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Volumetric and viscometric study and FT-IR analysis of binary and ternary mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate, methyldiethanolamine and water

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ABSTRACT

Densities and viscosities of binary mixtures {[Bmim][BF_4] + MDEA}, {MDEA + H_2O} and ternary mixture {[Bmim][BF_4] + MDEA + H_2O} were measured at $T = (293.15–333.15)$ K. The volumetric and viscometric properties of binary and ternary mixtures, such as excess molar volume (V^E), viscosity deviation ($\Delta\eta$), excess Gibbs energy of activation of viscous flow (ΔG^{*E}), and Grunberg-Nissan interaction parameter (G_{12}), were deduced from experimental data. The excess molar volumes and viscosities data were used to calculate the Redlich-Kister and Jouyban-Acree equations coefficients for binary mixtures, and Singh et al. and Jouyban-Acree extended equations coefficients for ternary mixtures. The intermolecular interactions in binary and ternary mixtures were discussed through volumetric and viscometric properties and FT-IR spectroscopic analysis.

1. Introduction

Currently, the development of economical and environmentally friendly CO_2 capture and recycling technology has become an urgent task all over the world due to the greenhouse effect stemming from the increasing CO_2 emission. In industry, alkanolamine aqueous solutions have been widely used for CO_2 capture [1]. Primary and secondary alkanolamines could rapidly chemically trap CO_2 to form carbamates. However, the high heat of absorption associated with the carbamate formation leads to high solvent regeneration cost [2]. In tertiary alkanolamines, methyldiethanolamine (MDEA) exhibits many advantages over other amines in CO_2 capture process, such as lower corrosivity [3], higher thermal stability and less regeneration cost [4]. Unfortunately, no hydrogen atom attaches to the nitrogen atom in the tertiary amine group of MDEA molecule. Thus it is unable to conduct carbamation reaction with CO_2, which results in a low reactivity with CO_2 [2,5]. Effectively, the combination of MDEA and other absorbents is usually applied for the enhancement of CO_2 absorption rate [6–9].

Many researches have shown that ionic liquids (ILs) exhibit great potential for CO_2 absorption due to their unique characteristics including wide liquid range, high thermal stability, negligible vapor pressure, tunable physicochemical characteristic and high CO_2 solubility, etc. [10,11]. Moreover, the mixture of ionic liquids and MDEA could improve the absorption performance for CO_2, by not only affording many desired properties for CO_2 capture, but also overcoming some inherent drawbacks [12]. In recent years, the aqueous solution of MDEA and 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) has received extensive attention in CO_2 capture [13–17]. Ahmady et al. [13,17] thought that the presence of ionic liquid could increase the initial rate of CO_2 absorption into MDEA aqueous solution under specified conditions.

The density and viscosity are basic and necessary physical property parameters for process design and optimization. Yusoff et al. [18] measured the densities and viscosities of aqueous mixture of MDEA/[Bmim][BF_4] with the [Bmim][BF_4] concentrations (0.5–2.0) mol·L^{-1}, and MDEA concentrations (2.0 and 4.0) mol·L^{-1} at atmospheric pressure and temperature $T = (303.15–363.15)$ K. Ahmady et al. [19] measured the densities and viscosities of the same mixture with [Bmim][BF_4] concentrations (0–2.0) mol·L^{-1} and MDEA concentration 4.0 mol·L^{-1} over a temperature range of $T = (303 - 333)$ K and atmospheric pressure. All the two measurements were conducted at low concentrations of MDEA and ionic liquid, up to now, the understanding of the physical property of the complicated ternary mixture is still far from sufficient. As is well known, the pure compounds and binary mixtures data could be used for the analysis and prediction of properties of ternary solutions. In previous work [20], the densities and viscosities of binary mixture {[Bmim][BF_4] + H_2O} have been measured, but the density and viscosity data of solution {[Bmim][BF_4] + MDEA} remain still lacking.

Theoretically, it is quite necessary to investigate the intermolecular interactive behavior in mixtures, since these kinds of interactions may

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Table 1
Specifications of studied chemicals.

