MDEA.

Correlation of Viscosity as a Function of Temperature, Concentration of MDEA, and Concentration of [bmim][BF$_4$], [bmim][DCA], and [emim][OTf]. An extended Arrhenius equation can be applied to correlate the temperature dependence of pure MDEA, pure ILs, and aqueous mixtures of MDEA + IL viscosity. The Arrhenius equation is expressed as eq 8.

$$\ln \eta = \frac{E_a}{RT} + \ln \eta_\infty \tag{8}$$

$\ln \eta$ vs $1/T$ for temperature from (303.15 to 363.15) K is plotted, and E_a and η_∞ are obtained by determining the slope and y-intercept of the resulting straight line graph. Thus, the E_a and η_∞ parameters are represented by eqs 9 to 14.

The equations for the aqueous mixture of MDEA + $[bmim][BF_4]$ can be expressed as

$$
\begin{aligned}
E_a = {} & (-5.4968[MDEA] + 12.278)([bmim][BF_4])^3 \\
& (16.597[MDEA] - 39.074)([bmim][BF_4])^2 \\
& + (-14.957[MDEA] + 37.903)([bmim][BF_4] \\
& + 3.2227[MDEA] + 3.1582) \tag{9}
\end{aligned}
$$

$$
\begin{aligned}
\eta_\infty \cdot 10^2 = {} & (4.5545[MDEA] - 11.09)([bmim][BF_4])^3 \\
& + (-13.645[MDEA] + 35.353)([bmim][BF_4])^2 \\
& + (11.918[MDEA]) - 33.414)([bmim][BF_4]) \\
& - 2.0428[MDEA] + 9.1816 \tag{10}
\end{aligned}
$$

The equations for the aqueous mixture of MDEA + $[bmim][DCA]$ can be expressed as

$$
\begin{aligned}
E_a = {} & (1.8006[MDEA] - 5.2401)([bmim][DCA])^3 \\
& + (2.2643[MDEA] - 0.3955)([bmim][DCA])^2 \\
& + (-8.1043[MDEA] + 16.031)([bmim][DCA]) \\
& + (3.0728[MDEA] + 3.758) \tag{11}
\end{aligned}
$$

Table 12. Experimental Results of Viscosity for Aqueous MDEA and [bmim][BF$_4$]^a

	sample concentration mass fraction		viscosity (mPa·s)				
			303.15 K	313.15 K	333.15 K	353.15 K	363.15 K
1	MDEA	0.234	2.285	1.612	1.418	1.121	1.112
2	MDEA	0.233	2.686	1.924	1.540	1.229	1.207
	[bmim][BF$_4$]	0.111					
3	MDEA	0.231	3.211	2.360	1.640	1.325	1.289
	[bmim][BF$_4$]	0.219					
4	MDEA	0.229	3.230	2.493	1.757	1.506	1.452
	[bmim][BF$_4$]	0.326					
5	MDEA	0.227	3.366	2.754	1.860	1.658	1.462
	[bmim][BF$_4$]	0.431					
6	MDEA	0.459	2.850	2.238	1.621	1.485	1.337
7	MDEA	0.464	3.174	2.423	1.884	1.678	1.485
	[bmim][BF$_4$]	0.110					
8	MDEA	0.459	3.475	2.785	2.075	1.755	1.568
	[bmim][BF$_4$]	0.217					
9	MDEA	0.454	3.611	2.995	2.197	1.797	1.664
	[bmim][BF$_4$]	0.323					
10	pure MDEA		58.621	37.682	15.256	6.756	4.539
11	pure [bmim][BF$_4$]		71.633	46.961	23.799	13.936	11.325

^{a}The uncertainty for mass fraction is ± 0.002, and the uncertainty of measured viscosity at the corresponding temperature was estimated to be ± 0.05 mPa·s and ± 0.01 K, respectively.

