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Review

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Sterically Hindered Amine-Based Absorbents for the Removal of CO_2 from Gas Streams

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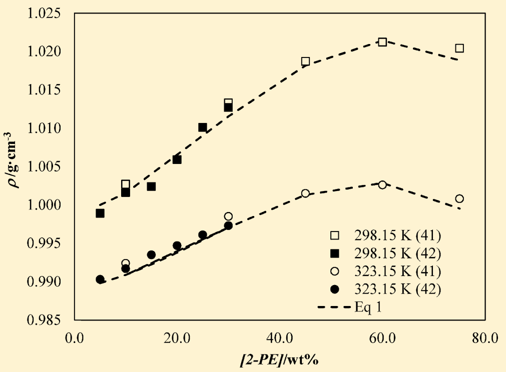
ABSTRACT: The gas absorption process for CO_2 separation from gas streams is of high interest in various applications in chemical, oil, and gas industries, as well as in environmental protection. The choice of a certain amine (single or blended amine) for CO_2 capture is mainly based on the absorption capacity, reaction kinetics, and regenerative potential and facility. The application of sterically hindered amines in gas-treating technology offers absorption capacity, absorption rate, and degradation resistance advantages over conventional amines for CO_2 removal from gases. The aim of this review is to bring an update of different aspects concerning several binary and multicomponent systems of CO_2-sterically hindered amine-based absorbents essential for the design and operation of absorption equipment (physical properties like density, viscosity, vapor pressure, heat capacity and heat of absorption, CO_2 and amine diffusivity, CO_2 absorption capacity and kinetics, regeneration capability).



1. INTRODUCTION

It is well-known that approximately one-third of all anthropogenic CO_2 emissions come from fossil fuels such as coal and oil used for generating energy. In addition, different industrial processes emit large amounts of CO_2 from each plant, such as oil refineries, cement works, and iron production.[1] A typical CO_2 generation rate from power plant is $400 \cdot 10^3$ $kg \cdot h^{-1}$ with stack gas flow rates of 484 $m^3 \cdot s^{-1}$ and approximately 13 % CO_2 (Rangwala, 1996).[2] There is growing political and public concern supported by consensus among the scientific community that global emissions growth will soon drive atmospheric CO_2 concentrations to very high levels, bringing a growing risk of fast climate change. In Canada, the Canadian Environmental Protection Act[3] is the legislative authority that pushes the companies to reduce their greenhouse gas production. The CO_2 emissions could be reduced substantially by capturing and storing CO_2.

Industrially often used alkanolamines are monoethanolamine (MEA), diethanolamine (DEA), *N*-methyldiethanolamine (MDEA), and 2-amino-2-methyl-1-propanol (AMP).[4] The choice of a certain amine (single or blended amine) is mainly based on the absorption capacity, reaction kinetics, and regenerative potential and facility. The key advantage of the primary and secondary alkanolamines such as MEA and DEA is their fast reactivity due to the formation of stable carbamates. Conversely, this will lead to very high solvent regeneration costs. On the absorption capacity side, they have the drawback of a relatively low CO_2 loading (limited to 0.5 mol $CO_2 \cdot$mol amine^{-1}). Tertiary alkanolamines, like MDEA, have a low reactivity with respect to CO_2, due to the exclusive formation of bicarbonates by CO_2 hydrolysis. However, this will lead to a very low solvent regeneration cost. Another advantage of these amines is the high CO_2 theoretical loading capacity of 1 mol of $CO_2 \cdot$mol of amine^{-1}. The application of sterically hindered amines (SHAs), for example, AMP, in gas-treating technology offers absorption capacity, absorption rate, selectivity, and degradation resistance advantages over conventional amines for CO_2 removal from gases (Sartori and Savage, 1983;[5] Say et al., 1984;[6] Goldstein et al., 1984[7]). Due to the hindrance of the bulky group adjacent to the amino group, sterically hindered amines form unstable carbamates. The hydrolysis of the voluminous carbamates leads to a preferential bicarbonate formation process, resulting in the theoretical loading capacity up to 1.0. Significantly higher reaction kinetics in respect to tertiary amines, coupled with a low solvent regeneration cost offer to SHA important industrial advantages. The use of blended alkanolamine solutions has also become very attractive because of the combination of each amine advantage: a fast reactivity from a primary or secondary alkanolamine (e.g., MEA, DEA) coupled with the high absorption capacity and low solvent regeneration cost from a tertiary or sterically hindered alkanolamine (e.g., MDEA, AMP).

The aim of this review is to bring an update of different aspects concerning several binary and multicomponent systems of CO_2-sterically hindered amine-based absorbents essential for the design and operation of absorption equipment (physical properties like density, viscosity, vapor pressure, heat capacity and heat of absorption, CO_2 and amine diffusivity, CO_2 absorption capacity and kinetics, regeneration capability).

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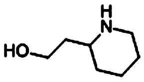
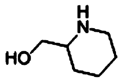
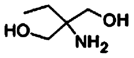
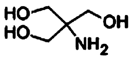
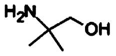
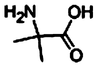
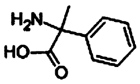
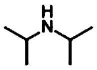
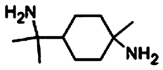
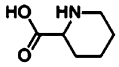
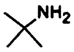
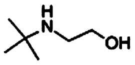
Table 1. Structure of Several Sterically Hindered Amines

Acronym	Name	CAS number	Structure	M/g·mol^{-1}
2-PE	2-piperidineethanol	1484-84-0		129.20
2-PM	2-piperidinemethanol	3433-37-2		115.17
AEPD	2-amino-2-ethyl-1,3-propanediol	115-70-8		119.16
AHPD	2-amino-2-hydroxymethyl-1,3-propanediol	77-86-1		121.14
AMP	2-amino-2-methyl-1-propanol	124-68-5		89.14
AMPA	2-amino-2-methylpropionic acid	62-57-7		103.12
AMPD	2-amino-2-methyl-1,3-propanediol	115-69-5		105.14
APPA	2-amino-2-phenylpropionic acid	565-07-1		165.19
DIPA	diisopropylamine	108-18-9		101.19
MDA	1,8-p-menthanediamine	80-52-4		170.30
PA	pipecolinic acid	4043-87-2		129.16
TBA	tert-butylamine	75-64-9		73.14
TBAE	2-(tert-butylamino)ethanol	4620-70-6		117.19

2. STRUCTURE AND PROPERTIES OF SHAS

2.1. Structure of SHAs. A hindered amine was originally defined by Sartori and Savage (1983)[5] as an amine belonging to one of the following categories:

(i) a primary amine in which the amino group is attached to a tertiary carbon;
(ii) a secondary amine in which the amino group is attached to at least one secondary or tertiary carbon.

An example of SHA, the well-known AMP, is the hindered form of MEA obtained by substituting two hydrogen atoms attached to the α-carbon atom to the amino group in MEA by two methyl groups. These substitutions influence significantly amine properties and absorption capacity.[8] All sterically hindered amines found in the literature that were linked to CO_2 absorption (solubility, kinetics) or for which any other properties necessary to operate a gas–liquid contactor are important (density, viscosity, superficial tension, vapor pressure) are given in Table 1.

2.2. Physical Properties of Single and Mixed SHA Aqueous Mixtures. Physical properties of amine solutions, as it will be explained in the following sections, are necessary to design properly CO_2 absorption and regeneration processes. It should be mentioned here that, without indication, all data presented in the next sections are for fresh (unloaded) solutions. It seems however that CO_2 loading could have a significant effect on parameter values for conventional amines (MEA, DEA, and MDEA), as it can be demonstrated in Weiland et al. (1998).[9] Unfortunately, except for some studies

Table 2. Density Data of AMP Systems

	T	ΔT	[AMP]	[amine[a]]	Δ[AM[b]]	$\Delta\rho$	
system	K	K	wt %	wt %	wt %	$g\cdot cm^{-3}$	reference
AMP	313		2–27				14
AMP	293–363	0.05	9–100			$1\cdot10^{-5}$	16
AMP	303		1–45			$5\cdot10^{-5}$	17
AMP	288–313		4.5–18				18
AMP	303–353	0.05	100			0.50 %	11
AMP	303–353		100			0.002 %	19
AMP	293–353		40–99			0.002 %	19
AMP	298–353		4–100			$8\cdot10^{-5}$	20
AMP	298–343		21–100		0.05	$5\cdot10^{-5}$	22
AMP	313–333	0.002	100			$6\cdot10^{-4}$	21
AMP	293–353		100				12
AMP	298–323		100		0.2	$5\cdot10^{-5}$	13
AMP	298		15–30		0.01 %		23
AMP + DEA	303–353	0.05	5–24	5–24		0.05 %	26
AMP + DEA	313–333	0.002	5–95	5–95		$6\cdot10^{-4}$	21
AMP + DEA	293–323	0.2	21–28.5	1.5–9		0.04 %	25
AMP + DEA	313	0.2	25.5–30	1.5–4.5		0.04 %	30
AMP + DEA	303–313	0.05	9–13	1–4	0.2	0.05 %	31
AMP + DEA	293–313		1.7–25	2–28			32
AMP + EMEA	298–323		10–50	10–40	0.2	$5\cdot10^{-5}$	13
AMP + MDEA	283–353	0.05	10–50	10–50	0.05 %	0.004	33
AMP + MDEA	283–333	0.05	25	5–20	0.05	0.001	34
AMP + MDEA	313–333	0.002	5–50	5–50		$6\cdot10^{-4}$	21
AMP + MEA	303–353	0.05	5–30	5–24		0.50 %	11
AMP + MEA	293–323	0.2	21–30	1.5–9		0.04 %	25
AMP + MEA	302–353	0.05	10	10		0.05 %	26
AMP + MEA	303–313	0.05	13–15	1–4	0.2	0.05 %	28
AMP + MEA	313	0.2	25.5–30	1.5–4.5		0.04 %	29
AMP + MMEA	298–323		10–50	10–40	0.20	$5\cdot10^{-5}$	13
AMP + MMEA	298–323	0.04	18–27	3–12	0.007 %	$7.7\cdot10^{-4}$	38
AMP + NMP	313–333	0.002	5–60	5–60		$6\cdot10^{-4}$	21
AMP + Pz	303–313	0.05	9–13	1–3.5	0.2	0.05 %	35
AMP + Pz	288–333	0.1	18–27	3–12		$4.8\cdot10^{-4}$	36
AMP + Pz	298–333	0.1	22–30	2–8		$4.5\cdot10^{-5}$	37
AMP + MDEA + DEA	303–343	0.005	2–10	*c*	0.002	0.01 %	39

[a] DEA, EMEA, MDEA, MEA, MMEA, NMP, or Pz. [b] Concentration uncertainty of all amines in solutions. [c] 32.5 (MDEA) + 12.5 (DEA).

concerning the heat of absorption and the vapor pressure, information concerning the loading effect on SHA solution properties is extremely scarce, and future research on the topic would be very welcome.

2.2.1. Density and Viscosity. Knowledge of physical properties like density and viscosity of solutions is necessary for the operation of process equipment such as pumps and heat exchangers as well as for the design of gas–liquid contactors. In addition, these data are useful for estimating the liquid diffusivity and reaction rate constant, for example when a wetted-wall column is used for kinetic studies. Solution density and viscosity are also important in the mass transfer rate modeling of absorbers and regenerators because these properties affect the liquid film coefficient for mass transfer, k_L. Viscosity was also found to significantly affect membrane contactor performance as mentioned by Lin et al. (2008).[10] Tables 2 and 3 report, respectively, all density information found in the literature concerning AMP and the various SHA (other than AMP). In the same way, Tables 4 and 5 concern viscosity data. AMP is the most studied SHA, and this is reflected by the large amount of reported density and viscosity values. More than 30 articles giving densities and/or viscosities were found in the open literature concerning this alkanolamine. Therefore, AMP-based systems will be discussed in a separate section. For SHA solutions under a temperature range related to CO_2 capture and regeneration, it was found that the values of density and viscosity data are almost always in the range of (0.85 to 1.11) $g\cdot cm^{-3}$ and (0.40 to 8.0) mPa·s (total amine concentration less than 40 wt %), respectively.

2.2.1.1. AMP Systems. 2.2.1.1.1. Pure and Binary Systems: AMP and AMP + H_2O. Li and Lie (1994)[11] reported densities and viscosities of pure AMP from (303 to 353) K to correlate tertiary systems containing AMP by a Redlich–Kister equation for density and a Grunberg and Nissan equation for viscosity. Kundu et al. (2003)[12] does not report experimental data but derived an empirical expression to calculate pure AMP density at (293 to 353) K. Álvarez et al. (2006)[13] measured densities as well as kinematic viscosities of pure AMP at temperatures from (298.15 to 323.15) K. Pure AMP data were also reported along with the aqueous binary data, as it will be mentioned further.

Yih and Shen (1988)[14] were among the first to report some density and viscosity data for the aqueous binary system, being necessary for kinetic studies using a wetted-wall column. The

Table 3. Density Data of Various SHA Systems

system	T	ΔT	[SHA]	[amine[a]]	Δ[AM[b]]	$\Delta\rho$	reference
	K	K	wt %	wt %	wt %	$g\cdot cm^{-3}$	
2-PE	313		1–13				40
2-PE	298–358	0.05	10–100			$1\cdot 10^{-5}$	41
2-PE	313–333	0.002	30–100			$6\cdot 10^{-4}$	21
2-PE	288–333	0.2	5–30			0.06 %	42
2-PE + DEA	313	0.002	5–50	5–50		$6\cdot 10^{-4}$	21
2-PE + DEA	288–333	0.2	3–27	3–27		0.06 %	42
2-PE + MDEA	313–333	0.002	5–60	5–60		$6\cdot 10^{-4}$	21
2-PE + MEA	303–353	0.05	5–24	5–24		0.05 %	26
2-PE + MEA	288–333	0.2	3–27	3–27		0.06 %	42
2-PE + Pz	288–333	0.1	18–27	3–12	0.007 %	$3.7\cdot 10^{-4}$	43
2-PE + TMS	293–358	0.05	10–65	2–44		$1\cdot 10^{-4}$	44
AEPD	303–318		5–25				45
AEPD	303–343	0.05	20–100			$2\cdot 10^{-4}$	46
AHPD	303–343	0.05	5–25			$3\cdot 10^{-4}$	49
AHPD	283–313	0.1	0.2–10		0.02 %	$3\cdot 10^{-4}$	50
AHPD	298–323	0.3	2.2–21.7			$3.5\cdot 10^{-5}$	51
AHPD + Pz	303–323	0.1	11.8	1–3.5		$3\cdot 10^{-4}$	52
AMPD	303–343	0.01	10–30			$4\cdot 10^{-5}$	47

[a] DEA, MDEA, MEA, Pz, or TMS. [b] Concentration uncertainty of all amines in solutions.

Table 4. Viscosity Data of AMP Systems

system	T	ΔT	[AMP]	[amine[a]]	Δ[AM[b]]	$\Delta\mu$	reference
	K	K	wt %	wt %	wt %	mPa·s	
AMP	313		2–27				14
AMP	298		2–22				15
AMP	296–350	0.05	18–27			0.001	16
AMP	303		1–35.5			$1\cdot 10^{-3}$	17
AMP	294–318		4.5–18				18
AMP	303–353	0.05	100			1.0 %	11
AMP	298–343	0.01	21–100		0.05	0.50 %	22
AMP	298–323	0.05	100		0.20	$5\cdot 10^{-4}$[c]	13
AMP + DEA	303–353	0.05	5–24	5–24	0.2	1.0 %	27
AMP + DEA	293–323	0.2	21–28.5	1.5–9		0.03 %	25
AMP + DEA	293–323	0.05	2–14	2–17	0.02 %	0.2 %	24
AMP + DEA	313	0.2	25–30	1.5–4.5		0.03 %	30
AMP + DEA	303–313	0.05	9–13	1–4	0.2	1.0 %	31
AMP + DEA	293–313		1.7–25	2–29			32
AMP + EMEA	298–323	0.05	10–50	10–40	0.2	$5\cdot 10^{-4}$[c]	13
AMP + MDEA	283–333	0.05	5–50	5–50	0.05 %	0.4 %[d]	33
AMP + MEA	303–353	0.05	5–30	5–24		1.0 %	11
AMP + MEA	293–323	0.05	2–15	1–10	0.02 %	0.2 %	24
AMP + MEA	293–323	0.2	21–30	1.5–9		0.03 %	25
AMP + MEA	303–353	0.05	10	10	0.2	1.0 %	27
AMP + MEA	303–313	0.05	13–15	0.5–2.5	0.2	1.0 %	28
AMP + MEA	313	0.2	25.5–30	1.5–4.5		0.03 %	29
AMP + MMEA	298–323	0.05	10–50	10–40	0.2	$5\cdot 10^{-4}$[c]	13
AMP + Pz	303–313		9–13	1–3.5	0.2	1.0 %	35
AMP + Pz	288–333	0.1	18–27	3–12		0.005	36
AMP + Pz	298–333	0.1	22–30	2–8		1.0 %	37
AMP + MDEA + DEA	303–333	0.005	2–10	[e]	0.002	0.3 %	39

[a] DEA, EMEA, MDEA, MEA, MMEA, or Pz. [b] Concentration uncertainty of all amines in solutions. [c] Value in $mm^2\cdot s^{-1}$. [d] Kinematic viscosity. [e] 32.5 (MDEA) + 12.5 (DEA).

amine concentration was varied between (0.258 and 3.0) $kmol\cdot m^{-1}$ ((2 to 27) wt %), and the temperature was kept at 313 K. Bosch et al. (1990)[15] reported later viscosity of AMP aqueous solutions of concentrations between (0.258 and 2.484) $kmol\cdot m^{-3}$ ((2 to 22) wt %) at 298 K. Xu et al. (1991)[16] measured densities and viscosities over a large temperature and concentration range ((293 to 363) K and (9.05 to 100) wt %). Data were found in good agreement with those by Yih and Shen (1988).[14] However, at around 298 K and 18 wt %, viscosities differed from those of Bosch et al. (1990).[15] Littel et al. (1992)[17]

Table 5. Viscosity Data of Various SHA Systems

	T	ΔT	[SHA]	[amine[a]]	Δ[AM[b]]	$\Delta\mu$	
system	K	K	wt %	wt %	wt %	mPa·s	reference
2-PE	313		1−13				40
2-PE	298−358	0.05	10−100			0.001	41
2-PE	288−333	0.2	5−30			0.69 %	42
2-PE + DEA	288−333	0.2	3−27	3−27		0.69 %	42
2-PE + MEA	288−333	0.2	3−27	3−27		0.69 %	42
2-PE + MEA	303−353	0.05	5−24	5−24	0.2	1.0 %	27
2-PE + Pz	288−333	0.1	18−27	3−12	0.007 %	0.005	43
2-PE + TMS	293−364	0.05	45−55	10−40		0.001	44
AEPD	303−318		5−25				45
AEPD	303−343	0.05	20−80			1 %[c]	46
AHPD	303−343	0.05	5 −25			1 %[c]	49
AHPD	283−313	0.1	0.2−10		0.02 %	1.5 %[c]	50
AHPD	298−323	0.3	2.2−21.7			1 %	51
AHPD + Pz	303−323	0.1	11.8	1−3.5		2 %	52
AMPD	303−343	0.05	10−30			0.5 %[c]	47

[a] DEA, MEA, Pz, or TMS. [b] Concentration uncertainty of all amines in solutions. [c] Kinematic viscosity.

