Experiment and model for the viscosity of carbonated MDEA–MEA aqueous solutions

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ABSTRACT

The viscosities of carbonated N-methyldiethanolamine (MDEA)–monoethanolamine (MEA) aqueous solutions were measured, with the temperature, mass fraction of amines and CO$_2$ loading (α, mole number of CO$_2$/mole number of MDEA + MEA) respectively ranging from 293.15 K to 343.15 K, 0.2 to 0.5 and 0 to 0.5. A modified Grunberg–Nissan equation was proposed for correlation and prediction of the viscosities of carbonated MDEA–MEA aqueous solutions. The effects of temperature, amine concentration and CO$_2$ loading on the viscosities were demonstrated.

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1. Introduction

In recent decades, atmospheric levels of CO$_2$ have increased rapidly due to the utilization of grand amount of fossil fuel. The reduction of CO$_2$ emission became a global issue [1,2]. Aqueous solutions of alkanol amines including monoethanolamine (MEA), diethanolamine (DEA), 2-amino-2-methyl-1-propanol (AMP) and N-methyldiethanolamine (MDEA) are popularly used for the removal of CO$_2$ from a variety of gas streams [3–12].

Among the alkanol amine series, MDEA takes the advantages of high resistance to thermal and chemical degradation, low solution vapor pressure and low enthalpy of absorption. However, compared with other amines like MEA and DEA, MDEA aqueous solution has a lower absorption rates. Adding small amounts of MEA to an aqueous solution of MDEA has found widespread application in the removal of CO$_2$ [6]. The mixtures of MEA and MDEA preserve relatively high rate of reaction of MEA with CO$_2$, and relatively low enthalpy of reaction of MDEA with CO$_2$, hence lead to higher absorption rates in the absorber column yet lower heat of regeneration in the stripper section.

The viscosities of alkanol amine aqueous solutions are required when designing or simulating an absorption column for CO$_2$ absorption. In particular, solution viscosity is important in the mass transfer rate modeling of absorbers and regenerators because these properties affect the liquid film coefficient for mass transfer. By far, there are some experiments concerning the viscosities of aqueous solutions containing MEA and MDEA [13–20]. For example, Li and Lie [19], and Mandal et al. [20] measured the viscosities of MDEA–MEA aqueous solutions at series of temperatures and amine concentrations (total amine mass fraction = 0.3) and modeled the viscosities with high accuracy. However, the experiments and theoretical work for the viscosities of CO$_2$-loaded amine aqueous solutions are rare [21,22]. Weiland et al. [21] measured the viscosities of carbonated MDEA–MEA aqueous solutions at 298.15 K and proposed a model for the correlation and prediction of their experiments. Amundsen et al. [22] measured the viscosities of carbonated MEA aqueous solutions in a wide temperature ranges and modeled their experiments with high accuracy.

The main purpose of this work is to investigate the viscosities of carbonated MDEA–MEA aqueous solutions in wide temperature and amine concentration ranges, so as to demonstrate the temperature, amine concentration and CO$_2$ loading dependence of the viscosities on the basic of experiments and calculations. To this end, the viscosities of carbonated MDEA–MEA were measured at temperatures from 293.15 K to 343.15 K and CO$_2$ loading from 0 to 0.5. The Grunberg–Nissan equation [23] was modified in this work so that it is able to correlate and predict the viscosities of carbonated aqueous solutions.

2. Experimental

2.1. Materials

Both MDEA and MEA were purchased from Huaxin Chemical Co., with mass purity ≥99%. The sample description is shown in Table 1. They were used without further purification. Aqueous solutions of

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Table 1
Sample description.

Chemical	CAS no.	Purity (in mass fraction %)	Molecular mass	Density (g cm^{-3}) at 293.15 K
MEA	141-43-5	99.4	61.09	1.0179
MDEA	105-59-9	99.5	119.16	1.0377

MDEA–MEA were prepared by adding doubly distilled water. The mass fractions of MEA and MDEA respectively range from 0.05 to 0.2 and 0.15 to 0.45. The total mass fractions were no greater than 0.5.