Chemical name	CAS NO.	Molar mass/g·mol^{-1}	Mass fraction of water	Mass fraction purity[a]	Source
[Bmim][BF_4]	174,501-65-6	226.02	0.0019	≥0.995	Henan Lihua Pharamaceutical Co. Ltd., in China.
MDEA	105–59-9	119.16	0.002	≥0.99	Aladdin Chemical Reagent Co. Ltd.
water	7732–18-5	18.01524	–	–	Hangzhou Wahaha Group Co. Ltd., in China.

[a] Declared by the supplier.

significantly affect the reaction rate and kinetic mechanism [21]. The association, hydrogen bond and interactions of different molecules could be investigated through analyzing the shift of band using Fourier-transform infrared (FT-IR) spectroscopy [22–30]. Rao et al. [27] found that the addition of *N*-methyl-2-pyrrolidinone (NMP) to [Bmim][BF_4] could affect the C—H vibration of cation of [Bmim][BF_4], B—F stretching of anion of [Bmim][BF_4], and C═O vibration and C—N stretching of NMP. These phenomena might be due to the ion-dipole interaction in the binary mixture, which leads to the negative V^E in the mixture. Cammarata et al. [31] studied the IR spectra of *v*(O—H) region of water in several ionic liquids involving the 1-alkyl-3-methylimidazolium cation with different anions, and the results revealed that the hydrogen bonds were formed between anions of these ionic liquids and O—H of water.

In this paper, the densities and viscosities of binary mixtures {[Bmim][BF_4] + MDEA and MDEA + H_2O} and ternary mixtures {[Bmim][BF_4] + MDEA + H_2O} were measured experimentally at atmospheric pressure and $T = (293.15–333.15)$ K. In addition, measured data were used to calculate the volumetric and viscometric properties, such

Table 2
Comparisons of experimental densities (ρ) and viscosities (η) for pure MDEA with literature values at $T = (293.15–333.15)$ K and $P = 0.101$ MPa.

	ρ/g·cm^{-3}					η/mPa·s			
T/K	Exp.	Lit.				Exp.	Lit.		
293.15	1.03966	1.041604 [45]	1.04060 [35,39]	1.042201 [50]	1.0399 [37]	103.091	102.7 [55]	104.50 [58]	103.3 [40]
		1.0406 [40,54]	1.0416 [52]	1.04006 [38]	1.04012 [44]		101.18 [60]		
303.15	1.03213	1.0315 [41,42]	1.03200 [32]	1.03228 [33]	1.034100 [45]	57.615	57.95 [55]	57.8599 [42]	57.86 [58]
		1.034493 [49]	1.03306 [35]	1.034358 [50]	1.03374 [51]		57.37 [33]	57.69 [51]	57.14 [57]
		1.0324 [36,37]	1.03325 [53]	1.0328 [40,54]	1.0341 [52]		59.76 [53]	57.3 [40]	57.23 [60]
		1.03247 [38]	1.03302 [39]	1.0347 [18]			57.28 [61]		
313.15	1.02452	1.0249 [41]	1.0249 [42]	1.02445 [32]	1.0250 [43]	34.043	34.02 [55]	34.11 [56]	34.3085 [42]
		1.02475 [33]	1.02519 [34]	1.026523 [45]	1.0272 [46–48]		34.31 [58]	34.617 [59]	34.60 [33]
		1.026993 [49]	1.02545 [35]	1.026484 [50]	1.02672 [51]		34.110 [34]	34.73 [46–48]	34.79 [51]
		1.0248 [36]	1.0249 [37]	1.02565 [53]	1.0254 [54]		34.04 [57]	37.9 [53]	34.1 [40]
		1.0265 [52]	1.02486 [38]	1.02540 [39]	1.0271 [18]		34.10 [60]	34.41 [61]	
		1.0254 [40]	1.02474 [44]						
323.15	1.01687	1.0174 [41–43]	1.01666 [32]	1.01708 [33]	1.01699 [34]	21.466	21.5 [55]	21.6716 [42]	21.67 [58]
		1.018877 [45]	1.019469 [49]	1.01778 [35]	1.018576 [50]		21.59 [33]	21.973 [34]	21.88 [51]
		1.01948 [51]	1.0172 [36,37]	1.01801 [53]	1.0178 [40,54]		21.53 [57]	24.7 [53]	21.6 [40]
		1.0189 [52]	1.01721 [38]	1.01774 [39]	1.01727 [44]		21.60 [60]		
333.15	1.00915	1.0098 [41,42]	1.00900 [32]	1.0096 [43]	1.00941 [33]	14.179	14.3 [56]	14.3856 [42]	14.39 [58]
		1.0096 [34]	1.011430 [45]	1.0126 [46–48]	1.011796 [49]		14.377 [59]	14.43 [33]	14.300 [34]
		1.01232 [51]	1.0094 [36]	1.0095 [37]	1.0010 [54]		14.66 [46–48]	14.6 [51]	14.3 [40]
		1.00951 [38]	1.01003 [39]	1.0130 [18]	1.0100 [40]		14.19 [60]		
		1.00956 [44]							