presented polynomial equations to calculate density and viscosity values at 303 K and for concentrations up to 5.009 kmol·m^{-3} (45 wt %) and 3.979 kmol·m^{-3} (35.5 wt %), respectively. However, these two correlations are not very useful as they are limited to one temperature only and they require concentration expressed in molarity instead of molality or mass fraction. Saha et al. (1993)[18] measured viscosity values at temperatures between (294 and 318) K and for AMP concentrations of (0.5 to 2.0) kmol·m^{-3} (4.5 to 18 wt %). Density values were unfortunately only graphically represented over the same concentration range and for temperatures between (288 and 313) K. Zhang et al. (2002)[19] measured densities for aqueous AMP solutions (293.15 to 353.15 K) and pure AMP (303.15 to 353.15 K). All reported densities for the aqueous solutions are relative to the density of pure water at the same temperature. The work by Chan et al. (2002)[20] represents one of those reporting the most density values for the aqueous binary system over a large temperature and concentration range ((298 to 353) K and (4 to 100) wt %). Data of that work were found to be excellent agreement with those of Zhang et al. (2002)[19] and Aguila-Hernandez et al. (2001).[21] Henni et al. (2003)[22] reported density and viscosity of aqueous solutions at six temperatures in the range (298 to 343) K and over a wide concentration range ((21 to 100) wt %). Pure AMP densities were found to be in excellent agreement, but consistently higher, than those by Li and Lie (1994),[11] Zhang et al. (2002),[19] and Aguila-Hernandez et al. (2001).[21] On average, the reported experimental values were 0.17 % higher than those of Li and Lie (1994),[11] well below their reported accuracy of 0.5 % and 0.24 % higher than those of Aguila-Hernandez et al. (2001).[21] The only data available at high pressure were given for AMP densities at 298.32 K and concentrations of (15 and 30) wt %.[23]

2.2.1.1.2. *Tertiary and Other Systems AMP + Amine(s) +* H_2O. *AMP + MEA +* H_2O. The aqueous system AMP + MEA has been widely studied in the literature. Density and viscosity data for this system were reported mainly by Li and Lie (1994),[11] Chenlo et al. (2001),[24] and Mandal et al. (2003),[25] covering a wide range of temperatures and concentrations. Data reported by Li and Lie (1994)[11] for density and viscosity from (303 to 353) K and concentrations between (20 and 30) wt % were correlated by a Redlich−Kister equation for the density and a Grunberg and Nissan equation for the viscosity. Chenlo et al.[24] measured kinematic viscosities at various concentrations from (0.25 to 2.0) mol·kg^{-1} and temperatures from (293.1 to 323.1) K, but dynamic viscosity values are not available as no density data are given for the studied concentrations and temperature. Densities and viscosities measured by Mandal et al. (2003)[25] at (293 to 323) K for a total amine concentration of 30 wt % were found in good agreement with previous data. For 30 wt % AMP and 24.0 wt % AMP + 6.0 wt % MEA blend, over the temperature range (303 to 323) K, densities showed 0.04 % and 0.05 % deviations, respectively, while viscosities showed 3.02 % and 3.08 % deviations, respectively, from the experimental data of Li and Lie (1994).[11] In addition to these three works, some other publications were found reporting density and viscosity values over a limited range of temperatures and concentrations. Hsu and Li (1997)[26,27] reported densities and viscosities of aqueous mixtures of AMP + MEA over a temperature range of (303 to 353) K and for a 10:10 wt % amine blend. Data were correlated together with those by Li and Lie (1994)[11] using a Redlich−Kister equation for the excess volume and viscosity deviation. Xiao et al. (2000)[28] measured the density and viscosity at (303 and 313) K for solutions containing (1.5 or 1.7) kmol·m^{-3} ((13.5 or 15.3) wt %) AMP with small additions of MEA ((0.1 to 0.4) kmol·m^{-3}; (0.6 to 2.5) wt %). Mandal and Bandyopadhyay (2006)[29] gave the density and viscosity at 313 K for various solutions of 30 wt % AMP, 28.5 wt % AMP + 1.5 wt % MEA, 27 wt % AMP + 3 wt % MEA, and 25.5 wt % AMP + 4.5 wt % MEA. Values were found to be in good agreement with those of Li and Lie (1994)[11] and of Mandal et al. (2003).[25]

AMP + DEA + H_2O. The system AMP + DEA + H_2O has also been widely studied in the literature. Density and viscosity data for this system were mainly reported by Hsu and Li (1997),[26,27] Aguila-Hernández et al. (2001),[21] and Mandal et al. (2003),[25] covering a wide range of temperatures and concentrations. Hsu and Li (1997)[26,27] reported densities and viscosities at (303 to 353) K and total amine concentration of 30 wt % (6:24, 12:18, 18:12, and 24:6 AMP/DEA wt %) and 20 wt % (5:15, 10:10, and 15:5 AMP/DEA wt %). At constant temperature, the increase of AMP concentration leads to the decrease in density and the increase in viscosity. Aguila-Hernández et al. (2001)[21] measured density at (313.15, 323.15, and 333.15) K, and the total amine concentration was in the range of (30 to 95) wt %. The correlations made by Hsu and Li

(1997)[26] applied to data of Aguila-Hernández et al. (2001)[21] were found to represent them with good agreement. Data by Mandal et al. (2003)[25] given at (293 to 323) K and a total amine concentration of 30 wt % were in good agreement with previous data: 0.19 % and 3.12 % deviations, respectively, from experimental density and viscosity data of Hsu and Li (1997)[26,27] for the system 24.0 wt % AMP + 6.0 wt % DEA, over the temperature range (303 to 323) K. In addition to these four works, some other publications were found reporting density and viscosity values over limited range of temperatures and concentrations. Chenlo et al. (2001)[24] reported kinematic viscosities at (0.25 to 2.0) mol·kg^{-1} and between (293.1 and 323.1) K. Mandal et al. (2003)[30] reported densities and viscosities at 313 K for four aqueous blends of total amine concentration of 30 wt %. Wang and Li (2004)[31] reported the density and viscosity of (1.0 and 1.5) kmol·m^{-3} AMP ((9 and 13.5) wt %) aqueous solution containing small additions of DEA ((0.1 to 0.4) kmol·m^{-3}; (1.1 to 4.2) wt %). Mandal and Bandyopadhyay (2005)[32] studied the absorption of CO_2 and H_2S in AMP + DEA aqueous solutions in a wetted-wall column. For complete system characterization, the authors measured density and viscosity for a total amine concentration of 3.0 kmol·m^{-3} and temperatures between (293 and 313) K. Density data showed excellent correspondence with those of Hsu and Li (1997),[26] Mandal et al. (2003),[30] and Aguila-Hernández et al. (2001)[21] while it was possible to observe a good agreement between their viscosity data and those of Hsu and Li (1997).[27]

Other AMP Based Systems. Densities and kinematic viscosities of aqueous blends of AMP + MDEA have been reported by Welsh and Davis (1995)[33] within the temperature range of (283 to 353) K for densities and (283 to 333) K for viscosities for a total amine concentration of 50 wt % for density ((10 to 50) wt % AMP) and (5 to 50) wt % for viscosity. By extending the range of compositions, the same research group published in Davis and Pogainis (1995)[34] densities for aqueous amine solutions of 25 wt % AMP + (5 to 20 wt %) MDEA over the temperature range (283 to 333) K. Aguila-Hernández et al. (2001)[21] published density at (313.15, 323.15, and 333.15) K and for solutions of total amine concentration of (30, 40, and 50) wt %. The same paper also reported the only density data available for the aqueous AMP + NMP system.

Density and viscosity for the aqueous AMP + Pz system were reported by Sun et al. (2005),[35] Paul and Mandal (2006),[36] and Samanta and Bandyopadhyay (2006),[37] covering the temperature range of (288 to 333) K and total amine concentrations between (9 and 30) wt % Pz. Densities and viscosities decreased with increasing temperature and decreasing mass fraction of P_Z in the mixture. For 30 wt % AMP, a 0.04 % deviation was found between density data of Li and Lie (1994)[11] and those by Samanta and Bandyopadhyay (2006).[37] Viscosity values of Paul and Mandal (2006)[36] and Samanta and Bandyopadhyay (2006)[37] showed excellent agreement.

Density and viscosity for aqueous ternary solutions of 2-(methylamino)ethanol (MAE; MMEA) and 2-(ethylamino)-ethanol (EAE; EMEA) with AMP are given by Álvarez et al. (2006)[13] at (298.15 to 323.15) K and a total amine concentration of 50 wt % (AMP/(MMEA or EMEA) wt % ratio was varied from 10:40 to 50:0, with 10 wt % increments). Similar data for density were reported by Venkat et al. (2010)[38] for 30 wt % total amine concentration. It was observed that the density of the ternary mixture decreased with increasing temperature and with decreasing mass fraction of MMEA in the mixtures. No similar data are available for viscosity.

Only one quaternary system was studied in the literature. Density and viscosity were reported between (303.15 and 343.15) K for aqueous solutions of three alkanolamines composed by 32.5 wt % MDEA + 12.5 wt % DEA + ((2, 4, 6, 8, or 10) wt %) AMP.[39] Since the pure AMP density was always lower than that of DEA or MDEA in the range of temperature considered, the density values of the studied solutions decreased as the AMP concentration increased. It was also found that the viscosity values increased as the AMP concentration increased. Equations were developed to allow the calculation of density and viscosity for aqueous solutions of MDEA and DEA as a function of AMP concentration and temperature.

2.2.1.2. Other SHA Systems. 2-PE Systems. Data for binary aqueous 2-PE systems were given by Shen et al. (1991),[40] Xu et al. (1992),[41] Aguila-Hernández et al. (2001),[21] and Paul and Mandal (2006).[42] Densities for all concentrations and temperatures were found to be in good agreement when coming from Shen et al. (1991),[40] Xu et al. (1992),[41] and Paul and Mandal (2006).[42] For aqueous solutions of 10 wt % and 30 wt % 2-PE over the temperatures of (298 and 323) K, densities reported by Paul and Mandal (2006)[42] are different respectively only by (0.09 and 0.08) % from those of Xu et al.[41] Data from Aguila-Hernández et al. (2001)[21] agreed well with the others at 313 K but were significantly lower at temperatures of (323.15 and 333.15) K. Xu et al. (1992)[41] stated that viscosity of aqueous 2-PE solutions is difficult to correlate or estimate, since in solution 2-PE has not only polarity but also molecule association effects. A comparison between viscosity data by Xu et al. (1992)[41] and Paul and Mandal (2006)[42] reported for 10 wt % and 30 wt % 2-PE over a temperature range of (298 to 313) K showed, respectively, 0.60 % and 3.27 % deviations. A comparison between viscosity data of Shen et al. (1991)[40] and Paul and Mandal (2006)[42] was possible at 313 K and showed only a mean deviation of 0.90 % indicating good correlation between these data.

Mixtures between 2-PE and commonly used CO_2 absorbents like MEA, DEA, MDEA, and piperazine (Pz) have also been of interest in the literature.

The system 2-PE + MEA was first considered by Hsu and Li (1997)[26,27] who reported densities[26] and viscosities[27] between (303 and 353) K for systems containing 30 wt % total amine (6:24, 12:18, 18:12, and 24:6 wt % of 2-PE and MEA, respectively) and 20 wt % total amine (5:15, 10:10, and 15:5 wt % of 2-PE and MEA, respectively). It was found that, for all temperatures, the increase in MEA concentration in the blend leads to an increase of the density and a decrease of the viscosity. Since 1997, the only data for this system were given by Paul and Mandal (2006).[42] The authors measured densities and viscosities between (288 and 333) K for a 30 wt % total amine concentration. At (303, 313, 323, and 333) K, density data showed 0.03 %, 0.06 %, 0.10 %, and 0.17 % deviations, respectively, from those reported by Hsu and Li (1997),[26] while viscosity data showed 0.68 %, 0.67 %, 0.77 %, and 0.85 % deviations, respectively, from those reported by Hsu and Li (1997),[27] which is quite satisfying.

The density for the system 2-PE + DEA was measured by Aguila-Hernández et al. (2001)[21] at 313 K (total amine concentration varying between (30 and 50) wt %) and by Paul and Mandal (2006)[42] between (288 and 333) K (total amine concentration kept at 30 wt %). For all temperatures, densities increased with the increase of DEA concentration in the blend. At 313 K and for a total amine content of 30 wt %, experimental data by Paul and Mandal (2006)[42] diverged at low 2-PE wt % ratio from data of Aguila-Hernández et al. (2001)[21]

but became similar for concentrations above 20 wt % of 2-PE. For this mixture, the only data available for viscosity are reported by Paul and Mandal (2006)[42] between (288 and 333) K and for a total amine concentration of 30 wt %. No similar data are then available in the open literature for comparison.

For the system 2-PE + MDEA, the only data available concern density at (313.15, 323.15, and 333.15) K, for total amine concentration of (30 to 60) wt %.[21] It was found that, for all temperatures, densities increase as the MDEA concentration increases. No similar data are available for comparison.

Densities and viscosities for the aqueous system 2-PE + Pz were reported by Paul and Mandal (2006)[43] between (288 and 333) K and for total amine mass fraction of 30 %. At constant temperature, the increase of Pz concentration in the blend leads to an increase in density and a decrease in viscosity. No similar data are available for comparison.

Mixed chemical/physical solvents can also been used to remove acid gases from gas streams. They combine the advantages of chemical (usually, aqueous solutions of alkanolamines) and physical solvents (usually, organic compounds with elevated boiling points). Xu et al. (1993)[44] reported and correlated densities and viscosities of aqueous blends of 2-PE and sulfolane (TMS), a physical solvent. At 298 K, densities and viscosities are given for various aqueous solution of 2-PE ((10 to 65) wt %) + TMS ((1.82 to 44.44) wt %). For blends of 45 wt % 2-PE + 40 wt % TMS and 55 wt % 2-PE + 10 wt % TMS, data were measured between (293 and 358) K for densities and over (293 to 364) K for viscosities. No similar data are available in the open literature for comparison.

AEPD Systems. Density and viscosity data for aqueous AEPD systems are very scarce in the open literature. Only two publications from the same research group[45,46] were found to report useful information. Yoon et al. (2002)[45] reported density and viscosity for AEPD for solution of (5 to 25) wt % by 5 wt % increments and from (303.15 to 318.15) K. The second publication[46] provided additional data by extending the range of concentration ((20 to 100) and (20 to 80) wt % AEPD for density and viscosity measurements, respectively) and temperature (up to 343.15 K).

AMPD Systems. Density and viscosity data for aqueous AMPD system are even scarcer than those concerning the AEPD system. Only one publication was found giving useful information. Baek et al. (2000)[47] published density and viscosity data of the AMPD binary system of (10, 20, and 30) wt % and over a temperature range of (303 to 343) K. Data were correlated with a polynomial equation for densities and an exponential one for viscosities. The maximum deviations between the measured and calculated data were less than 0.005 % for densities and 0.3 % for viscosities. Data by Baek et al. (2000)[47] were taken by Yoon et al. (2003)[48] in their kinetic study using a wetted-wall column absorber.

AHPD Systems. The system containing AHPD was quite well covered in the literature. Park et al. (2002)[49] measured densities and viscosities of aqueous AHPD solutions between (303.15 and 343.15) K and for AHPD concentrations ranging from (5 to 25) wt %. Le Tourneux et al. (2008)[50] brought new experimental data for solutions of concentrations between (0.15 and 10) wt % AHPD and temperatures of (283.15 to 313.15) K. The low concentration range was compatible with aqueous solutions required for developing an enzymatic CO_2 capture process. Density and viscosity values for AHPD aqueous solution of 10 wt % at (303.15 and 313.15) K are in excellent agreement with the results reported by Park et al. (2002)[49] (average absolute deviation of 0.025 % for density and 1.3 % for viscosity). Paul et al.[51] reported polynomial equations (no tabulated results) of density and viscosity of aqueous AHPD solutions under a temperature range from (298 to 323) K. The concentration of AHPD in the solution was varied between (2.17 and 21.7) wt %. For 10 wt % AHPD solution and over the temperatures of (298 to 313) K, density and viscosity data showed good agreement with respectively 0.18 % and 2.65 % deviations from data of Le Tourneux et al. (2008).[50] The only ternary system involving AHPD was considered by Bougie et al. (2009)[52] who measured density and viscosity of aqueous AHPD + Pz solutions containing 1 kmol·m^{-3} AHPD (11.8 wt %) and small amounts of piperazine ((0.1 to 0.4) kmol·m^{-3}; 0.8 to 3.4 wt %) at temperatures between (303.15 and 323.15) K. No similar data are available for comparison.

2.2.1.3. Density and Viscosity Correlations. Only reliable data from the available references were correlated using simple polynomial linear equations. They can be very useful for determining data at desired temperatures and concentrations in the ranges corresponding to data given in Tables 2 to 5 (information about data used for correlations are given in Sections 2.2.1.3.1 and 2.2.1.3.2).

2.2.1.3.1. Density Correlations. For pure and binary systems (SHA + H_2O), all of the references indicated in Tables 2 and 3 were used in our database at the exception of (i) for AMP: Littel et al. (1992),[17] Kundu et al. (2003),[12] Saha et al. (1993),[18] and Arcis et al. (2007),[23] (ii) for 2-PE: Aguila-Hernández et al. (2001)[21] at (323.15 and 333.15) K, and (iii) for AHPD: Paul et al. (2009)[51] for the reasons mentioned in Sections 2.2.1.1 and 2.2.1.2.

The equation correlating the selected pure and binary density data for these sterically hindered amines, where w is the amine mass percentage and T the absolute temperature, is the following:

$$\rho/\mathrm{g{\cdot}cm^{-3}} = \sum_{i=0}^{1} [a_i + b_i{\cdot}(w/\mathrm{wt\,\%}) + c_i{\cdot}(w/\mathrm{wt\,\%})^2 + d_i{\cdot}(w/\mathrm{wt\,\%})^3]{\cdot}(T/\mathrm{K})^{2i} \tag{1}$$

Table 6 gives the coefficients of eq 1 along with the determination coefficient (r^2) and the overall average deviation percentage (OAD %) of the calculated data relatively to the literature data. It should be mention that only the statistically significant coefficients were found; the others were equal to zero. This will apply also for the other presented correlations.