2.2. Apparatus and procedure

Aqueous solution of MDEA–MEA was put into a volumetric flask immersed in the thermostatic bath (CH-1006) with a built-in stirrer for uniform temperature distribution. The bath temperature was regulated within 0.1 K. CO_2 from a high-pressure tank was inlet into the volumetric flask with a flow rate 300 ml/min. Once the carbonated solution was prepared, varying proportions of the unloaded and loaded solutions were then mixed together to produce a set of samples having a fixed amine-to-water ratio but with varying CO_2 loading.

The mass of CO_2 can be determined by comparing the mass of the unloaded and carbonated solutions. The uncertainty of the electronic balance is ±0.1 mg. The CO_2 loading of the carbonated MEA–MDEA aqueous solution can be expressed as following:

$$\alpha = \frac{n_{CO_2}}{n_{MEA} + n_{MDEA}} \quad (1)$$

where n_{CO_2}, n_{MEA} and n_{MDEA} are the mole number of CO_2, MEA and MDEA, respectively.

The CO_2 loading of the diluted sample can also be obtained from Eq. (1) with n_{CO_2}, n_{MEA} and n_{MDEA} as input. We also determined the CO_2 loadings of some diluted samples using the analysis method based on the precipitation of $BaCO_3$, which has been well documented in the work of Amundsen et al. [22]. The estimated uncertainty in CO_2 loading was less than 2%.The viscosities of the carbonated aqueous solutions were measured by using a NDJ-1 rotational viscometer produced by Shanghai Hengping instrument factory. The measurement ranges for temperature and viscosity are respectively 273.15–383.15 K and 0.1–100 mPa s.

3. Results and discussion

To verify the reliability of the equipment, the viscosities of carbonated MEA aqueous solutions (α from 0.1 to 0.5 and w_{MEA} from 0.2 to 0.4) were measured at 298.15 K and compared with the experimental values from Amundsen et al. [22]. The results are shown in Table 2. The average relative deviation (ARD) between the experiments form this work and those from Amundsen et al. [22] is 2.3%, indicating that the experimental equipment is reliable.

Table 2
Viscosities for the carbonated MEA aqueous solutions at 298.15 K.

	The work of Ref. [22], η'			This work, η		
	$w = 0.2$	$w = 0.3$	$w = 0.4$	$w = 0.2$	$w = 0.3$	$w = 0.4$
0.1	1.8	2.6	4.0	1.72	2.51	3.88
0.2	1.9	2.9	4.6	1.88	2.82	4.69
0.3	1.9	3.1	5.1	1.95	3.18	5.17
0.4	2.1	3.5	6.0	2.14	3.44	5.89
0.5	2.2	3.9	7.0	2.26	3.97	6.93

$$ARD = \sum_{i=1}^{15} \left| 1 - \frac{\eta}{\eta'} \right| \times 100/15 = 2.3\%.$$

The viscosities of unloaded and carbonated MDEA–MEA aqueous solutions at different temperatures, CO_2 loadings and amine concentrations are shown in Table 3.

Besides experiments, models that can correctly correlate and predict the viscosities are also important. Among the popularly used equations [21,23,24], Eyring [24] equation can only quantitatively describe the temperature dependence of viscosity. Grunberg–Nissan equation [23] can well describe the temperature and amine concentration dependences, and Weiland equation [21] can simultaneously describe the temperature, amine concentration and CO_2 loading dependences. Comparison shows [25] that Grunberg–Nissan equation is more accurate for CO_2-unloaded aqueous solutions than Weiland equation, however, it is inapplicable for CO_2-loaded cases because the contribution of CO_2 loading has not been taken into account.

When applied to carbonated MDEA–MEA aqueous solutions, the Weiland equation can be expressed as

$$\eta_{mix} = \frac{w_1}{w_1 + w_2}\eta_1 + \frac{w_2}{w_1 + w_2}\eta_2 \quad (2)$$

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

$$\frac{\eta_i}{\eta_{water}} = \exp\left\{ \frac{[(a_i w + b_i)T + (c_i w + d_i)]w}{T^2} \times f(\alpha, w) \right\} \quad (3)$$

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

$$f(\alpha, w) = \alpha(e_i w + f_i T + g_i) + 1 \quad (4)$$

where a_i, b_i, c_i, d_i, e_i, f_i and g_i are adjustable parameters, as shown in Table 4.

