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Experiment and model for the viscosity of carbonated piperazine-N-methyldiethanolamine aqueous solutions

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ABSTRACT

The viscosities of both CO_2-unloaded and CO_2-loaded piperazine (PZ) promoted N-methyldiethanolamine (MDEA) aqueous solutions were measured by using a NDJ-1 rotational viscometer, with temperatures ranging from 293.15 to 323.15 K. The total mass fraction of amines was fixed as 0.5 and the mass fraction of PZ ranged from 0.025 to 0.15. The CO_2 loading ranged from 0 to 0.6. The Weiland equation was used to correlate the viscosities and the calculated results agreed well with the experiments. The effects of temperature, mass fraction of amines and CO_2 loading on the viscosity were demonstrated.

1. Introduction

In recent decades, atmospheric levels of CO_2 have increased rapidly due to the utilization of great amount of fossil fuel. The reduction of CO_2 emissions became a global issue [1,2].

Chemical absorption is one of the most effective approaches for CO_2 capture because CO_2 can be satisfactorily removed and the absorbents can be regenerated by heating. Currently, aqueous solutions of alkanolamines are widely used for the removal of CO_2 from a variety of gas streams [3–10]. Among the alkanolamine series, N-methyldiethanolamine (MDEA) has the advantages of high resistance to thermal and chemical degradation, low solution vapor pressure, and low enthalpy of absorption. However, MDEA has a low absorption rate. Adding a small amount of monoethanolamine (MEA) or piperazine (PZ) to the aqueous solution of MDEA has found widespread application in the removal of CO_2 [11–20]. PZ is considered as the most promising additive to MDEA aqueous solution. The mixtures of PZ and MDEA preserve the high rate of the reaction of PZ with CO_2, and the low enthalpy of the reaction of MDEA with CO_2, hence leading to higher absorption rates in the absorber column, yet lower heat of regeneration in the stripper section.

Solution viscosity is important in the mass transfer rate modeling of absorbers and regenerators because these properties significantly affect the liquid film coefficient for mass transfer. Viscosities of both CO_2-unloaded and CO_2-loaded MDEA-PZ aqueous solutions are required when designing or simulating an absorption column for CO_2 absorption using MDEA-PZ aqueous solutions. So far, there are some experiments concerning the viscosity of CO_2-unloaded MDEA-PZ aqueous solutions [19,20]. However, the viscosity of CO_2 loaded MDEA-PZ aqueous solutions has been rarely reported, and the influences of temperature, amine concentration and CO_2 loading on the viscosity of carbonated MDEA-PZ aqueous solutions have not been well described due to the lack of experiments.

The main purpose of this work is to investigate the viscosities of carbonated MDEA-PZ aqueous solutions in wide ranges of CO_2 loading, temperature and amine concentration, and then demonstrate the temperature, mass fraction of amines and CO_2 loading dependence of the viscosities on the basis of experiments and calculations. To this end, the viscosities of both CO_2-unloaded and CO_2-loaded PZ promoted MDEA aqueous solutions were measured, with the temperatures, mass fraction of PZ and CO_2 loading respectively ranging from 293.15 to 323.15 K, 0.025 to 0.15 and 0 to 0.6. The Weiland equation [21] was used to correlate the viscosities.

2. Experimental section

2.1. Materials

Both MDEA and PZ were purchased from Huaxin chemical Co. The sample description is shown in Table 1. They were used without further purification. Aqueous solutions of MDEA-PZ were prepared by adding doubly distilled water. The uncertainty of the electronic balance (FA1604A) is ±0.1 mg.

2.2. Apparatus and procedure

The carbonated MDEA-PZ aqueous solutions were prepared according to the methods mentioned in the work of Weiland et al.

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Table 1
Sample description.

Chemical	CAS no.	Purity (in mass fraction %)	Molecular mass	Density ($g \cdot cm^{-3}$) at 293.15 K
PZ	110-85-0	99.5	86.14	0.876
MDEA	105-59-9	99.5	119.16	1.0377

[21] and Amundsen et al. [22]: CO_2-unloaded MDEA-PZ aqueous solutions were put into a volumetric flask immersed in a thermostatic bath with a built-in stirrer for uniform temperature distribution. CO_2 from a high-pressure tank was inlet into the volumetric flask at certain temperatures (CO_2 pressure is atmosphere). Once the carbonated solution was prepared, varying proportions of the unloaded and loaded solutions were mixed together to produce a set of samples having fixed ratios of MDEA/PZ-to-water, but with varying CO_2 loadings. CO_2 loading is defined as $\alpha = n_{CO_2}/(n_{MDEA} + n_{PZ})$, in which n_{CO_2} is the mole of loaded CO_2, and n_{MDEA} and n_{PZ} are respectively the moles of MDEA and PZ in the unloaded aqueous solutions.

It is worth noting that CO_2 loading is expected to be a major uncertainty in the experiment. In this work, the carbonated solution was prepared at non-equilibrium conditions, under which the thermodynamic equilibrium (saturated absorption, corresponding to maximum CO_2 loading, α_{max}) was not achieved. A certain amount of CO_2 escaped when the loaded solution was mixed with the unloaded solution and the atmospheric CO_2 and humidity have some effects on the CO_2 loading and solution concentration. The CO_2 loadings of some diluted samples were checked by using the analysis method based on the precipitation of $BaCO_3$ [21–26]. The estimated uncertainty in the CO_2 loading was less than 2%.