The standard uncertainties *u* in this work are: $u(T) = 0.03$ K for density, $u(T) = 0.05$ K for viscosity, $u(P) = 0.003$ MPa; the relative standard uncertainties u_r are: $u_r(\rho) = 0.0005$, $u_r(\eta) = 0.03$.

Table 3
Densities (ρ) and viscosities (η) for binary mixtures at $T = (293.15–333.15)$ K and $P = 0.101$ MPa.

x_1	$T = 293.15$ K		$T = 303.15$ K		$T = 313.15$ K		$T = 323.15$ K		$T = 333.15$ K	
	ρ/g·cm^{-3}	η/mPa·s	ρ/g·cm^{-3}	η/mPa·s	ρ/g·cm^{-3}	η/mPa·s	ρ/g·cm^{-3}	η/mPa·s	ρ/g·cm^{-3}	η/mPa·s
[Bmim][BF_4] (x_1) + MDEA (x_2)										
0.1002	1.06615	89.344	1.05845	49.934	1.05074	30.023	1.04310	18.935	1.03545	12.752
0.1974	1.08746	82.949	1.07991	46.203	1.07214	27.971	1.06458	17.770	1.05695	12.094
0.3000	1.10760	78.866	1.09993	43.666	1.09231	26.387	1.08471	17.237	1.07714	11.840
0.4001	1.12506	75.170	1.11753	42.355	1.10991	26.077	1.10238	17.219	1.09489	12.030
0.4998	1.14104	73.611	1.13340	42.397	1.12589	26.443	1.11840	17.684	1.11102	12.444
0.6000	1.15559	74.189	1.14814	43.828	1.14061	27.744	1.13317	18.796	1.12580	13.348
0.6997	1.16908	79.057	1.16167	47.485	1.15419	30.434	1.14679	20.649	1.13950	14.796
0.7998	1.18171	87.861	1.17437	53.140	1.16702	34.041	1.15962	23.330	1.15248	16.836
0.8999	1.19367	105.592	1.18645	63.525	1.17915	41.236	1.17205	27.798	1.16510	19.792
MDEA (x_1) + H_2O (x_2)										
0.1000	1.03876	7.325	1.03330	4.901	1.02728	3.458	1.02090	2.551	1.01403	1.904
0.1991	1.05357	26.191	1.04663	15.414	1.03945	9.684	1.03194	6.517	1.02422	4.582
0.2985	1.05644	56.540	1.04909	31.074	1.04148	18.139	1.03370	11.418	1.02572	7.616
0.3975	1.05514	84.733	1.04759	45.332	1.03993	25.738	1.03205	15.802	1.02404	10.248
0.4963	1.05250	103.228	1.04490	54.913	1.03727	31.504	1.02949	18.960	1.02149	12.184
0.5949	1.04967	113.880	1.04201	60.929	1.03433	34.140	1.02656	20.848	1.01873	13.408
0.6934	1.04676	115.534	1.03920	62.477	1.03161	35.728	1.02388	21.722	1.01607	14.066
0.7916	1.04440	113.565	1.03666	61.994	1.02905	35.443	1.02141	21.953	1.01363	14.318
0.8896	1.04204	109.801	1.03445	59.489	1.02685	35.117	1.01925	21.790	1.01159	14.318

The standard uncertainties *u* are: $u(x_1) = 0.002$, $u(T) = 0.03$ K for density, $u(T) = 0.05$ K for viscosity, $u(P) = 0.003$ MPa; The relative standard uncertainties $u_r(\rho) = 0.0005$, $u_r(\eta) = 0.03$.