The Grunberg–Nissan equation can be expressed as

$$\ln \eta_{mix} = \sum x_i \ln \eta_i + \sum \sum x_i x_j G_{ij} \quad (5)$$

$$G_{ij} = a_{ij} + b_{ij}T + c_{ij}T^2 \quad (6)$$

where x_i stands for the mole fraction of component i. The model parameters a_{ij}, b_{ij}, c_{ij} can be obtained by fitting to the experimental data of unloaded amine aqueous solutions. In particular, using the viscosities of pure MEA, MDEA and water [19] as input, Mandal et al. [20] regressed these parameters directly from the viscosities of unloaded MDEA–MEA aqueous solutions, as also shown in Table 4.

Fig. 1 shows the viscosities of the unloaded MDEA–MEA aqueous solutions calculated from different models, and the comparison with experiments. One finds that both the Grunberg–Nissan equation and the Weiland equation correctly capture the amine concentration and temperature dependence of the viscosities. The average relative deviations between the predictions and experiments are 8.1% for Grunberg–Nissan equation and 10.5% for Weiland equation, respectively.

To describe the viscosity of carbonated MDEA–MEA aqueous solutions using Grunberg–Nissan equation, there needs an additional formulation of the contribution of CO_2 loading to the viscosity. In this work, an empirical expression of the contribution of CO_2 loading was introduced into the Grunberg–Nissan equation. The modified equation is as following:

$$\ln \eta_{mix} = \sum x_i \ln \eta_i + \sum \sum x_i x_j G_{ij} + (e + f\alpha + g\alpha^2) \quad (7)$$

The model parameters e, f and g in the modified Grunberg–Nissan equation should be regressed by fitting to

Table 3
Viscosity for unloaded and CO_2-loaded MDEA–MEA aqueous solutions.

| w_{MEA}	w_{MDEA}	η (mPa s)					
		293.15 K	303.15 K	313.15 K	323.15 K	333.15 K	343.15 K
$\alpha = 0$							
	0.15	2.12	1.85	1.24	1.01	0.78	0.65
0.05	0.25	3.72	2.68	2.22	1.44	1.06	0.92
	0.35	5.38	3.95	3.46	2.55	1.79	1.44
	0.45	9.60	7.64	5.51	3.89	2.47	2.17
	0.10	2.21	1.72	1.41	0.95	0.81	0.61
0.10	0.20	3.09	2.49	2.05	1.24	1.09	0.82
	0.30	5.55	4.34	3.04	2.22	1.79	1.14
	0.40	9.25	7.03	4.54	3.32	2.93	1.91
	0.05	1.90	1.49	1.13	0.99	0.82	0.66
0.15	0.15	2.76	2.14	1.81	1.51	1.17	0.86
	0.25	4.84	3.22	2.75	2.01	1.75	1.25
	0.35	8.61	6.26	4.25	3.01	2.59	1.67
	0.05	2.22	1.65	1.29	1.02	0.85	0.67
0.20	0.10	2.65	2.05	1.74	1.42	1.07	0.84
	0.20	4.63	3.28	2.46	1.85	1.56	1.23
	0.30	8.01	5.89	4.08	2.77	2.2	1.55
$\alpha = 0.25$							
	0.15	2.15	1.94	1.65	1.29	1.03	0.86
0.05	0.25	4.01	3.2	2.65	2.04	1.32	1.1
	0.35	6.61	4.92	3.57	2.8	2	1.56
	0.45	13.41	9.89	7.06	4.43	3.47	2.51
	0.10	2.89	2.11	1.74	1.22	0.95	0.82
0.10	0.20	4.34	3.33	2.95	2	1.6	1.27
	0.30	6.3	4.81	3.69	2.97	2.19	1.71
	0.40	12.04	8.77	6.23	4.73	3.4	2.5
	0.05	2.8	2.06	1.61	1.17	0.92	0.76
0.15	0.15	4.15	3.01	2.6	1.95	1.51	1.14
	0.25	6.22	4.91	3.89	2.81	2.14	1.67
	0.35	11.91	8.32	5.94	4.31	3.49	2.77
	0.05	2.98	2.28	2.06	1.58	1.33	0.96
0.20	0.10	3.75	3.2	2.55	2.15	1.82	1.39
	0.20	6.04	4.96	3.85	2.96	2.29	1.63
	0.30	11.41	8.12	5.84	4.16	3.26	2.41
$\alpha = 0.50$							
	0.15	3.31	2.64	1.99	1.49	1.28	0.92
0.05	0.25	4.37	3.43	2.41	2	1.72	1.19
	0.35	8.22	5.76	4.28	3.17	2.3	1.83
	0.45	14.59	10.6	7.64	4.89	3.82	2.81
	0.10	3.15	2.36	1.85	1.31	1.22	0.86
0.10	0.20	4.77	3.71	3.08	2.09	1.78	1.44
	0.30	8.23	5.61	3.99	3.15	2.69	1.98
	0.40	14.27	9.45	6.98	5.04	3.98	2.89
	0.05	3	2.19	1.7	1.31	1.09	0.93
0.15	0.15	4.42	3.48	2.07	2.15	1.82	1.26
	0.25	8.3	5.31	4.2	3.06	2.56	2.06
	0.35	13.98	10.17	6.78	5.05	3.96	3.23
	0.05	3.25	2.66	2.08	1.85	1.53	1.1
0.20	0.10	4.24	3.41	2.67	2.48	2.06	1.63
	0.20	6.94	5.88	4.61	3.06	2.79	1.86
	0.30	13.33	9.34	6.33	4.94	3.76	2.86