The viscosities of the carbonated MDEA-PZ aqueous solutions were measured from 293.15 to 323.15 K by using a NDJ-1 rotational viscometer produced by the Shanghai Hengping instrument factory. The measurement ranges for temperature and viscosity are respectively 273.15–383.15 K and 0.1–100 mPa·s. The uncertainty of temperature is ±0.05 K. Taking into account the uncertainty in the CO_2 loading, the uncertainty of the viscosity in this work is about 2%.

3. Results and discussion

The viscosities of CO_2-unloaded and CO_2-loaded MDEA-PZ aqueous solutions are shown in Table 2.

Besides experiments, models that can correctly correlate the viscosities are also important. Among the popularly used equations [21,27,28], the Eyring equation [27] can only quantitatively describe the temperature dependence of viscosity. The Grunberg–Nissan equation [28] can well describe the temperature and amine concentration dependence, however, it is not applicable for CO_2-loaded cases because the contribution of CO_2 loading has not been taken into account. The Weiland equation [21] can simultaneously describe the temperature, amine concentration and CO_2 loading dependences.

When applied to carbonated MDEA-PZ aqueous solutions, the Weiland equation can be expressed as:

$$\eta_{mix} = \frac{w_1}{w_1 + w_2}\eta_1 + \frac{w_2}{w_1 + w_2}\eta_2 \quad (1)$$

where η_{mix} is the viscosity of carbonated aqueous solution, and w_1 and w_2 respectively stand for the mass fractions of MDEA and PZ. η_1 and η_2 are expressed as:

$$\eta_i/\eta_{water} = \exp\left\{\frac{[(a_i w + b_i)T + (c_i w + d_i)]w}{T^2} \times f(\alpha, w)\right\} \quad (2)$$

Table 2
Viscosities of CO_2-unloaded and CO_2-loaded MDEA-PZ aqueous solutions.

w_{MDEA}/w_{PZ}	α	η/(mPa·s)			
		293.15 K	303.15 K	313.15 K	323.15 K
0.475/0.025	0	10.7	7.3	5.1	3.6
	0.1	11.6	7.9	5.5	3.9
	0.2	12.5	8.5	5.9	4.2
	0.3	14.8	10.0	7.0	5.0
	0.4	16.6	11.2	7.9	5.6
	0.5	17.5	11.9	8.4	6.1
	0.6	19.5	13.3	9.5	7.0
0.45/0.05	0	10.1	7.6	5.7	4.3
	0.1	11.9	8.8	6.0	5.0
	0.2	13.5	10.5	6.9	5.5
	0.3	14.7	10.8	7.4	6.4
	0.4	16.7	11.3	7.9	6.7
	0.5	17.6	12.7	9.3	7.0
	0.6	20.1	15.5	12.0	8.0
0.40/0.10	0	12.5	8.9	6.1	3.7
	0.1	13.5	9.3	6.2	4.6
	0.2	15.1	10.9	7.0	5.6
	0.3	16.2	11.5	8.1	6.4
	0.4	17.3	12.0	9.2	8.2
	0.5	19.7	14.9	10.6	9.4
	0.6	20.0	17.6	12.0	11.0
0.35/0.15	0	11.8	8.4	6.0	4.6
	0.1	12.7	9.5	6.5	5.4
	0.2	13.9	10.9	8.0	6.6
	0.3	16.7	11.7	8.4	6.8
	0.4	18.4	12.7	9.4	8.3
	0.5	19.6	15.0	11.9	9.7
	0.6	21.0	16.6	14.0	11.3

where η_{water} is the viscosity of pure water, and $w = w_1 + w_2$ is the total mass fraction of amines. $f(\alpha, w)$ refers to the contribution of CO_2 loading:

$$f(\alpha, w) = \alpha(e_i w + f_i T + g_i) + 1 \quad (3)$$

where a_i, b_i, c_i, d_i, e_i, f_i and g_i are adjustable parameters. For MDEA, $a_1 = -0.1944$, $b_1 = 0.4315$, $c_1 = 80.684$ and $d_1 = 2889.1$ were directly taken from the work of Weiland et al. [21]. The parameters for PZ were regressed by fitting to the viscosities of CO_2-unloaded MDEA-PZ aqueous solutions from Derks et al. [20]. The objective function was expressed as:

$$fs = \sum_{i=1}^{n}\left[1 - \eta^{cal}/\eta^{exp}\right] \times 100\%/n \quad (4)$$

where the superscripts 'exp' and 'cal' respectively stand for the experimental and calculated data, and n is the data numbers. The optimized values are $a_2 = 0.1156$, $b_2 = 8.444$, $c_2 = -9.074$ and $d_2 = 3.224$. The average relative deviation (ARD) is 6.2%.

Figs. 1 and 2 show the viscosities of the CO_2-unloaded MDEA-PZ aqueous solutions calculated from the Weiland equation, and the comparison with experiments [20]. The viscosity increases with the increase of w_{PZ} at a given temperature and a given w_{MDEA}, and exponentially decreases with the increase of temperature at a given w_{PZ} and w_{MDEA}. The Weiland equation correctly captures the amine concentration and temperature dependence of the viscosities, and satisfactorily fits the experimental data, except that some data at low temperatures are underestimated.

To describe the viscosity of CO_2-loaded MDEA-PZ aqueous solutions using the Weiland equation, one should firstly determine the adjustable parameters e_i, f_i and g_i. For MDEA, $e_1 = 0.0106$, $f_1 = 0$ and $g_1 = 80.684$ were directly taken from the work of Weiland et al. [21]. The parameters for PZ were regressed by fitting to the viscosities of CO_2-loaded MDEA-PZ aqueous solutions from this work. The objective function is