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New polyalkylated imidazoles tailored for carbon dioxide capture

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ABSTRACT

Aqueous polyalkylated imidazoles have gained interest as potential CO_2 capture solvents due to their high oxidative stability and low vapor pressures compared to traditional amines. In this work, 21 aqueous solutions of polyalkylatedimidazoles were screened as absorbents for CO_2 capture and four solvent candidates were further characterized by measuring the vapor-liquid equilibria and the heat of absorption of CO_2. The pK_a values of the imidazoles were measured and a positive correlation between the absorption capacity and pK_a of polyalkylated imidazoles was found. Increasing the pK_a of imidazoles to 9 by alkylation improved the CO_2 absorption capacity significantly. Based on the equilibrium experiments, the cyclic capacities of the selected solvents varied from 0.8 to 2 mol CO_2/kg solvent. Furthermore, the heat of absorption of CO_2 of the studied imidazoles was lower compared to primary amines. In general, the tested polyalkylated imidazoles are more feasible for processes with partial pressures of CO_2 above 50 kPa. Trimethylimidazole that forms bicarbonate precipitate might be applicable for post combustion CO_2 capture as a high cyclic capacity is obtained even at CO_2 partial pressures around 10 kPa. The present study gives new important knowledge of the absorption properties of polyalkylated imidazoles.

1. Introduction

The predominant technology for CO_2 capture is the use of aqueous alkanolamine solutions for chemical absorption. Unfortunately, chemical absorption with these systems require substantial amounts of energy to regenerate the solvent system (Svendsen et al., 2011). Hence, it is important to study the potential of other amines for CO_2 capture. An interesting class of compounds is imidazoles. Imidazoles are *N*-heterocyclic compounds and have not been extensively studied as absorbents for CO_2 capture. Recently, evolutionary de novo design has been applied to propose new imidazoles for investigation as potential aborbents (Venkatraman et al., 2016). The attention given to imidazoles has mainly been as precursor for imidazolium ionic liquids as physical absorbents for CO_2 (Ramdin et al., 2012) or in imidazolium-based deep eutectic solvents for CO_2 capture (Cao et al., 2015). Furthermore, incorporating imidazole into CO_2 selective membranes has shown promising results (Lin et al., 2017) and highly efficient absorption of SO_2 have been obtained with imidazoles (Shannon et al., 2015). Other uses of imidazoles include natural products (Zhang et al., 2014) and as NHC-ligands in organometallic catalysis (Fortman and Nolan, 2011), Shannon et al. have previously reported that pure, non-aqueous *N*-alkylimidazoles exhibit both lower viscosities and greater physical absorption than their imidazolium counterparts (Shannon and Bara, 2011). As neat liquids, *N*-alkylimidazoles do not demonstrate chemical reaction with CO_2. However, significantly improved CO_2 absorption capacity was obtained for monoethanolamine in *N*-butylamine compared to aqueous monoethanolamine solutions (Shannon and Bara, 2011). In aqueous solutions, imidazoles react with CO_2 as tertiary amines (Tomizaki et al., 2010a). Chemical absorption of CO_2 with unsubstituted imidazole is not efficient due to imidazole not having sufficientlyhigh pK_a, and has been scarcely studied. Investigation of imidazoles with increased pK_a is therefore of interest. The absorption capacity and cyclic capacity of imidazole/piperazine blends increase with higher pK_a of the imidazole (Du et al., 2016a). Imidazoles can also be used to improve CO_2 mass-transfer rates into amine solvents (Du et al., 2016a) and have been applied to reduce the vapor pressure of volatile organic compounds in aqueous solution (Puxty et al., 2015). Very low vapor pressures are observed above neat alkylimidazole solutions (Emel'yanenko et al., 2011a,b). Furthermore, the thermal stability of imidazoles is improved by additional number of alkyl substituents on the imidazole (Du et al., 2016b). Imidazole has excellent oxidative stability compared to other amines (Martin et al., 2012). As alkyl substitution increases both the thermal stability and the pK_a (Lenarcik and Ojczenasz, 2002) of the imidazole, we decided to study the CO_2 absorption capacities of polyalkylated imidazoles. We have previously prepared a wide range (> 40) polyalkylated imidazoles in

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Table 1
pK_a Values: a) lit. data (Lenarcik and Ojczenasz, 2002) at 25 °C, b) measured at 25 °C and c) measured CO_2 loading (α) [mol CO_2/mol amine] at given pressure at 40 °C.