The uncertainties of temperature and viscosity are respectively ±0.05 K and ±0.01 mPa s.

the experimental viscosities of carbonated MDEA–MEA aqueous solutions. The objective function was expressed as:

$$fs = \sum_{i=1}^{n} \left[1 - \frac{\eta^{\text{cal}}}{\eta^{\text{exp}}} \right] \times 100\% \tag{8}$$

where the superscripts 'exp' and 'cal', respectively stand for the experimental and calculated data, n is the data numbers. The optimized results are shown in Table 3. The average relative deviation (for the cases of $\alpha = 0.25$ and 0.50) is 7.1%. The comparison of the calculated and experimental results is shown in Fig. 2. One finds from this figure that with 12 model parameters as input, the modified Grunberg–Nissan equation correctly captures the temperature and amine concentration dependence of viscosity of carbonated solutions, and fits the experiments fairly good. Compared with the modified Grunberg–Nissan equation, the Weiland equation also correctly describes the effects of amine concentration, temperature and CO_2 loading on the viscosities, the average relative deviation between the experiments and predictions (for the cases of $\alpha = 0.25$ and 0.50) is 10.7%.
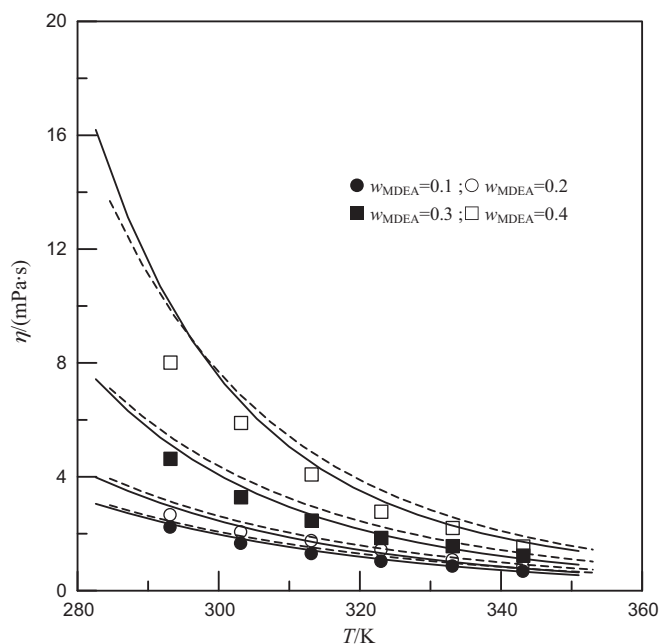
Fig. 1. Comparison of the viscosities of the unloaded solutions from different models. $w_{MEA} = 0.20$. Lines: calculated data. —: from the Grunberg–Nissan equation; - - -: from the Weiland equation. Symbols: experimental data.
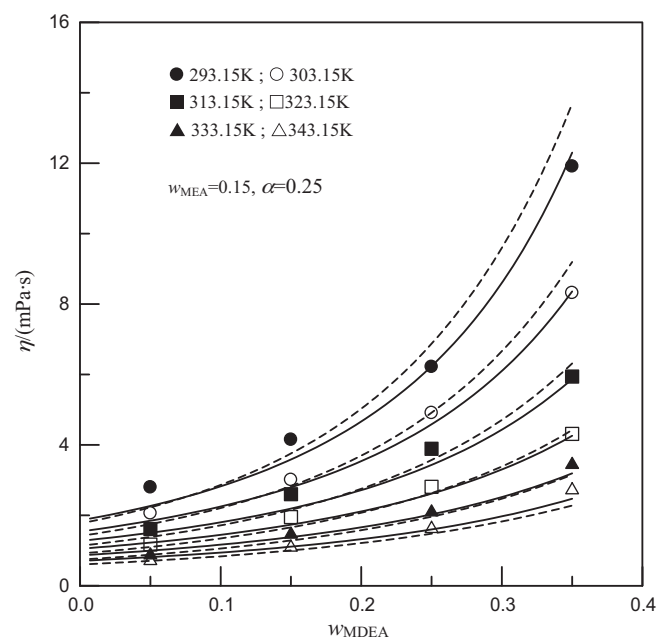