For ternary systems (SHA + other + H_2O), all of the references indicated in Tables 2 and 3 were used in our database with the exception of (i) for AMP + MDEA: the first data of Davis and Pogainis (1995)[34] for 25 wt % AMP + 5 wt % MDEA at 333.15 K which seem odd. The equation correlating the selected ternary density data, where w_1 is the mass percentage of the SHA, w_2 is the mass percentage of the other species, and T the absolute temperature, is the following:

$$\rho/\mathrm{g{\cdot}cm^{-3}} = \sum_{i=0}^{1} \left[a_i + \frac{b_i}{T/\mathrm{K}} + c_i{\cdot}(w_1/\mathrm{wt\,\%})^{i+1} + d_i{\cdot}(w_2/\mathrm{wt\,\%})^{i+1} + e_i{\cdot}(w_1/\mathrm{wt\,\%}{\cdot}w_2/\mathrm{wt\,\%})^{i+1} \right]{\cdot}(T/\mathrm{K})^{2i} \tag{2}$$

Table 6. Density Correlation Coefficients of Equation 1 for Binary Aqueous Amine Systems

	binary aqueous SHA systems				
parameter	2-PE	AEPD	AHPD	AMPD	AMP
a_0	1.04689	1.02865	1.05390	1.05608	1.06915
b_0	$1.49927 \cdot 10^{-3}$	$3.57266 \cdot 10^{-3}$	$2.56901 \cdot 10^{-3}$	$1.96949 \cdot 10^{-3}$	$6.44832 \cdot 10^{-4}$
c_0	$8.34750 \cdot 10^{-6}$	$-1.91885 \cdot 10^{-5}$			
d_0	$-1.82209 \cdot 10^{-7}$				$-8.30901 \cdot 10^{-8}$
a_1	$-5.54067 \cdot 10^{-7}$	$-4.85143 \cdot 10^{-7}$	$-6.40281 \cdot 10^{-7}$	$-6.65693 \cdot 10^{-7}$	$-7.81603 \cdot 10^{-7}$
b_1	$-1.32719 \cdot 10^{-8}$	$-1.75701 \cdot 10^{-8}$		$-5.50806 \cdot 10^{-9}$	$-8.45613 \cdot 10^{-9}$
c_1		$1.08868 \cdot 10^{-10}$			$2.75376 \cdot 10^{-11}$
d_1	$7.24406 \cdot 10^{-13}$				
r^2	0.9881	0.9992	0.9949	0.9992	0.9987
OAD %	0.08	0.06	0.11	0.03	0.10

Table 7. Density Correlation Coefficients of Equation 2 for Ternary Aqueous Amine Systems without AMP

	ternary systems without AMP					
parameter	2-PE + DEA	2-PE + MDEA	2-PE + MEA	2-PE + Pz	2-PE + TMS	AHPD + Pz
a_0	1.41097	1.08935	1.20039	1.10759	1.09639	1.02820
b_0	$-6.74390 \cdot 10^{1}$		$-2.83464 \cdot 10^{1}$			9.79061
c_0		$6.62278 \cdot 10^{-4}$	$1.02170 \cdot 10^{-3}$	$-3.62000 \cdot 10^{-4}$	$3.16279 \cdot 10^{-4}$	
d_0	$4.79490 \cdot 10^{-4}$	$1.18023 \cdot 10^{-3}$	$8.94935 \cdot 10^{-4}$		$2.04969 \cdot 10^{-3}$	$4.03960 \cdot 10^{-4}$
e_0		$-9.71944 \cdot 10^{-6}$	$-2.48945 \cdot 10^{-5}$			
a_1	$-1.98097 \cdot 10^{-6}$	$-1.03664 \cdot 10^{-6}$	$-1.27371 \cdot 10^{-6}$	$-9.52907 \cdot 10^{-7}$	$-1.07861 \cdot 10^{-6}$	
b_1						
c_1	$2.03541 \cdot 10^{-11}$	$-6.10764 \cdot 10^{-11}$	$-1.73320 \cdot 10^{-10}$			$-2.71715 \cdot 10^{-9}$
d_1	$1.04730 \cdot 10^{-10}$	$-5.54610 \cdot 10^{-11}$	$-8.69695 \cdot 10^{-11}$			
e_1	$2.72169 \cdot 10^{-13}$	$-2.53118 \cdot 10^{-14}$				
r^2	0.9889	0.9990	0.9963	0.9992	0.9807	0.9999
OAD %	0.08	0.03	0.05	0.02	0.3	0.002

Table 8. Density Correlation Coefficients of Equation 2 for Ternary Aqueous Amine Systems Involving AMP

	ternary systems involving AMP						
parameter	AMP + DEA	AMP + EMEA	AMP + MDEA	AMP + MEA	AMP + MMEA	AMP + NMP	AMP + Pz
a_0	1.22303	1.09425	1.08326	1.20585	1.04547	$7.40135 \cdot 10^{-1}$	1.34408
b_0	$-3.27527 \cdot 10^{1}$			$-3.07163 \cdot 10^{1}$		$7.61748 \cdot 10^{1}$	$-5.49795 \cdot 10^{1}$
c_0	$3.80116 \cdot 10^{-4}$	$1.49372 \cdot 10^{-4}$	$3.20405 \cdot 10^{-4}$	$6.93539 \cdot 10^{-4}$	$1.22377 \cdot 10^{-3}$	$4.79469 \cdot 10^{-4}$	
d_0	$1.49490 \cdot 10^{-3}$		$1.19843 \cdot 10^{-3}$	$9.97040 \cdot 10^{-4}$	$1.69268 \cdot 10^{-3}$	$1.11448 \cdot 10^{-3}$	$6.25989 \cdot 10^{-4}$
e_0	$-1.42683 \cdot 10^{-5}$		$-1.15025 \cdot 10^{-5}$	$-1.52999 \cdot 10^{-5}$	$-4.14561 \cdot 10^{-5}$	$-1.50504 \cdot 10^{-5}$	
a_1	$-1.34911 \cdot 10^{-6}$	$-1.22740 \cdot 10^{-6}$	$-9.95555 \cdot 10^{-7}$	$-1.27851 \cdot 10^{-6}$	$-8.02988 \cdot 10^{-7}$		$-1.82348 \cdot 10^{-6}$
b_1							
c_1	$-1.00459 \cdot 10^{-10}$		$-8.67675 \cdot 10^{-11}$	$-1.64584 \cdot 10^{-10}$	$-1.90872 \cdot 10^{-10}$	$-1.04511 \cdot 10^{-10}$	$-1.45128 \cdot 10^{-11}$
d_1	$-4.60396 \cdot 10^{-11}$		$-5.11136 \cdot 10^{-11}$	$-9.70532 \cdot 10^{-11}$	$-2.62090 \cdot 10^{-10}$	$-6.00757 \cdot 10^{-11}$	$-2.33775 \cdot 10^{-10}$
e_1	$-1.12208 \cdot 10^{-14}$		$-4.36394 \cdot 10^{-14}$	$-3.58123 \cdot 10^{-13}$	$-6.30596 \cdot 10^{-14}$	$-3.23054 \cdot 10^{-14}$	$7.83703 \cdot 10^{-13}$
r^2	0.9965	0.9994	0.9986	0.9956	0.9945	0.9985	0.9969
OAD %	0.08	0.01	0.05	0.04	0.04	0.04	0.03

Tables 7 and 8 give the correlation coefficients of eq 2 for the ternary systems without and with AMP, respectively. It should be mentioned that the coefficients found for the systems 2-PE + Pz and AMP + EMEA are only specific for the data considered here: total amine concentration of 30 wt % and 50 wt %, respectively, as only these data were available for correlations. In general, eqs 1 and 2 applied to correlate densities of pure, binary, and tertiary systems give excellent agreement as can be seen in Figure 1. Quaternary data presented by Rebolledo-Libreros and Trejo (2006)[39] were not used because the authors presented their own correlation, and no similar data were available in the literature.

Viscosity Correlations. In comparison with the density correlations (Section 2.2.1.3.1), it was much more difficult to find an accurate and simple linear correlation model for viscosity data with a limited number of correlation coefficients. Another difficulty arose from the fact that several studies reported kinematic viscosity data without the respective density value to calculate the dynamic viscosity what limited our database. Therefore, not all systems indicated in Tables 4 and 5 have been correlated here.

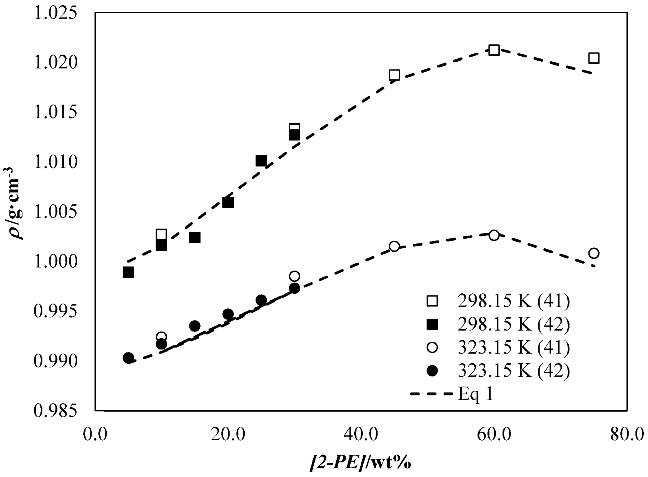


Figure 1. Literature density values of 2-PE + H_2O solutions and results calculated with eq 1 (references are given in parentheses).

For pure and binary systems, only AHPD and AMPD viscosity data were successfully correlated using this equation:

$$\ln(\mu/\text{mPa·s}) = \sum_{i=0}^{1}\left[a_i + \frac{b_i}{T/\text{K}} + c_i\cdot(w/\text{wt }\%) + d_i\cdot(w/\text{wt }\%)^2\right]\cdot(T/\text{K})^{2i} \tag{3}$$

For AHPD, the paper of Paul et al. (2009)[51] was not considered as no tabulated data were available. Table 9 gives the information about the correlation coefficients of eq 3 for these two systems. It should be mentioned that in Table 9, r^2 is linked to $\ln(\mu/\text{mPa·s})$, whereas the stated OAD % is associated directly to $\mu/\text{mPa·s}$. For comparison, eq 3 applied to pure and binary 2-PE, AEPD, and AMP viscosity data of Tables 4 and 5 gave respectively overall average deviations of (5.6, 3.6, and 8.4) % which seemed too high to be of interest.

Table 9. Viscosity Correlation Coefficients of Equation 3 for Pure and Binary Aqueous Amine Systems

	binary systems	
parameter	AHPD	AMPD
a_0	$2.06480\cdot10^{1}$	$1.93980\cdot10^{1}$
b_0		
c_0	$3.96451\cdot10^{-2}$	$2.62452\cdot10^{-2}$
d_0	$9.88914\cdot10^{-4}$	$1.31608\cdot10^{-3}$
a_1	$1.55017\cdot10^{-4}$	$1.34932\cdot10^{-4}$
b_1	$-1.15826\cdot10^{-1}$	$-1.05473\cdot10^{-1}$
c_1	$-1.78664\cdot10^{-7}$	
d_1	$-6.75681\cdot10^{-9}$	$-9.85184\cdot10^{-9}$
r^2	0.9995	0.9999
OAD %	0.6	0.4

Concerning the viscosity data of ternary systems, an equation similar to eq 2 was chosen (i.e., eq 4) to correlate them. Tables 10 and 11 display the regression coefficients found for the selected systems, only the AMP + MDEA system was discarded as the OAD % was too high. Our database was composed of the articles indicated in Tables 4 and 5 at the exception of Chenlo et al. (2001)[24] for AMP + DEA and AMP + MEA. The system AMP + MMEA was correlated with the kinematic viscosity instead of the dynamic one for more accuracy. It should be mentioned that the coefficients found for the system 2-PE + TMS are only specific for 45 wt % 2-PE + 40 wt % TMS and 55 wt % 2-PE + 10 wt % TMS at temperatures between (293 and 364) K. Also, the coefficients found for the system AHPD + Pz are only specific for the system containing 11.8 wt % AHPD, as only these data were available for correlations. Figure 2 shows some data of the literature along with values calculated with eq 4.

$$\ln(\mu/\text{mPa·s}) = \sum_{i=0}^{1}\left[a_i + \frac{b_i}{T/\text{K}} + c_i\cdot(w_1/\text{wt }\%)^{i+1} + d_i\cdot(w_2/\text{wt }\%)^{i+1} + e_i\cdot(w_1/\text{wt }\%\cdot w_2/\text{wt }\%)^{i+1}\right]\cdot(T/\text{K})^{2i} \tag{4}$$

2.2.2. Surface Tension.

2.2.2. Surface Tension. Surface tension of mixtures is an important property for the design of contacting equipment like packed columns and membrane contactors used in gas absorption. Surface tension affects the hydrodynamics and transfer rates of such systems where a gas–liquid interface exits. In packed columns, surface tension was found to be one of the most sensitive parameter in CO_2 absorption by influencing the effective mass transfer area.[53] In membrane contactors, surface tension of solutions and the hydrophobicity of the membrane strongly influence membrane wettability. In addition, values of surface tension are also necessary to estimate the breakthrough pressure of the solution through the pore of the membrane by using the Laplace–Young equation. Table 12 reports the aqueous amine systems for which data of surface tension were found in the literature. For conventional amine solution concentrations (less than 40 wt %) and under a temperature range of (293 to 393) K, surface tension values of SHA solutions were found to usually be between (38 and 72) mN·m^{-1}.

In a study concerning membrane wetting, Rongwong et al. (2009)[54] reported punctual values of surface tension of 1 kmol·m^{-3} AMP aqueous solution and of 0.25 kmol·m^{-3} AMP + 0.25 kmol·m^{-3} (DEA or MEA) at 303 K. Authors mentioned that important measures to prevent the wetting problems include the selection of liquids with suitable surface tension. It was reported that when the liquid surface tension decreased from about 33 mN·m to 30 mN·m, the transmembrane pressure difference in polypropylene (PP) membranes was decreased from about (0.9 to 0.1) bar, leading to the rapid increase of membrane wetting. Another study reporting surface tension of AMP and AMP + MEA aqueous solution was made by Vázquez et al. (1997).[55] They measured surface tension at temperatures from (298 to 323) K and total amine concentration varying between (5 and 100) wt % for the binary AMP system or kept at 50 wt % for tertiary mixtures. The experimental binary values were correlated with temperature and mole fractions. For all studied systems, surface tension decreased with increasing temperature for any given concentration and decreased when wt % ratio of AMP increased in the ternary system for a given temperature. Álvarez et al. (1998, 2003)[56,57] measured the surface tension of aqueous solutions of AMP + MDEA, AMP + 3-amino-1-propanol (AP), and AMP + 1-amino-2-propanol (MIPA) at (298 to 323) K. For these tertiary mixtures, the concentration range for each amine was (0 to 50) wt % by 10 wt % increments. Yoon et al. (2002)[46] reported surface tension of aqueous AEPD for temperature ranging from (303.15 to 343.15) K and AEPD concentration of (20 to 80) wt %. The experimental data were

Table 10. Viscosity Correlation Coefficients of Equation 4 for Ternary Aqueous Amine Systems without AMP

	ternary systems without AMP				
parameter	2-PE + DEA	2-PE + MEA	2-PE + Pz	2-PE + TMS	AHPD + Pz
a_0	$2.80407 \cdot 10^{2}$	$-1.67285 \cdot 10^{1}$	-5.10680	$-1.34308 \cdot 10^{2}$	-6.67761
b_0	$-2.53385 \cdot 10^{4}$	$4.10418 \cdot 10^{3}$	$2.53784 \cdot 10^{3}$	$1.90170 \cdot 10^{4}$	$2.05722 \cdot 10^{3}$
c_0	$2.17886 \cdot 10^{-2}$	$7.63385 \cdot 10^{-2}$	$-7.25504 \cdot 10^{-2}$		
d_0		$5.92013 \cdot 10^{-2}$			$4.31625 \cdot 10^{-2}$
e_0	$5.78432 \cdot 10^{-4}$	$-6.10503 \cdot 10^{-4}$		$1.25396 \cdot 10^{-4}$	
a_1	$1.13136 \cdot 10^{-3}$	$2.80800 \cdot 10^{-5}$		$-2.95581 \cdot 10^{-4}$	
b_1	$-9.90823 \cdot 10^{-1}$			$3.34791 \cdot 10^{-1}$	
c_1		$-7.77203 \cdot 10^{-9}$			
d_1	$6.04752 \cdot 10^{-9}$	$-5.31004 \cdot 10^{-9}$			
e_1		$-2.88500 \cdot 10^{-11}$	$-1.14183 \cdot 10^{-10}$		
r^2	0.9956	0.9988	0.9970	0.9999	0.9995
OAD %	1.9	1.4	1.9	0.9	0.3

Table 11. Viscosity Correlation Coefficients of Equation 4 for Ternary Aqueous Amine Systems Involving AMP

	ternary systems involving AMP				
parameter	AMP + DEA	AMP + EMEA	AMP + MEA	AMP + MMEA[a]	AMP + Pz
a_0	$2.32656 \cdot 10^{2}$	$-3.54098 \cdot 10^{1}$	$-2.38985 \cdot 10^{1}$	$-3.00208 \cdot 10^{1}$	$-1.05998 \cdot 10^{1}$
b_0	$-2.11896 \cdot 10^{4}$	$8.96897 \cdot 10^{3}$	$5.65724 \cdot 10^{3}$	$7.78275 \cdot 10^{3}$	$3.11621 \cdot 10^{3}$
c_0	$4.54955 \cdot 10^{-2}$	$1.13858 \cdot 10^{-2}$	$8.71964 \cdot 10^{-2}$	$1.73432 \cdot 10^{-2}$	$6.27013 \cdot 10^{-2}$
d_0	$1.52046 \cdot 10^{-2}$		$6.82753 \cdot 10^{-2}$		$3.28742 \cdot 10^{-2}$
e_0	$8.90657 \cdot 10^{-4}$	$1.65873 \cdot 10^{-4}$	$-1.23642 \cdot 10^{-3}$		
a_1	$8.91034 \cdot 10^{-4}$	$8.03854 \cdot 10^{-5}$	$4.92136 \cdot 10^{-5}$	$6.48099 \cdot 10^{-5}$	
b_1	$-8.07688 \cdot 10^{-1}$				
c_1			$-9.22850 \cdot 10^{-9}$	$-1.43395 \cdot 10^{-9}$	$-5.81697 \cdot 10^{-9}$
d_1	$8.51917 \cdot 10^{-9}$	$1.75843 \cdot 10^{-9}$	$-5.89416 \cdot 10^{-9}$	$1.25089 \cdot 10^{-9}$	$1.75049 \cdot 10^{-8}$
e_1			$-1.88802 \cdot 10^{-11}$		
r^2	0.9958	0.9998	0.9960	0.9998	0.9954
OAD %	2.6	0.4	2.4	0.4	2.6

[a] Correlation of the kinematic viscosity.