Table 13. Experimental Results of Viscosity for Aqueous MDEA and [bmim][DCA]^a

	sample concentration mass fraction		viscosity (mPa·s)				
			303.15 K	313.15 K	333.15 K	353.15 K	363.15 K
1	MDEA	0.235	2.365	1.982	1.557	1.200	1.120
	[bmim][DCA]	0.101					
2	MDEA	0.239	2.467	2.181	1.663	1.310	1.193
	[bmim][DCA]	0.202					
3	MDEA	0.234	3.222	2.782	2.176	1.523	1.243
	[bmim][DCA]	0.302					
4	MDEA	0.234	3.273	2.929	2.314	1.637	1.384
	[bmim][DCA]	0.402					
6	MDEA	0.466	2.858	2.402	1.910	1.563	1.445
	[bmim][DCA]	0.100					
7	MDEA	0.465	2.942	2.613	2.128	1.657	1.518
	[bmim][DCA]	0.200					
8	MDEA	0.462	5.032	3.972	2.759	1.854	1.569
	[bmim][DCA]	0.298					
9	pure [bmim][DCA]		23.916	17.116	10.490	6.773	5.523

^{a}The uncertainty for mass fraction is ± 0.002, and the uncertainty of measured viscosity at the corresponding temperature was estimated to be ± 0.05 mPa·s and ± 0.01 K, respectively.

$$\eta_\infty \cdot 10^2 = (-0.7577[MDEA] + 1.5698)([bmim][DCA])^3$$
$$+ (-3.0624[MDEA] + 7.3199)$$
$$([bmim][DCA])^2 + (7.1988[MDEA] - 18.481)$$
$$([bmim][DCA]) - 1.9462[MDEA] + 8.795$$
$$(12)$$

The equations for the aqueous mixture of MDEA + [emim]-[OTf] can be expressed as

$$E_a = (-1986.7[MDEA] + 12493)([emim][OTf])^3$$
$$+ (-1110[MDEA] - 8460)([emim][OTf])^2$$
$$+ 3281.7[MDEA] - 4033.3)([emim][OTf])$$
$$+ (3150[MDEA] + 3450)$$
$$(13)$$

$$\eta_\infty \cdot 10^2 = (0.4187[MDEA] - 2.6786)([emim][OTf])^3$$
$$+ (2.315[MDEA] - 5.98)([emim][OTf])^2$$
$$+ (-2.6377[MDEA] + 8.3406)([emim][OTf])$$
$$+ (-2.0150[MDEA] + 9.052)$$
$$(14)$$

To determine the viscosity, eqs 9 to 14 are substituted into eq 8, and it was found out for [bmim][BF$_4$] the percentage deviation of calculated viscosity from experimental value was less than 30 %. Hence, the viscosity can be fitted with high accuracy with eq 8 for the temperature range from (303.15 to 363.15) K. For [bmim][DCA] the percentage deviation of calculated viscosity from experimental value varies from 0.4 % to as large as 37 %. The large deviation in result only occurs in 2.0 M MDEA and 1.5 M [bmim][DCA]. For [emim][OTf], the percentage

Table 14. Experimental Results of Viscosity for Aqueous MDEA and [emim][OTf][a]

	sample concentration mass fraction		viscosity (mPa·s)				
			303.15 K	313.15 K	333.15 K	353.15 K	363.15 K
1	MDEA	0.231	2.488	2.290	1.816	1.468	1.314
	[emim][OTf]	0.139					
2	MDEA	0.226	2.711	2.446	2.029	1.598	1.402
	[emim][OTf]	0.273					
3	MDEA	0.221	5.177	4.345	2.955	1.975	1.609
	[emim][OTf]	0.401					
4	MDEA	0.216	5.333	4.598	3.371	2.350	1.948
	[emim][OTf]	0.522					
6	MDEA	0.457	7.549	6.482	4.598	2.738	2.253
	[emim][OTf]	0.138					
7	MDEA	0.447	8.278	7.215	5.393	3.531	2.897
	[emim][OTf]	0.271					
8	MDEA	0.438	9.234	8.149	6.231	4.313	3.328
	[emim][OTf]	0.397					
9	pure [emim][OTf]		36.141	26.651	16.452	12.166	11.144

[a]The uncertainty for mass fraction is ± 0.002, and the uncertainty of measured viscosity at the corresponding temperature was estimated to be ± 0.05 mPa·s and ± 0.01 K, respectively.