Fig. 2. Comparison of the viscosities of the carbonated solutions from different models. Lines: calculated data. —: from the modified Grunberg–Nissan equation; - - -: from the Weiland equation. Symbols: experimental data.

Table 4
Model parameters for Grunberg–Nissan equation and Weiland equation.

| Parameters	Grunberg–Nissan equation			Weiland equation [21]	
	G_{12} [20]	G_{13} [20]	G_{23} [20]	MEA	MDEA
a	2,061,147.2	−23,598.38	126,845.8	0	−0.1944
b	−12,381.298	196.2777	−625.3264	0	0.4315
c	18.523985	0.3298253	0.8442153	21.184	80.684
d	–	23,730	2889.1		
e	0.0502	0.01015	0.0106		
f	−0.2071	0.0093	0		
g	0.9400	−2.2589	−0.2141		
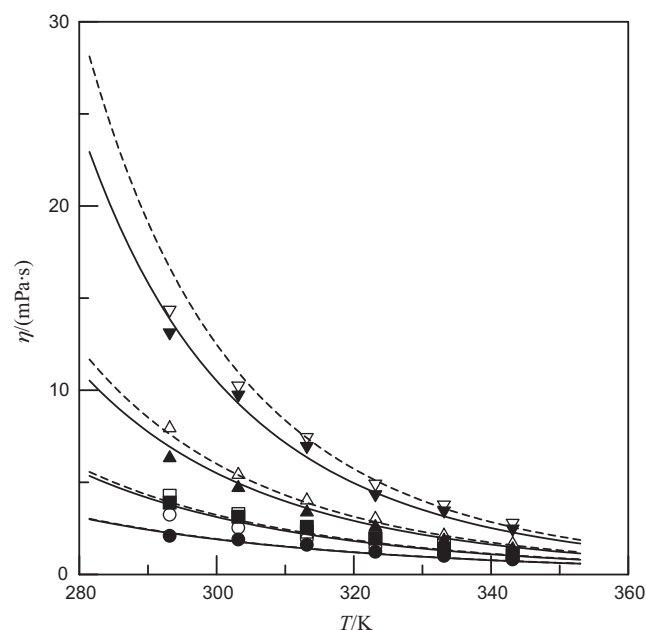
Fig. 3. Effect of CO_2 loading on the viscosities of carbonated MDEA–MEA aqueous solutions, $w_{MEA} = 0.05$. Solid symbols: $\alpha = 0.25$, ● ($w_{MDEA} = 0.15$), ■ ($w_{MDEA} = 0.25$), ▲ ($w_{MDEA} = 0.35$), ▼ ($w_{MDEA} = 0.45$); hollow symbols: $\alpha = 0.50$, ○ ($w_{MDEA} = 0.15$), □ ($w_{MDEA} = 0.25$), △ ($w_{MDEA} = 0.35$), ▽ ($w_{MDEA} = 0.45$). Lines: calculated from the modified Grunberg–Nissan equation, —: $\alpha = 0.25$; - - -: $\alpha = 0.50$.