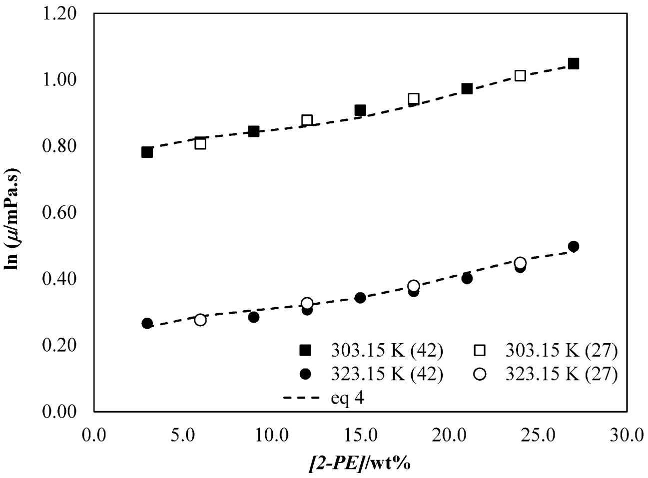


Figure 2. Literature viscosity values of 2-PE + MEA + H_2O solutions with a total amine content of 30 wt % and results calculated with eq 4 (references are given in parentheses).

correlated as a function of temperature and AEPD concentration with an average absolute deviation of 0.4 %. Paul and Mandal (2006)[43] measured the surface tension of aqueous blends of Pz as activator with 2-PE or AMP between (293 and 323) K and total amine mass fraction of 30 %. Surface tension of the ternary mixtures decreased with increasing temperature and decreasing mass fraction of Pz in the mixture. Ventak et al. (2010)[38] reported experimental surface tension data of aqueous blends of AMP + MMEA at (298 to 323) K and total amine mass fraction of 30 %, as well as correlations with temperature and amine concentration. The surface tension increased with decreasing temperature and increasing mass fraction of MMEA in the mixture. One study has been found in the literature concerning the surface tension of mixture of three alkanolamines. Águila-Hernández et al. (2007)[58] determined the equilibrium surface tension for aqueous solutions composed of 32.5 wt % MDEA + 12.5 wt % DEA + ((2, 4, 6, 8, or 10) wt %) AMP between (303.15 and 343.15) K. In the temperature range studied, the experimental surface tension values of the aqueous blends of three alkanolamines decreased linearly with the increase of AMP concentration and temperature. The authors mentioned that this behavior was highly consistent with the fact that the surface tension of pure AMP was lower than that of pure MDEA and pure DEA, and consequently, the surface tension of aqueous solutions at a given AMP concentration was lower than that of aqueous solutions of MDEA and DEA, individually, under the same conditions of concentration and temperature. This behavior led to the statement that the lower the solution surface tension, the larger its absorption capacity toward acid gases in conventional gas−liquid contactor. Furthermore, an analysis of the excess surface adsorption clearly indicated the

Table 12. Surface Tension of Various SHAs

	T	ΔT	[SHA]	[amine[a]]	Δ[AM[b]]	$\Delta\sigma$	
system	K	K	wt %	wt %	wt %	$mN \cdot m^{-1}$	reference
2-PE + Pz	293–323	0.1	18–27	3–12	0.007 %	0.12	43
AEPD	303–343	0.1	20–80			0.8 %	46
AMP	298–323	0.05	5–100		0.3 %	0.02	55
AMP	303		9				54
AMP + AP	298–323	0.01	10–50	10–50		0.02	57
AMP + DEA	303		2	2			54
AMP + MDEA	298–323	0.05	10–50	10–50	0.3 %	0.02	56
AMP + MEA	303		2	2			54
AMP + MEA	298–323	0.05	10–50	10–50	0.3 %	0.02	55
AMP + MIPA	298–323	0.01	10–50	10–50		0.02	57
AMP + MMEA	298–323	0.2	18–27	3–12	0.007 %	0.35	38
AMP + Pz	293–323	0.1	18–27	3–12	0.007 %	0.12	43
AMP + MDEA + DEA	303–343	0.005	2–10	*c*	0.002	0.21	58

[a] Pz, AP, DEA, MDEA, MEA, MIPA, MMEA, or Pz. [b] Concentration uncertainty of all amines in solutions. [c] 32.5 (MDEA) + 12.5 (DEA).

existence of an excess of amine molecules at the liquid–vapor interface with respect to those of solvent.

From all of these works, the only possible comparison can be made for AMP surface tension at 303.15 K and 10 wt %: 52.87 $mN \cdot m^{-1}$ from Vázquez et al. (1997)[55] versus 58.81 $mN \cdot m^{-1}$ from Rongwong et al. (2009).[54]

2.2.3. Vapor Pressure. For solubility measurements or modeling CO_2 absorption in aqueous amine solutions, the vapor phase needs to be analyzed to determine the exact CO_2 content. Most studies consider that only water and CO_2 are volatile compounds, and therefore, amine volatility can be neglected. However, it is often stated that MEA, the most used conventional alkanolamine, has a high vapor pressure and high amine losses occur industrially. Studies on SHA volatility should then be made to explore the potential use of these amines.

Nguyen et al. (2010)[59] mentioned that an excessive volatility may result in significant economic losses and environmental impact. According to the authors, volatility is of greatest interest at the top of the absorber at 313 K and at nominal lean loading because aqueous amine absorbers are designed to operate near this temperature and that cleaned flue gas leaving the absorber will tend to be in equilibrium with lean amine solution. Their study reported amine volatility in 7 $mol \cdot kg^{-1}$ MEA, 8 $mol \cdot kg^{-1}$ Pz, 7 $mol \cdot kg^{-1}$ MDEA + 2 $mol \cdot kg^{-1}$ Pz, 12 $mol \cdot kg^{-1}$ EDA (ethylenediamine), and 5 $mol \cdot kg^{-1}$ AMP at (313 to 333) K with lean and rich loadings giving CO_2 partial pressures of (0.5 and 5) kPa at 313 K. Data were obtained from Fourier transform infrared (FTIR) spectroscopy for both unloaded and nominal lean and rich CO_2 systems. The results showed that amine solutions were ranked in order of increasing amine volatility as follows: 7 $mol \cdot kg^{-1}$ MDEA + 2 $mol \cdot kg^{-1}$ Pz (6/2 ppm), 8 $mol \cdot kg^{-1}$ Pz (8 ppm), 12 $mol \cdot kg^{-1}$ EDA (9 ppm), 7 $mol \cdot kg^{-1}$ MEA (31 ppm), and 5 $mol \cdot kg^{-1}$ AMP (112 ppm). The 5 $mol \cdot kg^{-1}$ AMP was found the most volatile amine at the CO_2 partial pressure of interest, (0.1 to 0.5) kPa at 313 K. This behavior may come from the fact that SHA, as they do not form stable carbamates, existed in their free form and not in reacted, nonvolatile species in solution, increasing therefore their volatility.

AMP volatility was also studied by Pappa et al. (2006).[60] In that work, AMP vapor pressures were measured in the temperature range of (373.3 to 436.9) K. Data were correlated with an Antoine expression with a mean deviation of 0.5 %:

$$P_{\mathrm{AMP}}^{\mathrm{sat}}/\mathrm{kPa} = \exp\left[15.155 - \left(\frac{3472.6}{T/\mathrm{K} - 107.32}\right)\right] \quad (5)$$

2.2.4. Heat Capacity. In a conventional industrial CO_2 absorption process, a lean aqueous solution first absorbs CO_2 and is then sent to a stripper where CO_2 is recovered and compressed. The absorption takes usually place at room temperature or slightly above (298 to 323 K), whereas solution regeneration is around 383 K. Heat capacity data for alkanolamine solutions are required for the design of heat-exchangers included in the absorption/desorption installation. Table 13 reports the works where heat capacity data for various SHA were found in the open literature. It was found that usually SHA solution heat capacity values can fluctuate between around (90 and 300) $J \cdot mol^{-1} \cdot K^{-1}$.

Some estimation methods to predict molar heat capacity can be found in the literature, like for example those of Missenard (1965),[61] Chueh and Swanson (1973),[62,63] and Nagvekar and Daubert (1987).[64] However, these estimations cannot always be considered as reliable as true experimental data. It is worth mentioning that, except for aqueous AMP for which several works have been published, no comparable experimental data are available for comparison for the other systems.

Since 1999, the group of Li published several studies concerning heat capacity of pure or aqueous alkanolamine solutions used in CO_2 absorption. Chiu and Li (1999)[65] and Chiu et al. (1999)[66] reported heat capacities of pure and aqueous solutions of 2-PE, AMP, and several other conventional amines from (303 to 353) K. A comparison showed that, at 323 K, good agreement was found between the reported AMP C_p value (2.80 $kJ \cdot kg^{-1} \cdot K^{-1}$) and the one estimated from Missenard (1965)[61] (2.734 $kJ \cdot kg^{-1} \cdot K^{-1}$) with a deviation of 2.4 %. However, at temperatures of (293 and 298) K, both C_p estimation methods of Missenard (1965)[61] and Chueh and Swanson (1973)[62,63] yielded poor results compared to the measured AMP C_p values, but good results compared to the 2-PE ones. It was observed that the order of C_p for alkanolamine aqueous solutions generally follows the order of C_p for pure alkanolamines. Among the eight studied alkanolamine aqueous solutions (MEA, DEA, DGA, DIPA, TEA, MDEA, AMP, and 2-PE), the AMP system showed the strongest nonideality

Table 13. Heat Capacity of Various SHA Solutions

	T	ΔT	[SHA]	[amine^a]	Δ[AM^b]	ΔC_p	
system	K	K	mole fraction	mole fraction	mole fraction	J·mol·K^{-1}	reference
2-PE	303−353	0.1	0.2−0.8			3 %	65
2-PE	303−353	0.1	1.0			3 %	66
2-PE + MEA	303−353	0.1	0.04−0.8	0.04−0.8		2 %	67
AMP	303−353	0.1	0.2−0.8			3 %	65
AMP	303−353	0.1	1.0			3 %	66
AMP	303−368		1.0			2 %	19
AMP	278−368		0.06−0.90			2 %	19
AMP	303−353	0.1	1.0			2 %	69
AMP	303−353	0.1	0.2−0.8			2 %	69
AMP	323−398	0.08	1.0			0.9 %	70
AMP + DEA	303−353	0.1	0.04−0.9	0.04−0.9		2 %	68
AMP + MEA	303−353	0.1	0.04−0.8	0.04−0.8		2 %	69
AMP + TMS	303−353	0.1	0.04−0.8	0.04−0.8	$1.5\cdot10^{-4}$	1 %	71

[a] MEA, DEA, or TMS. [b] Concentration uncertainty of all amines in solutions.

behavior. Shih et al. (2002)[67] determined the heat capacity of aqueous and nonaqueous mixture of 2-PE + MEA from (303 to 353) K. The Redlich−Kister equation correlated the ternary system with an overall average absolute deviation of 0.2 % for 176 data points. Shih and Li (2002)[68] measured heat capacities of nonaqueous AMP + DEA ((0.1 to 0.9) AMP mole fractions) and of 16 aqueous ternary solutions. It was observed that, at constant temperature, the heat capacity of AMP + DEA increased as the mole fraction of DEA increased. Heat capacities of aqueous AMP and aqueous and nonaqueous AMP + MEA solutions from (303 to 353) K (eight binary and sixteen ternary systems) were given by Chen and Li (2001).[69] Probably due to the use of higher AMP purity, the values of C_p obtained in this study were slightly higher than those of Chiu et al. (1999).[66] However, excellent agreement with Maham et al. (1997)[70] was found.

Ho et al. (2007)[71] reported heat capacities of aqueous solutions of AMP with sulfolane (TMS) over a temperature range from (303.15 to 353.15) K. Since the mole fraction of water in aqueous alkanolamine solution is normally greater than 0.5 (Kohl and Nielsen, 1997),[4] 12 solutions of AMP + TMS + water that covered the mole fractions of water from 0.6 to 0.8 were studied. Heat capacities of AMP + sulfolane were also determined. For 132 data points of AMP + sulfolane + water, the fitted results of heat capacity calculations using a Redlich−Kister equation (overall average absolute percentage deviation (AAD %)) were (0.3 and 7.7) % for the molar heat capacity and the excess molar heat capacity, respectively.

In addition to studies from Li's research group, some works concerning AMP over different temperature ranges are worth to be mentioned. Maham et al. (1997)[70] measured molar heat capacities of 14 pure alkanolamines (including AMP) at various temperatures from (299.1 (323 for AMP) to 397.8) K. The molar heat capacity was represented through a structural dependence model, where the molar heat capacity of one molecule was considered as the sum of various group (CH_2, OH, NH, and N) contributions. An analysis of their model indicated that the molar heat capacities of alkanolamines were dominated by CH_2 and OH group contributions and that these contributions increased with increasing temperature. In the work by Zhang et al. (2002),[19] heat capacities of pure and aqueous solutions of AMP were measured, respectively, at temperatures from (303.15 to 368.15) K and from (278.15 to 368.15) K. Experimental C_p data for pure AMP were compared with literature values. While the values from Zhang et al. (2002)[19] and those from Chiu et al. (1999),[66] Chen and Li (2001),[69] and Maham et al. (1997)[70] were in good agreement considering the uncertainties, some deviations appeared with the data estimated from the works of Chueh and Swanson (1973)[62,63] and Missenard (1965).[61]

Based on the studies reporting the pure and binary C_p AMP value indicated in Table 13, our own correlation was elaborated using this equation:

$$C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = \sum_{i=0}^{1} [a_i + b_i\cdot(w/\text{wt }\%) + c_i\cdot(w/\text{wt }\%)^2 + d_i\cdot(w/\text{wt }\%)^3]\cdot(T/\text{K})^{2i} \qquad (6)$$

Table 14 reports the correlation coefficient of eq 6. Based on the five studies,[19,65,66,69,70] 328 data were correlated with an overall mean deviation of only 1.1 % which is quite satisfying.

Table 14. Heat Capacity Correlation Coefficients of Equation 6 for Pure and Binary AMP Aqueous Solutions

parameter	pure and binary AMP systems
a_0	$3.99560\cdot10^{1}$
b_0	3.80351
c_0	$-8.38391\cdot10^{-2}$
d_0	$5.79857\cdot10^{-4}$
a_1	$-1.71029\cdot10^{-4}$
b_1	$6.52042\cdot10^{-6}$
c_1	
d_1	$3.44363\cdot10^{-10}$
r^2	0.9983
OAD %	1.1

2.2.5. Heat of Absorption. When designing absorption with a chemical reaction there are several factors to account for. One of the most important considerations is the temperature variation within the absorber arising from the heat of absorption of the acid gas. The temperature influences not only the equilibrium line, but also the rate of the chemical reactions involved and the physical properties of the liquid and the gas.[53] The use of constant heat of absorption values in the calculations often leads to inaccurate results since the magnitude of this phenomenon varies with temperature and CO_2 content in the alkanolamine solutions (CO_2 loading). Experimental data are then necessary, and they can be derived either from solubility data or by direct calorimetric measurements. The exothermic effect of the CO_2 absorption causes an increase of the enthalpy of solution (referred as the differential enthalpy of solution, ΔH_{sol}), and this can be calculated from solubility data using eq 7. The differential enthalpy is then integrated following eq 8 to get the enthalpy of solution H_{sol}.

$$\left(\frac{\mathrm{dln}\, P_{CO_2}}{\mathrm{d}(1/T)}\right)_{\alpha} = \frac{\Delta H_{sol}}{R} \tag{7}$$

$$H_{sol} = \frac{1}{\alpha}\int_0^{\alpha} \Delta H_{sol} \mathrm{d}\alpha \tag{8}$$

There are few direct measurements of the enthalpy of solution, and the available measurements showed considerable scatter with respect to both temperature and concentration of alkanolamine.[72] Based on solubility data of CO_2 in aqueous alkanolamine solutions, Murrieta-Guevara et al.[73] derived the differential enthalpy of solution (ΔH_{sol}) at 343.15 K for systems of 10 wt % AMP + 20 wt % DEA and 5 wt % AMP + 25 wt % DEA. Values were obtained for CO_2 loadings of 0.5, 0.6, and 0.7. It was seen that, within ± 10 %, ΔH_{sol} was a linear function of α for all systems considered and it changed slightly with the concentration of each amine of the blend. From the same research group, Rebolledo-Libreros and Trejo (2004)[72] obtained experimental gas solubility data for CO_2 in aqueous solutions of 32.5 wt % MDEA + 12.5 wt % DEA + (4, 6, or 10) wt % AMP at (313.15, 343.15, and 393.15) K. They showed that the plots of ln P_{co_2} versus $1/T$ were linear with a correlation coefficient of 0.99, indicating that ΔH_{sol} was independent of temperature over the range of temperature studied. For each temperature, pressure values were smoothed with a polynomial function to carry out interpolations of ΔH_{sol} at constant values of α. Differential enthalpies of solution were extracted at a mean temperature of 350 K for loadings from 0.1 to 0.7. They found that, within ± 20 %, the calculated values of ΔH_{sol} were not influenced by the change of AMP concentration. An explicit model for CO_2 solubility in an aqueous solution of AMP has been proposed by Gabrielsen et al. (2006),[53] and an expression for the heat of absorption of CO_2 has been developed as a function of loading and temperature.

$$\Delta H_{sol}/\mathrm{J \cdot mol^{-1}} = R\left(-8161 + 47652\frac{\alpha}{T/\mathrm{K}}\right) \tag{9}$$

A rate-based steady-state model for CO_2 absorption into an AMP solution has also been developed,[53] using both the proposed expression for the CO_2 solubility and the expression for the heat of absorption along with an expression for the enhancement factor and physicochemical data from literature. The proposed model was successfully applied to absorption of CO_2 into an AMP solution in a packed tower and validated against pilot-plant data from literature. Arcis et al. (2007)[23] measured the enthalpies of solution of CO_2 in (15 and 30) wt % AMP aqueous solutions at 322.5 K and for total pressures from (0.2 to 5) MPa. The experimental enthalpies of solution were compared to the values derived from vapor−liquid equilibrium data available in the literature. The enthalpies estimated from Park et al. (2002)[74] for a 30 wt % AMP aqueous solution were found to be in good agreement with their experimental enthalpies, but only for CO_2 loading over 0.4. The calorimetric data also allowed the determination of gas solubility in the liquid phase.

2.2.6. Corrosion and Amine Degradation. According to Kohl and Nielsen (1997),[4] the most serious operating problem encountered in acid gas separation plants is corrosion. The corrosion problem leads to direct impacts on a plant's economy since it causes unplanned downtime, production losses, reduced equipment life, and even injury or death. Veawab et al. (1996, 1997, 1999)[75−77] studied corrosion and corrosion inhibition in AMP aqueous solutions ((1, 2.5, 5, and 7) $\mathrm{kmol \cdot m^{-3}}$; (9 to 63.3) wt %) by static weight loss tests. The corrosion data were obtained under boiling conditions to simulate the service environment in reboilers and regenerators and were compared with those of MEA, tested under the same conditions. The results indicated that AMP solutions were less corrosive to carbon steel than MEA ones in environments of both pure CO_2 and a mixture of CO_2 and air (10 % O_2).

It is also often related that amine degradation products can influence significantly corrosion caused by amine solutions. Thermal degradation occurs as the amine solution is circulating from the absorber (temperature up to 330 K) to the regeneration column where temperature can go as far as 413 K. Oxidative degradation is mainly caused by the presence of oxygen in the flue gas and is then occurring in the absorber where oxygen concentration is higher. Interesting studies[78−80] were found in the literature describing existing degradation mechanisms, giving the degradation rate and indicating all possible degradation products found in solutions for conventional alkanolamines (e.g., MEA, DEA, MDEA). Unfortunately, details concerning SHA are very scarce and concern mainly AMP solutions where AMP was found more stable than usual alkanolamines.[81,82] It appeared that corrosion and amine degradation are linked and that this field of research is very complex as many degradation mechanisms exist, degradation products are abundant (e.g., more than 15 for MMEA[83]), and because many other parameters can be taken into account: the presence of metal ions, dissolved CO_2, other reactive sour gas, or oxygen, and so forth. Therefore, this section will not be discussed in depth in this review, and readers are encouraged to read selected literature on the subject for more information.