Table 15. Comparison of Viscosity as Function of Temperature Using the Correlation and Data of the Experiment for the Aqueous Mixture of MDEA and [bmim][BF₄] at 303 K[a]

	sample concentration mass fraction		viscosity (mPa·s)		
			exptl	calcd	% deviation
1	MDEA	0.234	2.285	2.302	0.74
2	MDEA	0.233	2.686	2.720	1.25
	[bmim][BF₄]	0.110			
3	MDEA	0.231	3.211	2.778	13.48
	[bmim][BF₄]	0.219			
4	MDEA	0.229	3.230	3.361	3.89
	[bmim][BF₄]	0.326			
5	MDEA	0.227	3.366	3.131	6.98
	[bmim][BF₄]	0.431			
6	MDEA	0.459	2.850	2.719	4.58
7	MDEA	0.464	3.174	2.949	7.09
	[bmim][BF₄]	0.110			
8	MDEA	0.459	3.475	3.327	4.26
	[bmim][BF₄]	0.217			
9	MDEA	0.454	3.611	3.516	2.7
	[bmim][BF₄]	0.323			

[a]The uncertainty for mass fraction is ± 0.002, and the uncertainty of measured viscosity at the corresponding temperature was estimated to be ± 0.05 mPa·s and ± 0.01 K, respectively.

Table 16. Summaries of E_a and η_∞ Values for Pure MDEA and ILs

	characteristic parameter	
pure substance	$E_a/(\text{kJ}\cdot\text{mol}^{-1})$	$\eta_\infty/(\cdot 10^2 \text{ mPa}\cdot\text{s})$
MDEA	39.14	0.001
[bmim][DCA]	22.06	0.368
[emim][OTf]	18.07	2.628
[bmim][BF₄], this work	28.14	0.097
[bmim][BF₄], Sanchez et al.[32]	33.53	0.140

deviation is less than 8.9 %. Thus, the viscosity can be fitted with high accuracy with eq 8 except for the sample 2.0 M MDEA, 1.5

M [bmim][DCA] for the temperature range from (303.15 to 363.15) K.

The percentage deviations for aqueous MDEA + [bmim]-[BF₄] mixtures at 303 K are shown in Table 15. Meanwhile the E_a and η_∞ parameters for pure MDEA, pure ILs from this work, and pure [bmim][BF₄] from literature were presented in Table 16. The E_a and η_∞ parameters for pure [bmim][BF₄] of this work is slightly deviated from literature. The temperature range used for both correlations is different where this will cause the deviation of E_a and η_∞ parameters.

■ **CONCLUSIONS**

The density and viscosity data for the pure and aqueous MDEA + [bmim][BF₄], MDEA + [bmim][DCA], and MDEA + [emim]-[OTf] mixtures were measured over the whole range of composition at temperatures ranging from (303.15 to 363.15) K and atmospheric pressure. The experimental results show that both densities and viscosities decrease with temperature from (303.15 to 363.15) K. As the concentration of [bmim][BF₄], [bmim][DCA], and [emim][OTf] increases, the viscosities and densities of aqueous solution increase as well. It was also found that the density for the ILs can be correlated to an empirical linear equation with high accuracy, whereas a developed Arrhenius equation was applied to correlate viscosity for both pure and aqueous substances with good accuracy. The derived linear equation can excellently represent the dependence of density on composition and temperature. The percentage deviations of calculated density from experimental density of [bmim][BF₄], [bmim][DCA], and [emim][OTf] at temperatures ranging from (303.15 to 353.15) K are less than 0.26 %, 0.21 %, and 0.98 %, respectively . Furthermore, the extended Arrhenius equation can be used to estimate viscosities from (303.15 to 363.15) K with acceptable accuracy where the percentage deviation of calculated viscosity from experimental viscosity was less than 30 %.

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Notes

The authors declare no competing financial interest.

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