Fig. 3 shows the CO_2 loading dependence of the viscosity of carbonated MDEA–MEA aqueous solutions. At given temperature and given amine concentrations, with the increase of α, the solubility of CO_2 increases, and the concentration of ions increases subsequently. In general, the increase of the concentration of ions tends to increase the viscosity, hence the viscosity of carbonated MDEA–MEA aqueous solutions increases with increasing α. One may also find that the viscosities increase more rapidly at relatively lower temperatures, in particular, at 343.15 K, in the cases of $w_{MEA} = 0.05$ and $w_{MDEA} = 0.15$, the viscosities corresponding to $\alpha = 0.25$ and 0.5 are respectively 0.86 mPa s and 0.92 mPa s, while

at 293.15 K, they become 2.15 mPa s and 3.31 mPa s, respectively. Figs. 4 and 5 show the temperature and amine concentration dependences of the viscosity of carbonated MDEA–MEA aqueous solutions. One finds that at given α, T and w_{MEA}, the viscosity increases with increasing w_{MDEA} due to the increase of the solubility of CO_2.

4. Summary

The viscosities of carbonated MDEA–MEA aqueous solutions ($\alpha = 0$, 0.25 and 0.5) have been measured in wide temperature and concentration ranges. The experiments have been modeled by using a modified Grunberg–Nissan equation and the results are satisfactory. The effects of temperature, amine concentration and CO_2 loading on the viscosities of carbonated solutions have been demonstrated based on the experiments and calculations. Our results showed that:

(1) By taking into account the contribution of CO_2 loading, the modified Grunberg–Nissan equation can correctly correlate and predict the viscosities of carbonated MDEA–MEA aqueous solutions. The agreement with experiments is satisfactory.
(2) The increase of CO_2 loading tends to increase the viscosity of carbonated MDEA–MEA aqueous solutions due to the increase of ion concentration.
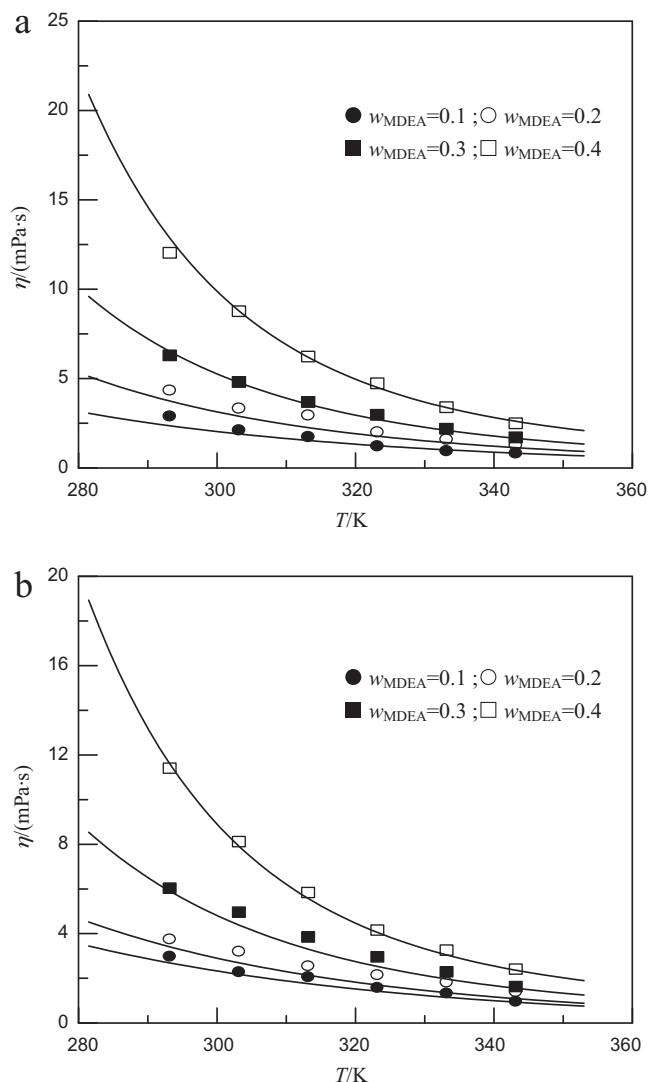
Fig. 4. Effect of temperature on the viscosities of carbonated MDEA–MEA aqueous solutions. $\alpha = 0.25$. (a) $w_{MEA} = 0.10$, (b) $w_{MEA} = 0.20$. Symbols: experimental data, lines: calculated from the modified Grunberg–Nissan equation.