2.2.7. CO_2 Diffusivity in SHA Solutions. Gas diffusivity in solutions is one essential parameter for the design of gas/liquid contactors. It is also needed for the operation of certain types of contactors, in particular the wetted-wall column, often used for kinetic studies. D_{co_2} is used to calculate the enhancement factor (E) and the liquid-side mass-transfer coefficient. However, the diffusion coefficient of CO_2 in amine solution cannot be measured directly as the acid gas reacts with the amine. Therefore, some methods are usually adopted to estimate it, namely, the N_2O analogy and the Stokes−Einstein relation. In the N_2O analogy, the CO_2 diffusion coefficient in amine aqueous solution can be estimated from the N_2O diffusion coefficient in the same solution and the diffusivity ratio of these two gases in water at the same temperature, according to the following equation:

$$(D_{CO_2})_{amine} = (D_{N_2O})_{amine} \cdot \left(\frac{D_{CO_2}}{D_{N_2O}}\right)_{water} \tag{10}$$

It is commonly accepted that values of nitrous oxide and carbon dioxide diffusion coefficients in water can be calculated from equations proposed by Versteeg and van

Table 15. N_2O Diffusion Coefficient in Various SHA Solutions

system	T K	ΔT K	[SHA] wt %	[amine[a]] wt %	Δ[AM[b]] wt %	ΔD_{N_2O} $m^2 \cdot s^{-1}$	reference
2-PE[c]	313		1−13				40
2-PE	293−313		5−40				92
AEPD[c]	303−318	0.1	5−25				45
AHPD[c]	303−323	0.1	6−27			2 %	93
AHPD	298−323	0.2	2.17−21.7			2 %	51
AMP[c]	313		2.3−27				14
AMP	294−348.5	0.1	18−27			5 %	16
AMP	294−318	0.1	4.5−18			5 %	18
AMP[c]	293−313		3.6−18				85
AMP	303−313		4.5−22.4			2 %	86
AMP	298		1.8−21.5				15
AMP + DEA	303−313		6−24	6−30		2 %	90
AMP + DEA	303−313		9−13.4	1−4	0.2	2 %	31
AMP + DEA	293−313	0.2	21−30	1.5−9		4 %	87
AMP + MEA	303−313		6−30	6−30		2 %	88
AMP + MEA	303−313		13.4−15.2	1−4	0.2	2 %	28
AMP + MEA	293−313	0.2	21−30	1.5−9		2 %	89
AMP + Pz	303−313		9−13.5	1−3.5	0.2	2 %	35
AMP + Pz	298−313	0.1	22−30	2−8		4 %	91
AMPD	303−323	0.1	2.5−30				48

[a] DEA, MEA, or Pz. [b] Concentration uncertainty of all amines in solutions. [c] Authors reported the ratio ${D_{CO_2}}^{1/2}/H_{CO_2}$ by using the N_2O analogy.

Swaaij (1988).[84]

$$(D_{CO_2})_{water}/m^2 \cdot s^{-1} = 2.35 \cdot 10^{-6} \cdot \exp\left(\frac{-2119}{T/K}\right) \quad (11)$$

$$(D_{N_2O})_{water}/m^2 \cdot s^{-1} = 5.07 \cdot 10^{-6} \cdot \exp\left(\frac{-2371}{T/K}\right) \quad (12)$$

The use of the Stokes−Einstein relation allows the reduction of the number of experiments. In eq 13, the N_2O diffusion coefficient is estimated based on the viscosities of amine solution and water and on the diffusion coefficient of N_2O in water; the last parameter can be calculated by eq 12 at a given temperature. However, many uncertainties concern the exponent value (β) related to viscosities.

$$(D_{N_2O} \cdot \mu^{\beta})_{amine} = \text{constant} = (D_{N_2O} \cdot \mu^{\beta})_{water} \quad (13)$$

Table 15 presents experimental values of the N_2O diffusion coefficient in various SHA aqueous solutions. It is traditional to get values between (0.6 and 2.0)·10^{-9} $m^2 \cdot s^{-1}$, but higher diffusivity values can be found at higher temperatures. As mentioned earlier, these values can be used to estimate the CO_2 diffusion coefficient in the same solution by the N_2O analogy. When the ratio $D^{1/2}_{CO_2}/H_{CO_2}$ is obtained experimentally, the diffusivity can be calculated on the basis of Henry's constant obtained from solubility measurements.

2.2.7.1. AMP Systems. AMP + H_2O. Yih and Shen (1988)[14] measured the ratio $D^{1/2}_{CO_2}/H_{CO_2}$ in aqueous AMP solutions using the N_2O analogy. Nitrous oxide absorptions were performed at 313 K for AMP solutions of (0.258 to 3.0) kmol·m^{-3} ((2.3 to 27) wt %). Data by Xu et al. (1991)[16] obtained at (294 to 348.5) K for AMP solutions of (2 and 3) kmol·m^{-3} ((18 and 27) wt %) differ by 15 % for the 3 kmol·m^{-3} AMP solution in respect to those given by Yih and Shen (1988).[14] The authors recommended the use of the N_2O analogy method to estimate the diffusivity of CO_2 in AMP solutions, instead of the Stokes−Einstein relation. Even a value of 0.80 for β in the Stokes−Einstein relation, as recommended by Versteeg and van Swaaij (1988),[84] did not result in satisfactory estimations. Saha et al. (1993)[18] measured N_2O solubility and diffusivity between (294 and 318) K in (0.5, 1.0, 1.5, and 2.0) kmol·m^{-3} ((4.5 to 18) wt %) AMP aqueous solutions. It was observed that the diffusivity results did not follow the Stokes−Einstein relation strictly. Authors also recommended the use of the N_2O analogy. Messaoudi and Sada (1996)[85] reported the ratio $D^{1/2}_{N_2O}/H_{N_2O}$ in AMP solutions of (0.4 to 2.0) kmol·m^{-3} ((3.6 to 18) wt %) and for temperatures of (293, 303, and 313) K. The results were correlated using the eq 14, and linear relationships were obtained at constant temperatures.

$$\log\left(\left(\frac{D^{1/2}_{N_2O}}{H_{N_2O}}\right)_{water} \Bigg/ \left(\frac{D^{1/2}_{N_2O}}{H_{N_2O}}\right)_{amine}\right) = a(C_{AMP}/\text{kmol} \cdot m^{-3})^{b} \quad (14)$$

where a and b are regressed parameters.

Equation 14 was also applied to represent data reported by Yih and Shen (1988),[14] Xu et al. (1991),[16] and Saha et al. (1993),[18] and a comparison was made between all these sources. Data of Messaoudi and Sada (1996),[85] Yih and Shen (1988),[14] and Xu et al. (1991)[16] exhibited a moderate dependence on amine concentration, but slightly diverge from each other. Data of Saha et al. (1993)[18] showed a strong amine concentration dependence, and it was hard to distinguish data at 293 K from those at 303 K.

In Ko et al. (2001),[86] diffusivities of nitrous oxide (N_2O) were measured in several aqueous alkanolamine solutions (MEA, DEA, DIPA, TEA, and AMP) at (303, 308, and 313) K and for AMP concentration from (0.5 to 2.5) kmol·m^{-3} ((4.5 to 22.4) wt %).

Taken all available N_2O diffusion coefficient data in AMP−H_2O solutions from the literature, it appeared that the values from Xu et al. (1991),[16] Saha et al. (1993),[18] Ko et al. (2001),[86] and Xiao et al. (2000)[28] deviate respectively by 5.9 %, 2.8 %, 3.5 %, and 1.3 % from our correlation based on all data reported in these four papers (eq 15). Data of Xu et al. (1991)[16] were found to deviate more significantly, reaching for some data a maximum deviation of 22.8 %. OAD % indicated in Table 16, without considering data of Xu et al. (1991),[16] reduced to 2.8 %. Ko et al. (2001)[86] also indicated that some data from that study[16] deviated considerably. N_2O diffusion coefficient data reported in Bosch et al. (1990)[15] were not considered in this correlation because they were based on estimation only. N_2O diffusivity data in 30 wt % AMP solutions reported by Mandal et al. (2004)[87] and Li and Lai (1995)[88] were also not included in the correlation because, for all temperatures, these data were clearly above the trend created by all of the other considered data.

Table 16. N_2O Diffusion Correlation Coefficients of Equation 15 in AMP Solutions

parameter	pure and binary AMP solutions
a_0	$-8.86770 \cdot 10^{1}$
b_0	$1.68285 \cdot 10^{4}$
c_0	$2.02569 \cdot 10^{-1}$
d_0	$-6.07155 \cdot 10^{-3}$
a_1	$3.83315 \cdot 10^{-4}$
b_1	
c_1	$-2.87647 \cdot 10^{-6}$
d_1	$7.18194 \cdot 10^{-8}$
r^2	0.9933
OAD %	3.7

$$D_{N_2O} \cdot 10^9/\mathrm{m^2 \cdot s^{-1}} = \sum_{i=0}^{1} \left[a_i + \frac{b_i}{T/\mathrm{K}} + c_i \cdot (w/\mathrm{wt}\,\%) + d_i \cdot (w/\mathrm{wt}\,\%)^2 \right] \cdot (T/\mathrm{K})^{2i} \tag{15}$$

AMP + MEA + H_2O. Three works are available for this system, covering the temperature range of (293 to 313) K.[28,88,89] Li and Lai (1995)[88] measured the solubility and diffusivity of N_2O in several AMP + MEA aqueous systems of total amine concentration of 30 wt % at (303, 308, and 313) K. In their study, Xiao et al. (2000)[28] measured the diffusivity of N_2O in AMP + MEA aqueous systems of (1.5 and 1.7) kmol·m^{-3} AMP + (0.1 to 0.4) kmol·m^{-3} MEA. Mandal et al. (2005)[89] measured N_2O diffusivity between (293 and 313) K for total amine concentration of 30 wt %. Good agreement was found between these data and those by Li and Lai (1995)[88] for 24 wt % AMP + 6 wt % MEA, over the temperature range of (303 to 313) K.

AMP + DEA + H_2O. As in the case of the aqueous AMP + MEA, three works are also available for this system, covering the temperature range of (293 to 313) K.[31,87,90] Li and Lee (1996)[90] measured N_2O solubility and diffusivity in solutions of 30 total amine mass percent. It was observed that the experimental diffusivities at (303 and 313) K did not follow the Stokes–Einstein relation strictly. In their kinetics study, Wang and Li (2004)[31] measured N_2O diffusivity in aqueous solutions of (1.0 and 1.5) kmol·m^{-3} (9 and 13.4 wt %) AMP + (0.1 to 0.4) kmol·m^{-3} (1.1 to 4.2 wt %) DEA at (303, 308, and 313) K. It was found that diffusivities in 1.5 kmol·m^{-3} AMP + DEA + H_2O are smaller than in 1.0 kmol·m^{-3} AMP + DEA + H_2O, due to the higher viscosity values of the former system. Also, the diffusivity of N_2O was found to decrease as the concentration of DEA increased at a given temperature and increased as the temperature increased at a given concentration. Mandal et al. (2004)[87] reported the diffusivity of N_2O in aqueous solutions of total amine concentration of 30 wt % between (293 and 313) K. For 24 wt % AMP + 6 wt % DEA, over the temperature range of (303 to 313) K, the deviation of the experimental data was within 2.5 % in respect to those by Li and Lee (1996).[90] As in Li and Lee (1996),[90] it was observed that the experimental diffusivities of N_2O in AMP + DEA + H_2O did not follow the Stokes–Einstein relation strictly.

AMP + Pz + H_2O. Sun et al. (2005)[35] measured the solubility and diffusivity of N_2O in aqueous mixtures of AMP and Pz using a wetted-wall column with an estimated error of ± 2 %. The diffusivity was measured between (303 and 313) K for solutions containing (1.0 and 1.5) kmol·m^{-3} AMP ((9 and 13.5) wt %) and a small addition of Pz ((0.1 to 0.4) kmol·m^{-3}; (0.9 to 3.5) wt %). Data were necessary to interpret kinetic results.

Samanta and Bandyopadhyay (2009)[91] also reported N_2O diffusivity in aqueous solutions of AMP + Pz, over a temperature range of (298 to 313) K and for solutions with a total amine content of 30 wt %. By a parametric sensitivity analysis, this study showed that Henry's law constant and the estimated CO_2 diffusivity in aqueous amine solutions were among the most influential parameters for the prediction of the absorption rate. The importance of reliable diffusivity data was also reported by Mandal and Bandyopadhyay (2006).[29]

2.2.7.2. Other SHA Systems.

The aqueous 2-PE system was studied by Shen et al. (1991)[40] and Xu et al. (1993)[92] At 313 K, the ratio $D_{CO_2}^{1/2}/H_{CO_2}$ was found to decrease with the increase of the amine concentration. Xu et al. (1993) [92] mentioned that N_2O diffusivity decreased with the increase of amine concentration at a given temperature (at (293 and 313) K) and increased with an increase of the temperature for a given concentration (between (5 and 40) wt %). Only one publication was found reporting N_2O diffusivity values in aqueous AEPD solutions.[45] As mentioned by Shen et al. (1991),[40] it was found that the ratio $D_{CO_2}^{1/2}/H_{CO_2}$ decreased with the increase of amine concentration at a given temperature (between (303.15 to 318.15) K) and decreased when temperature increased at a given concentration (between (5 and 25) wt %). One work was also found for the aqueous AMPD system.[48] D_{CO_2} was determined by the N_2O analogy; the solubilities were taken from Baek et al.[47] Bougie and Iliuta (2009)[93] measured the ratio $D_{CO_2}^{1/2}/H_{CO_2}$ by the absorption of N_2O in AHPD solutions of (0.5 to 2.4) kmol·m^{-3} ((6 to 27) wt %) between (303.15 and 323.15) K for AHPD solution, and the values were found to follow the same trend as those obtained by Yoon et al. (2002)[45] for AEPD systems. For the same system, Paul et al. (2009)[51] reported distinctly Henry's law constants and N_2O diffusivity in aqueous solutions of (2.17 to 21.7) wt %, over the temperature range from (298 to 323) K. It was found that N_2O diffusivity in the aqueous AHPD does not follow the Stokes–Einstein relation strictly.

2.2.8. Amine Diffusivity in SHA Solutions.

In addition to the CO_2 diffusivity, the amine diffusivity in aqueous solutions is an important physical parameter necessary for reaction kinetics study. According to Snijder et al. (1993),[94] the alkanolamine diffusivity can also be estimated with a modified Stokes–Einstein relation ($\beta = 0.60$):

$$(D_{\mathrm{amine}} \cdot \mu^{\beta})_{\mathrm{solution}} = \mathrm{constant} = (D_{\mathrm{amine}} \cdot \mu^{\beta})_{\mathrm{water}} \tag{16}$$

However, as it was observed in the case of CO_2 (N_2O) diffusivity, the reliability of this relation is questionable. The calculations also require the values of amine diffusivity in water at infinite dilution. Several correlations were found in the literature to estimate amine diffusion in water at infinite dilution: Othmer and Thakar (1953),[95] Scheibel (1954),[96] Hayduk and Laudie (1974),[97] and the modified Wilke–Chang relation.[97] Recently, Mandal et al. (2003)[30] used Glasscock's correlation (Glasscock, 1990)[98] to estimate AMP diffusivity AMP in water. However, works reporting values of SHA diffusivities in their aqueous solution are quite scarce in the literature.

Chang et al. (2005)[99] measured the diffusion coefficients of AMP, 2-PE, and other conventional alkanolamines in water at infinite dilution, as well as in concentrated solutions (up to 4 kmol·m^{-3} (35.8 wt %) for AMP and 3 kmol·m^{-3} (38.1 wt %) for 2-PE), from (303 to 343) K and at atmospheric pressure. It was found that infinite dilution diffusivity coefficients of alkanolamines in water depended on the characteristics of the solutions, such as the sizes of solute and solvent and the intermolecular interactions between solute and solvent. The following order was given for diffusivity coefficients of alkanolamines in water: AMP (molar mass 89.14) > DGA (105.14) > 2-PE (129.2) > TEA (149.19). This indicated that a lighter solute (alkanolamine) moved faster in water. An equation representing the diffusion coefficient as a function of temperature and solution concentration was applied to correlate all experimental data. Deviations between calculated and experimental data for AMP and 2-PE solutions were 2.4 % and 4.5 %, respectively.

3. MECHANISM OF REACTION BETWEEN CO$_2$ AND SHA. INFLUENCE OF STERIC HINDRANCE ON CARBAMATE STABILITY

In general, only aliphatic and cycloaliphatic amines are suitable for gas treatment (Sartori et al., 1987).[100] Due to their lower basicity, aromatic amines have a low absorption capacity and rate. When CO$_2$ is absorbed in an amine aqueous solution, the following reactions can occur (reaction mechanisms are presented for primary, secondary, tertiary, and sterically hindered amines for comparison).

Primary (RNH$_2$) and Secondary (R$_2$NH) Amines. An example is given for a primary amine:

- Zwitterion (RNH$_2^+$COO$^-$) formation

$$CO_2 + RNH_2 \leftrightarrow RNH_2^+COO^- \qquad (17)$$

- Carbamate (RNHCOO$^-$) and protonated amine (RNH$_3^+$) formation

$$RNH_2^+COO^- + RNH_2 \leftrightarrow RNHCOO^- + RNH_3^+ \qquad (18)$$

Global reaction:

$$CO_2 + 2RNH_2 \leftrightarrow RNHCOO^- + RNH_3^+ \qquad (19)$$

The key advantage of the primary and secondary alkanolamines such as MEA and DEA is their fast reactivity due to the formation of stable carbamates. Conversely, this will lead to a high solvent regeneration cost. On the absorption capacity side, they have the drawback of a relatively low CO$_2$ loadings (stoichiometric loading limited to 0.5 mol CO$_2$·mol amine^{-1}). Loadings greater than 0.5 mol CO$_2$·mol amine^{-1} can be achieved only at high CO$_2$ partial pressures.

Tertiary (R$_3$N) Amines.

- Bicarbonate (HCO$_3^-$) formation

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \qquad (20)$$

- Amine protonation

$$R_3N + H^+ \leftrightarrow R_3NH^+ \qquad (21)$$

Global reaction:

$$R_3N + CO_2 + H_2O \leftrightarrow R_3NH^+ + HCO_3^- \qquad (22)$$

Tertiary alkanolamines, like MDEA and TEA, have a low reactivity with respect to CO$_2$, due to the formation of bicarbonates by CO$_2$ hydrolysis. However, this will lead to a very low solvent regeneration cost. Another advantage of these amines is the high CO$_2$ theoretical loading capacity of 1 mol of CO$_2$·mol of amine^{-1}.

Sterically Hindered Amines. The reaction between a sterically hindered amine and CO$_2$ be can described through three simultaneous mechanisms:

(a) Bicarbonate formation following the same mechanism as tertiary amines (eq 22).

(b) Bicarbonate formation by zwitterion hydrolysis:

$$RNH_2 + CO_2 \leftrightarrow RNH_2^+COO^- \qquad (17)$$

$$RNH_2^+COO^- + H_2O \leftrightarrow RNH_3^+ + HCO_3^- \qquad (23)$$

Global reaction:

$$RNH_2 + CO_2 + H_2O \leftrightarrow RNH_3^+ + HCO_3^- \qquad (24)$$

(c) Bicarbonate formation by carbamate hydrolysis

$$RNH_2 + CO_2 \leftrightarrow RNH_2^+COO^- \qquad (17)$$

$$RNH_2^+COO^- + RNH_2 \leftrightarrow RNHCOO^- + RNH_3^+ \qquad (25)$$

$$RNHCOO^- + H_2O + (RNH_3^+) \leftrightarrow RNH_2 + (RNH_3^+) + HCO_3^- \qquad (26)$$

Global reaction:

$$RNH_2 + CO_2 + H_2O \leftrightarrow RNH_3^+ + HCO_3^- \qquad (24)$$

Due to the hindrance of the bulky group adjacent to the amino group, sterically hindered amines form unstable carbamates whose hydrolysis leads to the formation of bicarbonate, resulting in the theoretical loading capacity up to 1.0, like the tertiary amines. Due to the very low kinetics of the physical CO$_2$ absorption, bicarbonate formation through mechanism a is much less probable than b and c.

4. ABSORPTION CAPACITY

CO$_2$ solubility data are of great interest because they are essential for the design and operation of absorption scrubbing equipment in many technical applications like the chemical industry, oil and gas industry, and in environmental protection as well. Tables 17 to 20 present all experimental data published in the open literature concerning the solubility of CO$_2$ in single SHA aqueous solutions (Tables 17 and 19) and in SHA based mixed aqueous solutions (Tables 18 and 20) up to date.

4.1. CO$_2$ Chemical Solubility in Single Amine Aqueous Solutions. *4.1.1. CO$_2$ Absorption in AMP Aqueous Solutions.* As the solubility measurements for the CO$_2$–AMP system attracted many researchers and the available data are abundant with respect to data for other SHAs, this system is discussed in its own section.