Compounds (purity wt%)		a) pK_a lit. data[a]	b) pK_a Measured[b]	c) CO_2 loading α [mol/mol] (pressure [kPa])
Monoethanolamine (99.5%)	 MEA		9.50	0.56 (65)
N- Methyldiethanolamine (≥99%)	 MDEA		8.57	0.75 (73)
Imidazole (≥99%)	 **1**	6.95	7.01	0.21 (96)
1-Methylimidazole (99%)	 **2**	7.21	7.04	0.12 (80)
2-Methylimidazole (99%)	 **3**	7.85	7.92	0.36 (80)
2-Ethylimidazole (98%)	**4**	7.99	7.88	0.29 (84)
4(5)-Methylimidazole (98%)	 **5**	7.69	7.58	0.29 (90)
1,2-Dimethylimidazole (98%)	 **6**	8.21	8.05	0.36 (87)
2-Ethyl-4(5)-methylimidazole (95%)	 **7**	8.68	8.38	0.47 (80)
2,4,5-Trimethylimidazole (98%)	 **8**	8.92	8.90	0.61 (78)
4-Ethyl-2,5-dimethylimidazole (97%)	 **9**	–	8.88	0.63 (84)
1,4,5-Trimethylimidazole (97%)	 **10**	–	8.02	0.34 (87)
1-Ethyl-4,5-methylimidazole (98%)	 **11**	–	8.24	0.33 (97)
4,5-Methyl-1-propylimidazole (97%)	 **12**	–	8.18	0.31 (86)
1-Isopropyl-4,5-dimethylimidazole (97%)	 **13**	–	8.04	0.31 (88)
1-(2-Hydroxyethyl)-4,5-dimethylimidazole (96%)	 **14**	–	7.94	0.50 (84)
2,4,5-Triethylimidazole (95%)	**15**	–	7.99	0.24 (90)
1,2,4,5-Tetramethylimidazole (98%)	 **16**	9.20	9.05	0.72 (89)
1-Ethyl-2,4,5-trimethylimidazole (98%)	 **17**	–	8.68	0.71 (83)
2,4,5-Trimethyl-1-propylimidazole (98%)	**18**	–	8.89	0.68 (84)
1-Isopropyl-2,4,5-trimethylimidazole (95%)	 **19**	–	8.80	0.58 (90)
2-Ethyl-1,4,5-trimethylimidazole (99%)	 **20**	–	9.03	0.66 (84)
1,4,5-Trimethyl-2-propylimidazole (95%)	 **21**	–	9.04	0.61 (81)

[a] Fixed ionic strength, I = 0.5 (KNO_3) (Lenarcik and Ojczenasz, 2002).
[b] Infinite dilution.

out laboratory for this purpose (Evjen and Fiksdahl, 2017).

In this work, we present newly synthesized imidazoles as potential candidates for CO_2 capture. The effect of increasing the number of alkyl substituents on pK_a and absorption capacity of imidazoles will be presented. The water solubility of imidazoles will be discussed. Furthermore, the heat of absorption and vapor-liquid equilibrium (VLE) data of selected imidazoles will be given.

2. Experimental section

2.1. Materials

The tested compounds **1–21** are presented in Table 1. Monoethanolamine (MEA), *N*-methyldiethanolamine (MDEA), imidazole **1**, 1-methylimidazole **2**, 2-methylimidazole **3**, 2-ethylimidazole **4**, 4(5)-methylimidazole **5**, 1,2-dimethylimidazole **6** and 2-ethyl-4-methylimidazole **7** were obtained from Sigma-Aldrich Merck (Germany). 1,2,4,5-Tetramethylimidazole **16** was obtained from TCI Europe (Belgium). Commercial compounds were used without further purification. Polyalkylated imidazoles **8–15**, **17–21** were readily prepared by a one-step procedure in our laboratory (Evjen and Fiksdahl, 2017) from corresponding diketone, aldehyde and amine with ammonium sulfate or ammonium carbonate as ammonium source.

2.2. Acid dissociation constant, pK_a

Potentiometric measurements were conducted with a Mettler Toledo G20 compact titrator with a pH-electrode DSC-115 (uncertainty ± 0.02 pH) and temperature sensor DT100 (uncertainty ± 0.1 °C) (Kim et al., 2011). The temperature was controlled at 25 °C with a Julabo M4 heating circulator (temperature stability ± 0.1 °C). Deionized water was used as heat transfer medium. Calibration of the pH electrode was performed using buffer solutions traceable to the National Bureau of Standards (pH 4.01, 7.00, 9.21 and