Fig. 5. The same as in Fig. 4, except that $\alpha = 0.5$.

(3) The increases of amine concentration and temperature respectively increase and decrease the viscosity of carbonated MDEA–MEA aqueous solutions.

List of symbols
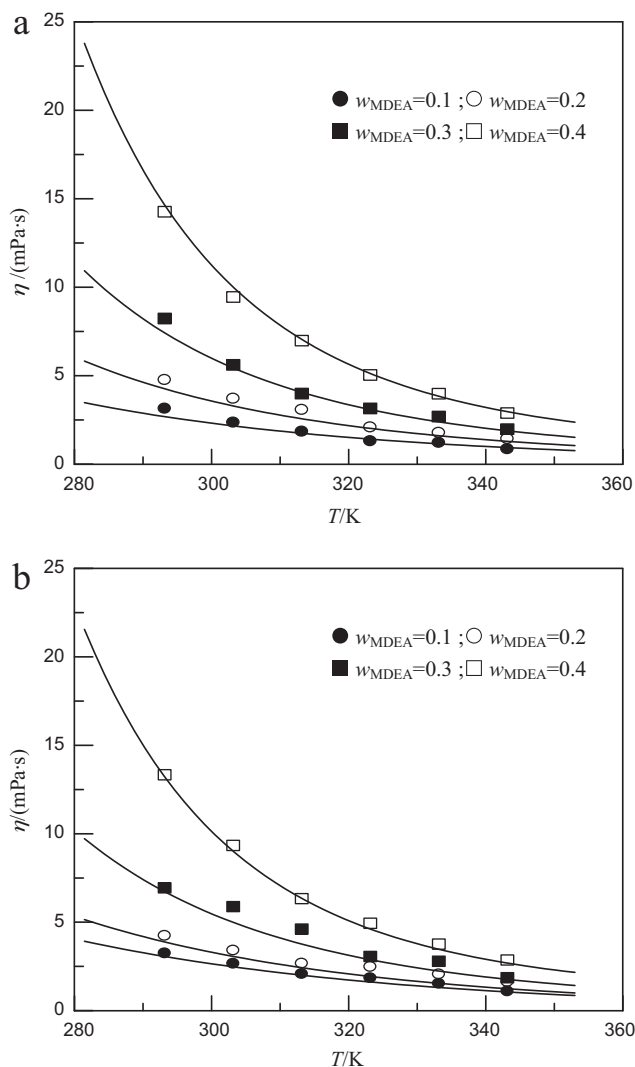
a, b, c, d, e, f, g model parameters
fs objective function
G temperature dependent parameter in Grunberg–Nissan equation
n mole number; data number
T absolute temperature, K
w mass fraction
x mole fraction

Greek letters

α CO$_2$ loading
η viscosity (mPa s)

Superscripts

cal   calculated results
exp   experimental results

Subscripts

1   MEA
2   MDEA
3   water
mix   mixture of MDEA–MDEA–water

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