Table 17. CO_2 Solubility in Single SHA Aqueous Solutions

	T	ΔT	P_{CO_2}	ΔP_{CO_2}	[SHA]	$\Delta\alpha$	
system	K	K	kPa	kPa	wt %	$mol \cdot mol^{-1}$	reference
AMP[a]	313, 393		0.55−2068		26.8		5
AMP	313	0.5	1.25−216	0.1 %	26.8	3 %	102
AMP	313	0.5	2.17−5740	0.1 %	18	3 %	102
AMP	373	0.5	8.53−5870	0.1 %	18	3 %	102
AMP	323	0.5	4.32−5645		30.7	3 %	105
AMP	293,313,333,353	0.5	1.59−98.93		18, 26.8		107
AMP[a]	303,313,323		0.1−100		18	12 %	112
AMP	313	0.1	43.7−159	1.4	18	5 %	114
AMP[a]	313, 333, 353	0.1	0.69−344	0.25 %	30		74
AMP[b]	288.5, 293, 298, 303	0.2	n.a.		4.5−18	2 %	18
AMP[b]	293, 298, 303, 308, 313	0.1	n.a.	0.2	18−26.8	2 %	89
AMP[b]	293, 298, 303, 308, 313	0.1	n.a.	0.2	18−26.8	2 %	87
AMP	313, 333, 353	0.1	3.94−336.6	0.1 %	30	3 %	115
AMP	303, 313, 323, 333		0.5−100		18	12 %	110
AMP	313, 333, 353, 373	0.1	1.05−197	1.4	30	3 %	116
AMP	303	0.1	4.41−90.1	0.2	18	2 %	12
AMP	303, 313, 323	0.1	3.20−94	0.2	25, 30.4	2 %	12
AMP	313, 333, 353	0.04	7.3−2743	0.2 %	17.6, 35.6	3 %	118
AMP	313	0.5	0.162−283.7		18	3 %	117
AMP	343	0.5	0.586−5279		18	3 %	117
AMP	313	0.01	0.89−151.9	5/10	26.8	3 %	120
AMPD	313		0.34−881	0.5 %	10.4		125
AMPD	313	0.1	1.04−2991	0.1 %	10	3 %	123
AMPD	303, 313, 333	0.1	0.6−3064	0.1 %	30	3 %	123
AMPD[b]	303, 313, 325	0.1	n.a.		10, 20, 30	3 %	47
AEPD	313, 323, 333	0.1	1.8−1927.4	0.1 %	10	3 %	126
AEPD	333	0.1	7.7−2849	0.1 %	30	3 %	126
AHPD	313, 323, 333	0.1	21.7−1839.8	0.1 %	10		49
AHPD	313	0.1	42.1−1451.5	0.1 %	20		49
AHPD	298	0.1	0.9−2427.3	0.1 %	10		128
AHPD	283, 298, 313	0.01	1.91−74.8	0.25 %	0.15−10	1 %	50
AHPD[b]	283, 298, 313	0.01	n.a.	0.25 %	0.15−10	1 %	50
AHPD	284, 293, 298, 303, 323, 333	0.1	0.31−2637.6		10−32.6		130
AHPD[b]	298, 303, 313, 323	0.3	n.a.	0.2	2.17−21.7	1.5 %	51

[a] d.n.t: data not tabulated. [b] p.s.: physical solubility; solubility uncertainties are on Henry's constant.

Sartori and Savage (1983)[5] measured CO_2 solubility in unhindered MEA and hindered AMP aqueous solutions (3.0 $kmol \cdot m^{-3}$; 26.8 wt %) at (313 and 393) K and studied the steric hindrance and basicity on CO_2−amine reactions. The higher CO_2 loadings observed at 313 K for the hindered amine, AMP, confirmed the formation of unstable carbamates. At 393 K, a temperature close to that of regeneration, CO_2 loadings in AMP were lower relatively to MEA, which was in agreement with the thermodynamic model predictions. Chakraborty et al. (1986)[101] investigated the behavior of CO_2 in AMP aqueous solutions using different experimental setups. Their data are not tabulated but graphically discussed. An acidic species such as CO_2 could, in principle, react with both the amino and alcohol groups present in the AMP molecule. However, the possible formation of an alkyl carbonic ion from the reaction between CO_2 and the alcohol group of AMP can be neglected because the solution pH never exceeds 12.0 (it is usually between 7.5 and 9). The CO_2 reaction with the amino group leads to the formation of chemically combined CO_2 forms: carbamate, bicarbonate, and carbonate ions. Since the basicity of AMP is low enough to guarantee that the carbonate−bicarbonate equilibrium is shifted toward the bicarbonate, the carbonate formation can entirely neglected. From C^{13} NMR spectra of liquid samples after reaction, the authors could not identify the carbamate peak, and they concluded that the concentration of carbamate was lower than the instrument sensitivity.

Roberts and Mather (1988)[102] studied the CO_2 absorption in aqueous AMP solutions at 313 K ((2.0 and 3.0) $kmol \cdot m^{-3}$ AMP; (17.9 and 26.8) wt %) and 373 K (2.0 $kmol \cdot m^{-3}$ AMP) over a wide range of CO_2 partial pressures (generally from (1.25 to 5870) kPa). Excellent agreement was found between their data and those reported by Sartori and Savage (1983).[5] Experimental data were also compared with previously reported solubility in aqueous MEA solutions. It was shown that the CO_2 solubility was much greater in aqueous AMP solutions than in MEA solutions at loadings between 0.5 and 1.0, which was in agreement with the behavior of SHA in respect to primary amines (see Section 3). The lower solubility in the aqueous MEA solution was due to the stable carbamate formation which limited the stoichiometric loading to 0.5. The formation of the unstable carbamate ion by reaction of AMP with CO_2 was followed by its hydrolysis, and thus a solution loading of 1.0 may be more easily attained. The experimental data reported in that work were used later by Hu and Chakma (1990)[103] for comparison with the predictions obtained using a mathematical model developed for the determination of the

Table 18. CO_2 Solubility in SHA Based Mixed Solvents

	T	ΔT	P_{CO_2}	ΔP_{CO_2}		$\Delta\alpha$	
system	K	K	kPa	kPa	concentration	$mol \cdot mol^{-1}$	reference
2-PE + TMS	313, 373	0.1	0.274−5548	0.1 %	55 wt % 2-PE + 10 wt % sulfolane		134
2-PE + TMS	298, 313, 343, 373, 403	0.1	0.00156−18900	0.1 %	45 wt % 2-PE + 40 wt % sulfolane	4 %	135
AHPD + Pz[a]	288, 298, 313, 333	0.1	n.a.		(1.1−4.2) $mol \cdot kg^{-1}$ AHPD + (0.1−0.65) $mol \cdot kg^{-1}$ Pz	2 %	130
AHPD + Pz	288, 298, 313, 333	0.1	2.1−2310		(1.1−4.2) $mol \cdot kg^{-1}$ AHPD + (0.01−0.66) $mol \cdot kg^{-1}$ Pz		130
AMP + DEA	313, 373	0.02	162−2908	3.5	5 wt % AMP + 25 wt % DEA	10 %	73
AMP + DEA	313, 373	0.02	22−2597	3.5	10 wt % AMP + 20 wt % DEA	10 %	73
AMP + DEA[a]	303,308,313	0.5	n.a.		(6−24) wt % AMP + (6−24) wt % MEA	2 %	90
AMP + DEA[a]	293, 298, 303, 308, 313	0.1	n.a.	0.2	(21−30) wt % AMP + (0−9) wt % DEA	2 %	87
AMP + DEA	313, 333, 353	0.1	0.69−344	0.25 %	(0−30) wt % AMP + (0−30) wt % DEA		74
AMP + DEA	313, 333, 353	0.1	1.61−357.3	0.1 %	(0−30) wt % AMP + (0−30) wt % DEA	3 %	115
AMP + MDEA	313	0.04	12.5−4020[b]	0.2 %/0.1 %	1.266 $mol \cdot kg^{-1}$ AMP + 1.278 $mol \cdot kg^{-1}$ MDEA	3 %	118
AMP + MDEA	303, 313, 323		0.1−100		2.0 $kmol \cdot m^{-3}$ total amine content	12 %	112
AMP + MEA[a]	303,308,313	0.5	n.a.		(0−30) wt % AMP + (0−30) wt % MEA	2 %	88
AMP + MEA[a]	293, 298, 303, 308, 313	0.1	n.a.	0.2	(21−30) wt % AMP + (0−9) wt % MEA	2 %	89
AMP + MEA	313, 333, 353	0.1	0.69−344	0.25 %	(0−30) wt % AMP + (0−30) wt % MEA		74
AMP + MEA	313, 333, 353, 373	0.1	1−199	1.4	(0−30) wt % AMP + (0−30) wt % MEA	3 %	116
AMP + Pz	313, 333, 353	0.01	0.97−139.9	5/10	(2.0, 3.0) $kmol \cdot m^{-3}$ AMP + (0.5, 1.0, 1.5) $kmol \cdot m^{-3}$ Pz	3 %	120
AMP + TMS	313, 373	0.5	2.63−6050	0.1 %	16.5 wt % AMP + 32.2 wt % sulfolane	3 %	122
AMP + DEA + MDEA	313, 343, 393	0.02/0.5	10−1929	3.5	4 wt % AMP + 12.5 wt % DEA + 32.5 wt % MDEA		72
AMP + DEA + MDEA	313, 343, 393	0.02/0.5	6.6−1999.1	3.5	6 wt % AMP + 12.5 wt % DEA + 32.5 wt % MDEA		72
AMP + DEA + MDEA	313, 343, 393	0.02/0.5	3.1−1968.7	3.5	10 wt % AMP + 12.5 wt % DEA + 32.5 wt % MDEA		72

[a] Physical solubility; solubility uncertainties are on Henry's constant. [b] Total pressure.

equilibrium solubility of CO_2 in aqueous AMP solutions. The same experimental method[104] was used by Teng and Mather (1989)[105] for measuring CO_2 solubility in 3.43 $kmol \cdot m^{-3}$ (30.7 wt %) aqueous AMP solutions at 323 K and CO_2 partial pressures varying between (4.32 and 5645) kPa. Solubility data were correlated using the Deshmukh and Mather model.[106] Based on the work of Sartori et al. (1987),[100] the authors neglected the carbamate formation. It was shown that the model reproduced the experimental data within the experimental uncertainty. Tontiwachwuthikul et al. (1991)[107] measured the CO_2 solubility in (2.0 and 3.0) $kmol \cdot m^{-3}$ ((17.9 and 26.8) wt %) aqueous AMP solutions at (293, 313, 333, and 353) K and CO_2 partial pressures varying between (1.59 and 98.93) kPa using a thermostatted gas/liquid contactor.[108] The authors found very good agreement between their data at 313 K and those found in the literature.[5,102] A modified Kent−Eisenberg model[109] was found to represent experimental data accurately. Haji-Sulaiman and Aroua (1996)[110] measured CO_2 solubility in aqueous 2.0 $kmol \cdot m^{-3}$ (17.9 wt %) AMP solutions at (303, 313, 323, and 333) K (1 data point) and 353 K (1 data point) and over CO_2 partial pressures of (0.5 to 100) kPa, by using a thermostatted stirred cell reactor. Data were correlated using the Deshmukh and Mather model.[106] Using a similar experimental setup,[110,111] additional measurements were provided later by the same research group at (303, 313, and 323) K, but data were not tabulated but graphically represented (Aroua et al., 2002).[112] Experimental data were graphically compared with predictions obtained by applying the electrolyte nonrandom two-liquid (NRTL) model,[113] using the AspenPlus software. Jane and Li (1997)[114] measured CO_2 solubility in 2.0 $kmol \cdot m^{-3}$ (17.9 wt %) aqueous AMP solutions at 313 K and a good agreement was found with data reported by Roberts and Mather (1988)[102] (5% deviation). Park et al. (2002)[74] measured CO_2 solubility in 30 wt % aqueous AMP solutions at (313, 333, and 353) K, but experimental data were not tabulated, only graphically represented. Based on the experimental data, a modified Kent−Eisenberg model[109] was used to determine the equilibrium constants corresponding to amine protonation and carbamate hydrolysis. The CO_2 solubility in aqueous 30 wt % AMP solution was also measured by Seo and Hong (1996)[115] at (313, 333, and 353) K, and data were in good agreement with those reported by Li and Chang (1994)[116] (see also Section 4.2). Kundu et al. (2003)[12] measured the solubility of CO_2 in (18, 25, and 30) wt % aqueous AMP solutions over a temperature range of (303 to 323) K and over CO_2 partial pressures ranging between (3.2 and 94) kPa. The modified Clegg−Pitzer equation was used to correlate and predict equilibria for this system. Generally, predicted results were found in good agreement with previous published data.[105,114−116] Teng and Mather (1990)[117] measured the CO_2 solubility in 2.0 $kmol \cdot m^{-3}$ (17.9 wt %) aqueous AMP solutions at (313 and 343) K and a wide range of pressures between (0.162 and 5279) kPa. Data at 313 K agreed well with those reported by Roberts and Mather (1988).[102] The authors observed that the solubility of CO_2 in AMP solutions was higher than that in comparable DEA or TEA solutions.

Table 19. Estimated Henry's Law Constants for CO_2 in Aqueous Single SHA Solutions Using the N_2O Analogy

	T	[SHA]	H_{CO_2}	
system	K	$kmol \cdot m^{-3}$	$kPa \cdot m^3 \cdot kmol^{-1}$	reference
AMP	288.5	0.5	2463.2	18
		1.0	2592.6	
		1.5	2696.2	
		2.0	2823.3	
	293.0	0.5	2801.7	
		1.0	2954.8	
		1.5	3072.4	
		2.0	3218.7	
	298.0	0.5	3062.5	
		1.0	3229.5	
		1.5	3351.4	
		2.0	3505.8	
	303.0	0.5	3466.8	
		1.0	3652.9	
		1.5	3779.7	
		2.0	3944.0	
AMP	293	2.0	3157	89, 87
		2.5	3241	
		3.0	3320	
	298	2.0	3636	
		2.5	3721	
		3.0	3818	
	303	2.0	3846	
		2.5	3911	
		3.0	4004	
	308	2.0	4405	
		2.5	4485	
		3.0	4551	
	313	2.0	4530	
		2.5	4619	
		3.0	4693	
AHPD	298	0.2	3170	51
		0.4	3202	
		0.9	3277	
		1.3	3390	
		1.9	3522	
	303	0.2	3535	
		0.4	3579	
		0.9	3670	
		1.3	3820	
		1.9	3982	
	313	0.2	4417	
		0.4	4492	
		0.9	4643	
		1.3	4810	
		1.9	4896	
	323	0.2	5527	
		0.4	5644	
		0.9	5767	
		1.3	5894	
		1.9	6027	
AHPD	283	0.01	1934	50
		0.04	1947	
		0.08	1952	
		0.2	1961	
		0.8	2087	
	298	0.01	3007	
		0.04	3017	
		0.08	3018	
		0.2	3041	
		0.8	3176	
	313	0.01	4242	
		0.04	4257	
		0.08	4262	
		0.2	4274	
		0.8	4463	

Moreover, at CO_2 loadings higher than unity, the temperature had little effect on gas solubility, as noted for MDEA solutions (Jou et al., 1982).[104] Silkenbäumer et al. (1998)[118] measured the CO_2 solubility in aqueous AMP solutions at different molal concentrations between (2.43 and 6.242) $mol \cdot kg^{-1}$ and at temperatures of (313, 333, and 353) K. A model taking into account CO_2 absorption coupled with the chemical reaction in the liquid phase was used to correlate experimental data. Activity coefficients for both molecular and ionic species were calculated from the Pitzer equation.[119] At low pressures, the authors found a good agreement between the correlation results and experimental data by Roberts and Mather (1988)[102] obtained at 313 K and AMP concentrations of (2.0 and 3.0) $kmol \cdot m^{-3}$. However, at high CO_2 partial pressures, previous data were systematically higher than the correlation results. A good agreement was also observed between the correlation results and solubility data by Tontiwachwuthikul et al. (1991)[107] measured from (293 to 353) K and for AMP concentrations of (2.0 and 3.0) $kmol \cdot m^{-3}$ (17.9 and 26.8 wt %), except for data at 313 K and 3.0 $kmol \cdot m^{-3}$ where the experimental partial pressures were higher that the calculated ones. Finally, solubility data by Teng and Mather (1990)[117] measured for 2.0 $kmol \cdot m^{-3}$ aqueous AMP solutions and at 343 K were found to agree well with the correlation results, at low and high pressures. CO_2 solubility given by Yang et al. (2010)[120] at 313 K and pressures between (0.89 and 151.9) kPa were found in good agreement with those reported by Roberts and Mather (1988)[102] and Tontiwachwuthikul et al. (1991).[107] Xu et al. (1992)[121] developed a mathematical model based on the extended Debye–Hückel equation for representing the CO_2 solubility in aqueous AMP solutions. Model parameters were obtained on the basis of selected experimental data reported by Roberts and Mather (1988)[102,122] and Teng and Mather (1989, 1990),[105,117] because they were measured using the same method and covered a wide range of amine concentration, temperature, and pressure. The stability constant of carbamate in solution was estimated. According to the correlation results, the authors concluded that the formation of protonated amine and bicarbonate ions is the dominant reaction. Carbamate ion concentration was found between the order of 10^{-5} and 10^{-2}.

4.1.2. CO_2 Absorption in Other SHA Aqueous Solutions. Two works are available for the aqueous CO_2–AMPD system. CO_2 solubility in 10 and 30 wt % aqueous solutions at (303, 313, and 333) K and over CO_2 partial pressures ranging between (0.6 and 3064) kPa was determined by Baek and Yoon

Table 20. Estimated Henry's Constants for CO_2 in Aqueous Mixed SHA Based Solutions, Using the N_2O Analogy

system	T	wt % (1) + wt % (2)	H_{CO_2}	reference
	K		$kPa \cdot m^3 \cdot kmol^{-1}$	
AMP (1) + MEA (2)	303.0	0 + 30	3181.9	88
		6 + 24	3317.3	
		12 + 18	3582.3	
		18 + 12	3949.8	
		24 + 6	4083.0	
		30 + 0	4271.5	
	308.0	0 + 30	3382.2	
		6 + 24	3601.1	
		12 + 18	4073.6	
		18 + 12	4292.8	
		24 + 6	4539.7	
		30 + 0	4713.7	
	313.0	0 + 30	3646.6	
		6 + 24	3943.8	
		12 + 18	4360.7	
		18 + 12	4846.1	
		24 + 6	5081.7	
		30 + 0	5356.3	
AMP (1) + MEA (2)	293.0	30 + 0	3328	89
		28.5 + 1.5	3306	
		27 + 3	3278	
		25.5 + 4.5	3247	
		14 + 6	3221	
		22.5 + 7.5	3182	
		21 + 9	3159	
	298.0	30 + 0	3829	
		28.5 + 1.5	3780	
		27 + 3	3731	
		25.5 + 4.5	3697	
		14 + 6	3667	
		22.5 + 7.5	3614	
		21 + 9	3560	
	303.0	30 + 0	4021	
		28.5 + 1.5	3970	
		27 + 3	3912	
		25.5 + 4.5	3856	
		24 + 6	3805	
		22.5 + 7.5	3750	
		21 + 9	3706	
	308.0	30 + 0	4569	
		28.5 + 1.5	4495	
		27 + 3	4434	
		25.5 + 4.5	4366	
		14 + 6	4307	
		22.5 + 7.5	4207	
		21 + 9	4141	
	313.0	30 + 0	4720	
		28.5 + 1.5	4622	
		27 + 3	4576	
		25.5 + 4.5	4521	
		14 + 6	4459	
		22.5 + 7.5	4405	
		21 + 9	4349	
AMP (1) + DEA (2)	303.0	6 + 24	4799.0	90
		12 + 18	4590.3	
		18 + 12	4496.4	
		24 + 6	4404.0	
	308.0	6 + 24	6179.3	
		12 + 18	5740.0	
		18 + 12	5357.4	
		24 + 6	5046.0	
	313.0	6 + 24	8193.9	
		12 + 18	7236.5	
		18 + 12	6440.1	
		24 + 6	5828.1	
AMP (1) + DEA (2)	293.0	30 + 0	3328	87
		28.5 + 1.5	3350	
		27 + 3	3381	
		25.5 + 4.5	3401	
		24 + 6	3405	
		22.5 + 7.5	3434	
		21 + 9	3447	
	298.0	30 + 0	3829	
		28.5 + 1.5	3862	
		27 + 3	3863	
		25.5 + 4.5	3886	
		24 + 6	3890	
		22.5 + 7.5	3916	
		21 + 9	3929	
	303.0	30 + 0	4021	
		28.5 + 1.5	4018	
		27 + 3	4024	
		25.5 + 4.5	4026	
		24 + 6	4034	
		22.5 + 7.5	4055	
		21 + 9	4071	
	308.0	30 + 0	4569	
		28.5 + 1.5	4576	
		27 + 3	4591	
		25.5 + 4.5	4604	
		24 + 6	4623	
		22.5 + 7.5	4632	
		21 + 9	4646	
	313.0	30 + 0	4720	
		28.5 + 1.5	4890	
		27 + 3	5109	
		25.5 + 4.5	5223	
		22.5 + 7.5	5267	
		22.5	5296	
		21 + 9	5308	

(1998).[123] A comparison between CO_2 solubility in aqueous AMPD solutions and that in aqueous MEA, MDEA, and AMP solutions[115,124] showed that the tendency of the solubility in AMPD solutions was similar to that in MDEA solutions. At low partial pressures, CO_2 solubility was lower in MDEA solutions and became higher at high pressures. Puxty et al. (2009)[125] measured CO_2 solubility in 1 $kmol \cdot m^{-3}$ (10 wt %) AMPD aqueous solutions at 313 K based on a synthetic method and by using a thermostatted glass reactor. Data by Puxty et al. (2009)[125] were higher than those reported by Baek and Yoon (1998)[123] at low partial pressures and became lower at higher pressures.

The CO_2 solubility in the aqueous AEPD system was only measured by Park et al. (2002)[126] at (313, 323, and 333) K and over CO_2 partial pressures ranging between (1.8 and 2849) kPa. A comparison with other amines such as MEA,[126,127] AMPD,[123] AMP,[115] and MDEA[124] showed that the tendency of CO_2 solubility in aqueous AEPD solutions was similar to those in MDEA and AMPD solutions. At low partial pressures, the CO_2 solubility in aqueous MEA solutions was higher than in AMP, MDEA, AMPD, or AEPD solutions but became lower at higher pressures (more than about (10 to 90) kPa, depending on the amine type).

The aqueous CO_2–AHPD system attracted more attention. The CO_2 solubility in (10 and 20) wt % aqueous solutions at (313, 323, and 333) K and over CO_2 partial pressures ranging between (21.7 and 1839.8) kPa was first determined by Park et al.[49] Solubilities in 10 wt % aqueous AHPD were compared with those in aqueous solutions of MEA[126] and other hindered amines such as AMPD[123] and AEPD.[126] At partial pressures higher than about 40 kPa, the CO_2 loading capacity of aqueous AHPD solutions was higher than that in MEA solutions. Moreover, the loading capacity of all sterically hindered amines analyzed (AMPD, AEPD, and AHPD) was found to be higher than that in MEA, following the order AHPD > AEPD > AMPD. At lower partial pressures, the CO_2 loading capacity in aqueous MEA solutions became higher than in AHPD. New data for this system at 298 K and aqueous AHPD solution concentration of 10 wt % were reported later by the same research group (Park et al., 2003).[128] Le Tourneux et al.[50] measured the CO_2 solubility in aqueous AHPD solutions of concentrations between (0.15 and 2.5) wt %, at (283, 298, and 313) K and over CO_2 partial pressures ranging between (1.91 and 74.8) kPa. The low concentration range was compatible with aqueous solutions in use in an enzymatic CO_2 capture process. It was shown that the enzyme did not influence the CO_2 solubility, but only accelerated reaching the equilibrium. Data were correlated using the modified Kent–Eisenberg model.[74,107,116,117,129] Additional solubility data for CO_2 in 10 wt % aqueous AHPD solutions were compared with those reported by Park et al.,[128] and it was shown that data by Park et al. were lower than those reported by Le Tourneux et al.[50] New CO_2 solubility data were recently measured by Bougie and Iliuta (2010)[130] for concentrations of (0.917, 2, 3, and 4) $mol \cdot kg^{-1}$, temperatures between (285 and 333) K, and over CO_2 partial pressures ranging between (0.314 and 2637.6) kPa. When comparison was possible, it was shown that data by Bougie and Iliuta[130] agreed well with those given by Le Tourneux et al.,[50] which were obtained using a different experimental setup. However, several data by Bougie and Iliuta[130] disagreed from those reported by Park et al.[49,128]

4.2. CO_2 Chemical Solubility in SHA Based Mixed Solvents.

4.2.1. CO_2 Absorption in AMP Based Mixed Solvents. Mixed solvents represent a combination of chemical and physical pure solvents. The use of blended alkanolamines for the removal of acid gases from gas streams has become very attractive because of their advantages over traditional treating solvents (single aqueous amine solutions). The mixed solvents combine the advantages of each amine present in the mixture: the fast reactivity of primary or secondary alkanolamine (e.g., MEA, DEA) is coupled with the high absorption capacity and low solvent regeneration cost of tertiary (e.g., MDEA) or SHA (e.g., AMP) amines.

Roberts and Mather (1988)[122] measured the CO_2 solubility in a mixed solvent consisting of AMP (16.5 wt %), sulfolane (tetramethylene sulfone, TMS) (32.2 wt %), and water at (313 and 373) K and at CO_2 partial pressures between (2.63 and 6050) kPa. The solubility in the mixed solvent was compared with the solubility in an aqueous solution of equivalent amine concentration. It was shown that the solubility of CO_2 was significantly lower in the mixed solvent than in the aqueous AMP solvent at low acid gas partial pressures. With the increase of the CO_2 partial pressure this difference in the solubility decreased, and at high partial pressures (much larger at 313 K (around 1400 kPa) than at 373 K (around 120 kPa)) the solubility of CO_2 became larger in the mixed solvent. Li and Chang (1994)[116] measured the CO_2 solubility in aqueous AMP + MEA solutions at (313, 333, 353, and 373) K for various ratios of AMP/MEA for a total amine concentration of 30 wt %. Based on the experimental data, a modified Kent–Eisenberg model[109,129] was used to determine the equilibrium constants corresponding to AMP and MEA protonation and MEA carbamate hydrolysis. Park et al. (2002)[74] measured the CO_2 solubility in aqueous AMP + MEA and AMP + DEA solutions at (313, 333, and 353) K, keeping the total amine concentration at 30 wt %. Experimental data were not tabulated, only graphically represented. As also observed by Li and Chang (1994),[116] the equilibrium curve P_{CO_2}/α for the system MEA + CO_2 crossed the one corresponding to AMP + CO_2 system. At low CO_2 partial pressures and up to a CO_2 loading of about 0.5, the addition of AMP to an aqueous MEA solution led to a decrease of CO_2 solubility. The AMP addition favored CO_2 solubility at higher pressures. These observations agreed to the behavior of SHA which can reach CO_2 loadings up to 1 due to carbamate formation followed by its hydrolysis and conversion to bicarbonate, coupled with the high reactivity of MEA which formed stable carbamate. Being less reactive than MEA, DEA did not have a similar influence on the solubility of CO_2 in AMP solutions. While the MEA addition to an aqueous AMP solution resulted in the increase of CO_2 solubility, the addition of DEA did not. It was observed that, at low loadings, DEA nearly had the same tendency to absorb CO_2 like AMP. However, at higher loadings DEA behaved in the same way like MEA due to the formation of stable carbamates. CO_2 solubility in aqueous AMP + DEA solutions at (313, 333, and 353) K was also measured by Seo and Hong (1996)[115] for the same total amine concentration of 30 wt % but different ratios between AMP and DEA than those considered by Park et al. (2002).[74] However, Park et al. (2002)[74] did not compare their data with those reported by Seo and Hong (1996),[115] even if they mentioned this reference in their work. Even if Park et al. (2002)[74] did not report any tabulated data, the results of these two studies were found to agree well. To test the predictive capability of the model used to correlate experimental data of CO_2 solubility in aqueous AMP solutions (described previously in Section 4.1.1), Silkenbäumer et al. (1998)[118] measured the CO_2 solubility in aqueous mixtures of AMP (1.266 $mol \cdot kg^{-1}$) and MDEA (1.278 $mol \cdot kg^{-1}$) at 313 K and for total pressures between (12.5 and 4020) kPa. It was found that, at constant total pressure, the addition of AMP, a stronger base than MDEA, to an aqueous MDEA solution increased CO_2 loadings. The model based only on data for the aqueous systems CO_2 + MDEA and CO_2 + AMP predicted the CO_2 solubility in the aqueous mixed solvent well. Murietta-Guevara et al. (1998)[73] reported the solubility of CO_2 in aqueous mixtures of AMP + DEA at (313 and 373) K for a total amine concentration of 30 wt %, with different compositions of the individual alkanolamines. Data analysis revealed a general trend: CO_2 solubility increased with the increase of AMP concentration. Using the same apparatus and methodology,[73,131,132] Rebolledo-Libreros and Trejo (2004)[72] measured the CO_2 solubility in aqueous solutions containing three amines: MDEA (32.5 wt %), DEA (12.5 wt %), and AMP ((4, 6, and 10) wt %). The authors found that the increase of AMP concentration in a mixture DEA + MDEA led to the increase of CO_2 solubility. Aroua et al. (2002)[112] measured the CO_2 solubility in aqueous AMP and MDEA mixtures (2.0 $kmol \cdot m^{-3}$ total amine concentration in all measurements) at (303, 313, and 323) K and over CO_2 partial pressures of (0.1 to 100) kPa. Data were not tabulated; an example was given graphically for 303 K and compared with predictions obtained by applying the electrolyte NRTL model[113] using the AspenPlus software. You et al. (2008)[133] studied the effect of AMP addition on CO_2 absorption in aqueous ammonia at 298 K. The mixed solvent contained 10 wt % ammonia and 1 wt % AMP. Data were not tabulated, and they were expressed graphically as CO_2 removal efficiency of the absorbent from a feed gas containing 15 vol % CO_2 and 85 vol % N_2. It was shown that the AMP addition led to the reduction of ammonia vaporization and slightly increased CO_2 absorption capacity. Yang et al. (2010)[120] measured CO_2 solubility in aqueous mixtures containing AMP and Pz (as the activator) at (313, 333, and 353) K and pressures up to 139.9 kPa. AMP concentrations in the mixed solvent were (2 and 3) $kmol \cdot m^{-3}$ ((17.9 and 26.8) wt %), while Pz concentrations were (0.5, 1, and 1.5) $kmol \cdot m^{-3}$ ((4.3 to 12.9) wt %). It was observed that, at constant temperature and total amine concentration, the CO_2 solubility increased with increasing partial pressure. At constant temperature and AMP concentration, the Pz addition led to an increase in the CO_2 solubility.

4.2.2. CO_2 Absorption in Other SHA Based Mixed Solvents.

You et al. (2008)[133] studied the effect of AMPD, AEPD, and AHPD (THAM) addition on CO_2 absorption in aqueous ammonia (AM) at 298 K. The mixed solvent contained 10 wt % ammonia and 1 wt % AMPD, AEPD, or AHPD. Data were not tabulated, and they were expressed graphically as CO_2 removal efficiency of the absorbent from a feed gas containing 15 vol % CO_2 and 85 vol % N_2. It was shown that the addition of all SHA tested led to the reduction of ammonia vaporization and maintained or slightly increased the CO_2 absorption capacity. The CO_2 removal capacity had the following trend (this includes the AMP effect described in the previous section): AM < (AM + AMPD) < (AM + AEPD) < (AM + AMP) < (AM + AHPD). The positive effect of SHA addition was attributed to intermolecular interactions between the alkanolamines and CO_2. The loss of ammonia decreased as following: AM > (AM + AMPD) > (AM + AEPD) > (AM + AMP) > (AM + AHPD). The effect of SHA addition was attributed to the interactions between the hydroxyl groups of SHA and ammonia via hydrogen bonding. Lal et al. (1998)[134] measured the CO_2 solubility in an aqueous mixed solvent containing 55 wt % 2-piperidineethanol (2-PE) and 10 wt % sulfolane at (313 and 373) K and over CO_2 partial pressures ranging between (0.274 and 5548) kPa. The same research group (Jou et al., 1998)[135] also reported the CO_2 solubility in the same mixed solvent but at a different concentration, namely, 45 wt % 2-PE and 40 wt % sulfolane, at (298, 313, 343, 373, and 403) K and over a very large CO_2 partial pressure range between (0.00156 and 18 900) kPa. The authors[135] mentioned that 50 % of their reported data "were determined in 1981 using a wet chemical analysis and the other values were determined in 1993 mainly using chromatographic analysis". However, it was not clear if these data have already been published elsewhere because the corresponding references were not given. The formation of a second liquid phase consisting in almost pure sulfolane was noted at certain conditions. The presence of the physical solvent (sulfolane) led to loadings larger than unity. Li and Mather (1998)[136] used simplified Clegg–Pitzer equations[137−139] to correlate solubility data of CO_2 in this aqueous mixed solvent containing 45 wt % 2-PE and 40 wt % sulfolane. Bougie and Iliuta (2010)[130] recently studied the effect of Pz addition (as the activator) on CO_2 absorption in AHPD aqueous solutions between (288 and 333) K. The AHPD concentration in the mixed solvent was varied from (1.1 to 4.2) $mol \cdot kg^{-1}$, while Pz concentration was varied from (0.01 to 0.66) $mol \cdot kg^{-1}$. It was shown that, at constant total amine concentration and CO_2 partial pressure, an increase in temperature led to a decrease of CO_2 loadings. At constant temperature, an increase in the total amine concentration led to a decrease of CO_2 solubility. As expected, at constant temperature the Pz addition in an aqueous AHPD solution increased the CO_2 loading capacity.

4.3. CO_2 Physical Solubility in Single and Mixed Solvents.

Physical solubility data of acid gases (like CO_2 and H_2S) in single and mixed amine solutions, usually expressed in term of Henry's law constants, H_{gas}, represent key parameters needed for the design of absorption scrubbing equipments. Henry's law constants are particularly useful to calculate the CO_2 diffusion coefficient, D_{gas}, in solution from experimental values of the ratio $D_{gas}^{1/2}/H_{gas}$. However, because of the gas reaction within the amines, the genuine gas physical solubility cannot be measured directly. Henry's law constants in these solutions can be determined by the application of the N_2O analogy method,[16,18,84,87−89,140−143] by using N_2O and CO_2 solubility in water and N_2O solubility in the single or the mixed solvent. Relying on artificial neural networks, Bensetiti et al. (1999)[144] used an exhaustive N_2O solubility database for developing correlation for N_2O solubility in water, AMP, DEA, MDEA, MEA, and their mixtures. Combined with the N_2O analogy method, this correlation allowed the calculation of CO_2 solubility in single or blend solutions over wide ranges of amine concentrations and temperatures.

Saha et al. (1993)[18] reported CO_2 physical solubility data in aqueous AMP solutions of concentrations between (0.5 and 2.0) $kmol \cdot m^{-3}$ ((4.5 and 17.9) wt %) at (288.5, 293, 298, and 303) K. It was observed that the CO_2 solubility decreased with the increase of temperature. At constant temperature, the solubility decreased when the amine concentration increased. The same system was also studied by Mandal et al. (2004, 2005)[87,89] who measured N_2O solubility at (293, 298, 303, 308, and 313) K and amine concentration between (2.0 and 3.0) $kmol \cdot m^{-3}$ (both papers[87,89] contain the same estimated CO_2 solubility data in aqueous AMP solutions). For 2.0 $kmol \cdot m^{-3}$ AMP aqueous solutions, data by Mandal et al. (2004, 2005)[87,89] agreed well with those reported by Saha et al. (1993)[18] (mean deviation of 2.8 %).

Li and Lai (1995)[88] used a similar apparatus as Saha et al. (1993),[18] Weiland and Trass (1971),[145] Haimour and Sandal (1984),[146] Al-Ghawas et al. (1989),[147] and Haimour (1990)[148] to determine physical CO_2 solubility in aqueous mixed AMP + MEA solution at (303, 308, and 313) K. Mandal et al. (2005)[89] estimated the CO_2 solubility in the same aqueous system, AMP + MEA, at (293, 298, 303, 308, and 313) K. In both works the amine concentration was kept at 30 wt % in the mixed solvent, but the ratios between AMP and MEA were different. A comparison of solubility data is given in Figure 3. Data by Mandal et al. (2005)[89] were constantly lower than those given by Li and Lai (1995).[88] The highest deviations of data by Mandal et al. (2005)[89] (from those reported by Li and Lai, 1995)[88] were observed at 313 K (e.g., 11.9 % at 30 wt % AMP). However, it was observed that, for constant total amine concentration, the CO_2 solubility decreased with the increase of temperature. At constant temperature, the CO_2 solubility decreased with the increase of AMP concentration.

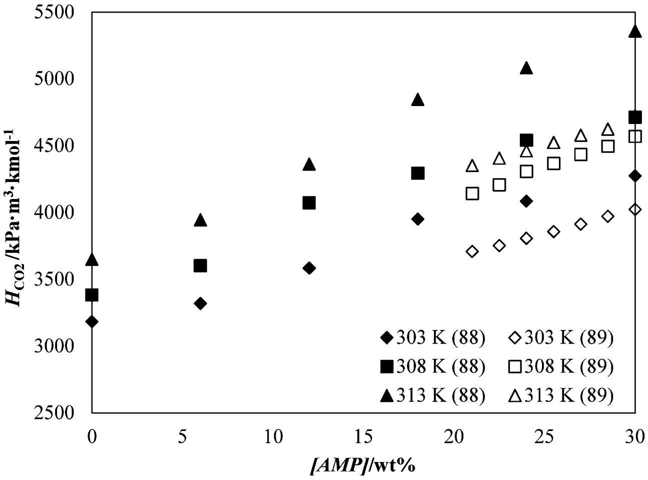


Figure 3. Henry's law constant of CO_2 in aqueous AMP + MEA mixtures for a total amine content of 30 wt % (references are given in parentheses).

Physical CO_2 solubility in aqueous mixed AMP + DEA solutions was studied by Li and Lee (1996)[90] at (303, 308, and 313) K and by Mandal et al. (2004)[87] at (293, 298, 303, 308, and 313) K. In both works, the total amine concentration in the mixed solvent was kept at 30 wt %. A comparison of solubility data is given in Figure 4. Data by Mandal et al. (2004)[87] were constantly lower than those given by Li and Lee (1996).[90] For a solution of 24 wt % AMP, the absolute deviation of data by Mandal et al. (2004)[87] (from those reported by Li and Lee, 1996)[90] was 9.6 %. As a general trend, for constant total amine concentration, the CO_2 solubility decreased with the increase of temperature. At a constant temperature, the CO_2 solubility increased with the increase of AMP concentration.

Baek et al. (2000)[47] measured N_2O solubility in (10, 20, and 30) wt % aqueous AMPD solutions at (303, 313, and 323) K. Data can be used to determine CO_2 physical solubility in these amine solutions. Le Tourneux et al. (2008)[50] measured the N_2O solubility in aqueous AHPD solutions of concentrations between (0.15 and 10) wt %, at (283.15, 298.15, and 313.15) K. Data were used to estimate Henry's law constant for CO_2 in the corresponding AHPD aqueous solutions. Paul et al. (2009)[51] estimated physical CO_2 solubility in aqueous AHPD solutions of concentrations between (2.17 and 21.7) wt %, at (298, 303, 313, and 323) K and atmospheric pressure. Data were correlated as a function of temperature and amine concentration. Bougie and Iliuta (2010)[130] measured the N_2O solubility in AHPD + Pz mixed solvent at (288, 298, 313, and 333) K. The AHPD concentration in the mixed solvent was varied from (1.1 to 4.2) mol·kg^{-1}, while Pz concentration was varied from (0.1 to 0.6) mol·kg^{-1}. Data can be used to determine CO_2 physical solubility in the mixed solvent.

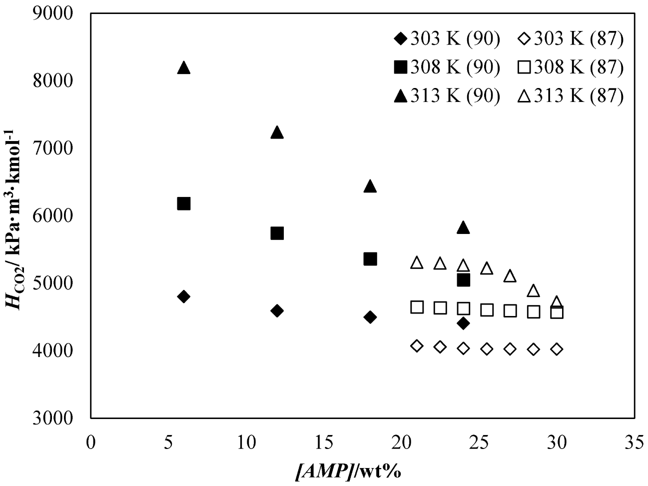


Figure 4. Henry's law constant of CO_2 in aqueous AMP + DEA mixtures for a total amine content of 30 wt % (references are given in parentheses).

5. ABSORPTION KINETICS

Kinetics data represent essential information in CO_2 absorption. To improve CO_2 capture, aqueous amine solutions not only require high absorption capacity but also an important absorption rate. For SHA applications in CO_2 separation, knowledge about the reaction mechanism and kinetic constants for various SHA is of major importance. Even though the available kinetic reviews (Mahajani and Joshi, 1988;[149] Vaidya and Kenig, 2007;[150] and Versteeg et al., 1996[151]) offer detailed descriptions on possible kinetic mechanisms between CO_2 and primary, secondary, and tertiary amine solutions, only very limited data on SHA are reported. We consider therefore that bringing together all kinetic available information related to SHA is highly needed.

The absorption rate of CO_2 in aqueous amine solution is usually described by a simple second-order reaction or by the zwitterion mechanism. The expression for the second-order reaction is given by:

$$r_{CO_2-\text{amine}} = k_2 C_A C_B \tag{27}$$

while with the zwitterion mechanism:

$$r_{CO_2-\text{amine}} = C_A C_B \Bigg/ \left(\frac{1}{k_2} + \frac{1}{\frac{k_2 k_{AM}}{k_{-1}} C_B + \frac{k_2 k_{OH^-}}{k_{-1}} C_{OH^-} + \frac{k_2 k_{H_2O}}{k_{-1}} C_{H_2O} + ...} \right) \tag{28}$$

It should be noted that the second term at the denominator contains kinetic parameters involved in the deprotonation of the zwitterion by bases in solution. The contribution of each base depends on its concentration as well as how strong the base is. Additional terms can therefore be present if mixtures of

Table 21. Kinetic Information of CO_2 Absorption by Various SHA (Other than AMP) Solutions

	T	[SHA]	k_2 at 298 K	k_2	k_2k_{Am}/k_{-1}	$k_2k_{H_2O}/k_{-1}$	
system	K	$kmol\cdot m^{-3}$	$m^3\cdot kmol^{-1}\cdot s^{-1}$	$m^3\cdot kmol^{-1}\cdot s^{-1}$	$m^6\cdot kmol^{-2}\cdot s^{-1}$	$m^6\cdot kmol^{-2}\cdot s^{-1}$	reference
2-PE	313	0.107–1.0		195			40
2-PE	283–313	0.25–2.5	620	$\exp(24.439 - 44621/RT)$	$\exp(24.619 - 41695/RT)$	$\exp(20.734 - 44206/RT)$	92
2-PE	303–323	0.14–1.13	495	$\exp(24.437 - 45171/RT)$			165
AEPD	303–318	0.417–2.154	242	$\exp(31.730 - 7820/T)$	$\exp(21.902 - 4809/T)$	$\exp(72.316 - 22843/T)$	45
AHPD	303–323	0.5–2.4	192	$\exp(26.953 - 6465/T)$	$\exp(15.999 - 3124/T)$	$\exp(11.695 - 3315/T)$	93
AHPD	303–323	0.179–1.789	329	$\exp(32.093 - 65155/RT)$			168
AMPD	278–303	0.025–1.6	194	$\exp(19.058 - 4110.2/T)$	$\exp(25.157 - 5381.3/T)$	$\exp(24.201 - 7043.5/T)$	169
AMPD	303–323	0.236–2.963	303[a]	$\exp(21.158 - 4602.6/T)$	$\exp(17.190 - 3434.7/T)$	$\exp(11.860 - 3476.8/T)$	48
TBAE	283–308		170	$\exp(31.330 - 7806/T)$			170

[a] Extrapolated value.

Table 22. Kinetic Information for CO_2 Absorption by AMP Solutions

	T	[AMP]	k_2 at 298 K	k_2	k_2k_{Am}/k_{-1}	$k_2k_{H_2O}/k_{-1}$	$k_2k_{Am\#2}/k_{-1}$	
system	K	$kmol\cdot m^{-3}$	$m^3\cdot kmol^{-1}\cdot s^{-1}$	$m^3\cdot kmol^{-1}\cdot s^{-1}$	$m^6\cdot kmol^{-2}\cdot s^{-1}$	$m^6\cdot kmol^{-2}\cdot s^{-1}$	$m^6\cdot kmol^{-2}\cdot s^{-1}$	reference
AMP	315			100				101
AMP	313	0.26–3.0		1270				14
AMP	278–298	0.01–1.5	520	$\exp(23.079 - 5013.7/T)$				153
AMP	298	0.202–2.373	10000	10000	127	8.36		15
AMP	294–318	0.5–2.0	555	$\exp(23.690 - 5176.49/T)$				155
AMP	288–318	0.17–3.5	782	$\exp(16.454 - 24261/RT)$	$\exp(16.005 - 20678/RT)$	$\exp(19.311 - 45670/RT)$		156
AMP	293–313	0.5–2.0	268	$\exp(26.500 - 6230.6/T)$				85
AMP	303	0.55–3.35	1105[a]	1150	1387	0.2611		158
AMP	313	0.55–3.35		1241	2057	1.875		158
AMP	293–313	0.2–2.8	570	$\exp(25.815 - 5801.7/T)$				32
AMP	298–313	0.05–0.35	578	$\exp(23.234 - 5028.5/T)$	$\exp(18.397 - 3522.1/T)$	$\exp(14.401 - 3413.9/T)$		157
AMP	313	3.3		731				159
AMP	288–313	0.1–3.0	27	$\exp(29.200 - 8186.9/T)$				164
AMP[b]	298	0.402–3.545	56	56.3	39			156
AMP + DEA	298–313	0.006–0.380	556	$\exp(22.829 - 4919.6/T)$	$\exp(13.996 - 2217.2/T)$	$\exp(14.424 - 3421/T)$	$\exp(23.799 - 4243.1/T)$	157
AMP + DEA	303–313	1.0–1.5	611	$\exp(19.509 - 3902/T)$				31
AMP + MEA	303–313	1.5–1.7	1098	$10^{(6.595-1059.2/T)}$	$10^{(13.23-3036.3/T)}$	$10^{(6.952-2392.9/T)}$	$10^{(19.607-5032.9/T)}$	28
AMP + MEA	298–313	0.073–0.256	559	$\exp(23.316 - 5063.2/T)$	$\exp(12.951 - 1872.1/T)$	$\exp(14.768 - 3532.7/T)$	$\exp(23.280 - 3547.6/T)$	157
AMP + Pz	303	0.55–3.35	1375[a]	1500	638.7	7.941	14693	158
AMP + Pz	313	0.55–3.35		1771	750.6	8.32	13767	158
AMP + Pz	303–313	1.0–1.5	1185[a]	$\exp(17.259 - 3034/T)$	$\exp(22.885 - 4241/T)$	$\exp(27.708 - 5893/T)$	$\exp(13.248 - 45861/T)$	35

[a] Extrapolated values. [b] In 1-propanol.

more than one amine are used. This mechanism also explains the shift in the order with respect to the amine often observed in kinetic experiments. For the same amine aqueous system and temperature, it should be expected that the values of k_2 determined from each of the eqs 27 and 28 are not exactly the same, because other kinetic constants are determined simultaneously in the zwitterion mechanism. However, these values should be of the same magnitude, as demonstrated by Shen et al. (1991).[40] Values of the kinetic constants for various SHA (except for AMP) and AMP, together with the corresponding temperature and amine concentration ranges, are indicated in Tables 21 and 22, respectively.

5.1. Single AMP Systems.

AMP is the most popular SHA; it is the reason why it will be discussed in the following two sections, separately from the other SHAs. Its high CO_2 loading capacity was first pointed out by Sartori and Savage (1983).[5] Since, a large amount of research was found in the literature concerning kinetics of AMP. More than 15 papers were found giving details on the reaction mechanism and/or kinetic constants on single and blended aqueous amine solutions.

Chakraborty et al. (1986)[101] studied the kinetics between pure CO_2 and aqueous AMP solutions at 315 K. The authors assumed that the forward reaction rate would be first order with respect to both CO_2 and AMP. A value as low as 100 $m^3 \cdot kmol^{-1} \cdot s^{-1}$ was found for k_2. However, the concentrations of the solutions used were not given, and only one temperature was considered, which is not quite sufficient to obtain reliable kinetic constants. Yih and Shen (1988)[14] mentioned that although Sartori and Savage (1983)[5] have noted that steric hindrance generally has an adverse effect on the CO_2-amine reaction rate constants, as indicated from data by Sharma (1965),[152] the above value of k_2 obtained by Chakraborty et al. (1986)[101] seemed too low in comparison with conventional amines. Therefore, the research by Yih and Shen (1988)[14] was undertaken to investigate the kinetic order with respect to both CO_2 and AMP and to obtain the second-order forward rate constant at 313 K. Concentrations of (0.258 to 3.0) $kmol \cdot m^{-3}$ were considered. The authors found that the reaction was first order in respect to both CO_2 and AMP, as it was also mentioned in Chakraborty et al. (1986).[101] The new k_2 value of 1270 $m^3 \cdot kmol^{-1} \cdot s^{-1}$ obtained in their study was about 6 times lower than the value of k_2 for CO_2–MEA, which confirmed the Sartori and Savage (1983)[5] statement that steric hindrance has an adverse effect on the CO_2-amine rate constants. Alper (1990)[153] investigated the mechanism and kinetics of the reaction between aqueous solutions of CO_2 and AMP ((0.013 to 1.5) $kmol \cdot m^{-3}$) at (278 to 298) K. Experiments were also carried out with MEA solution. They found that the reaction was first order with respect to CO_2 but 1.14 to 1.15 with respect to AMP. A fractional order between 1 and 2 would be expected if the deprotonation of the zwitterion was not instantaneous. However, kinetic constants were extracted as if the order with respect to AMP was unity. The corresponding second-order rate constants at 298 K were found to be (520 and 5545) $m^3 \cdot kmol^{-1} \cdot s^{-1}$ for AMP and MEA, respectively, with the corresponding activation energies of (41.7 and 46.7) $kJ \cdot mol^{-1}$. The predicted rate constant at 313 K was 1165 $m^3 \cdot kmol^{-1} \cdot s^{-1}$, which agreed well with the value of 1270 $m^3 \cdot kmol^{-1} \cdot s^{-1}$ reported by Yih and Shen (1988).[14] Bosch et al. (1990)[15] mentioned that, following their analysis of the paper of Chakraborty et al. (1986)[101] carried out in Bosch et al. (1989),[154] the CO_2 absorption rates observed in sterically hindered amine solutions could probably be explained satisfactorily with the zwitterion mechanism. To verify this hypothesis, new CO_2 absorption data for aqueous AMP solutions have been collected and were presented in their paper.[15] Experimental work was conducted at 298 K for AMP solutions of (0.202 to 2.373) $kmol \cdot m^{-3}$. Unfortunately, from the observed decrease of CO_2 pressure with time, it was concluded that for none of the absorption experiments the simple pseudofirst-order conditions prevailed. The reaction rate constant for the zwitterion formation, k_2, could not be calculated accurately (estimated inaccuracy of 100 %); however, a value of 10000 $m^3 \cdot kmol^{-1} \cdot s^{-1}$ was reported at 298 K. This value seemed quite high since steric considerations should have given a value of k_2 for AMP smaller than that for MEA, as reported in Alper (1990).[153] In the paper of Saha et al. (1995),[155] the mechanism and kinetics of the reaction between CO_2 and AMP aqueous solution were investigated at (294 to 318) K. The reaction was found to be first order with respect to both CO_2 and AMP. Values of the second-order rate constant were found to be (439, 687, 1179, and 1650) $m^3 \cdot kmol^{-1} \cdot s^{-1}$ at (294, 301.5, 311.5, and 318) K, respectively, in the amine concentration range (0.5 to 2.0) $kmol \cdot m^{-3}$. These results were in close agreement with those reported by Yih and Shen (1988)[14] and Alper (1990),[153] even though the latter adopted a completely different methodology. The corresponding value of the activation energy was found to be 43 $kJ \cdot mol^{-1}$. The study by Xu et al. (1996)[156] was among the first to treat absorption data over large concentration and temperature ranges in AMP solutions using the zwitterion mechanism. Reaction rate constants for the reaction between CO_2 and AMP were determined from measurements of the absorption rate of CO_2 into aqueous AMP and nonaqueous (1-propanol + AMP) solutions. The kinetic parameters for aqueous AMP solutions were obtained for temperatures from (288 to 318) K over an AMP concentration range of (0.17 to 3.5) $kmol \cdot m^{-3}$ and at 298 K over a concentration range of (0.40 to 3.55) $kmol \cdot m^{-3}$ of AMP in 1-propanol solutions. The absorption of CO_2 in AMP + L-propanol was studied to help confirming the validity of using the zwitterion mechanism to interpret the kinetics between CO_2 and AMP. The authors found that the partial order in respect to AMP was larger than unity in both solutions. In aqueous solutions, the reaction orders for AMP varied from 1.15 at 288 K to 1.32 at 318 K, while it was 1.28 in 1-propanol solutions at 298 K. The second-order rate constant, k_2, and the kinetic constants $k_2 k_{H_2O}/k_{-1}$ and $k_2 k_{AM}/k_{-1}$ were correlated as a function of temperature using Arrhenius type equations. The authors compared their results with data from literature using the overall pseudofirst-order reaction rate constant. Their values of k_{ov} obtained at 298 K were in good agreement with those of Bosch et al. (1990)[15] and Alper (1990)[153] at lower concentrations of AMP but were slightly higher when the concentration of AMP was greater than about 0.7 $kmol \cdot m^{-3}$. Also, the k_{ov} values measured at 288 K[156] were slightly higher than those determined from Alper's results; at 313 K, the values were somewhat lower than those of Yih and Shen (1988).[14] The use of k_{ov} as a basis of comparison assumed that all experiments were carried out in the pseudofirst-order reaction regime, which may have not been the case in Bosch et al. (1990).[15] Messaoudi and Sada (1996)[85] investigated the absorption of CO_2 into aqueous AMP solutions ((0.5 to 2.0) $kmol \cdot m^{-3}$). The reaction was found to be first order with respect to both CO_2 and AMP. The second-order reaction rate constants at (293, 303, and 313) K were found to be (190, 369, and 740) $m^3 \cdot kmol^{-1} \cdot s^{-1}$, respectively. These values were constantly lower than those of Saha et al. (1995),[155] although almost the same concentration and temperature ranges were considered. Mandal and Bandyopadhyay (2005)[32] performed an experimental and theoretical investigation of the simultaneous absorption of CO_2 and H_2S in aqueous solutions of AMP + DEA. Kinetic information concerning AMP was taken from Mandal's thesis who reported an equation for the second-order rate constant, k_2. It was assumed that the temperature and concentration ranges considered were adequately covered by this equation. Kinetic constants calculated with that equation were in good agreement with the values reported by Saha et al. (1995).[155] Ali (2005)[157] studied the effect of mixing AMP with a primary amine (MEA) and a secondary amine (DEA) on the kinetics of the reaction with carbon dioxide in aqueous media. Experimental work was conducted at (298, 303, 308, and 313) K using aqueous AMP solutions of concentrations varying between (0.05 and 0.35) $kmol \cdot m^{-3}$. For blended aqueous solutions, AMP + MEA and AMP + DEA, various amine concentrations were used, and MEA/AMP and DEA/AMP molar ratios of (0.05, 0.09, 0.15, 0.22, and 1.08) and (0.06, 1.01, and 19) were respectively selected. A model based on the zwitterion mechanism for all the amines involved (AMP, MEA, and DEA) was applied. Blending AMP with either MEA or DEA resulted in overall pseudofirst-order reaction rate constant values (k_{ov}) larger than the sum of the k_{ov} values corresponding to the respective pure amines. This should be due to the role played by one amine in the deprotonation of the zwitterion of another one. The k_{ov} values of Ali (2005)[157] at a given temperature were found comparable with those reported by Alper (1990)[153] (using the stopped-flow technique), Xu et al. (1996)[156] (derived from absorption experiments using a stirred cell reactor) and Bosch et al. (1990).[15] The activation energy for the zwitterion formation step for AMP (a primary amine) was found closer to that for MEA (a primary amine) than that for DEA (a secondary amine). This appeared to suggest that the nature of the amine (i.e., whether it is primary or secondary) had a great bearing on the energy barrier that had to be overcome to form the zwitterion intermediate in the first step. For the aqueous AMP system, the activation energy value for the zwitterion formation step obtained in Ali (2005)[157] (41.9 kJ·mol^{-1}) was found to be very close to that obtained by Alper (1990)[153] (41.7 kJ·mol^{-1}) and comparable to that obtained by Saha et al. (1995)[155] (43.0 kJ·mol^{-1}), despite the fact that these two last studies treated their data using an overall second-order reaction. Also, the E_a value obtained by Xu et al. (1996)[156] (24.3 kJ·mol^{-1}) was found to be lower, while the data obtained by Messaoudi and Sada (1996)[85] (51.5 kJ·mol^{-1}) were found to be higher, as compared to the value obtained by Ali (2005).[157] An analysis of the kinetic parameter involved in the zwitterion mechanism showed that MEA had a higher deprotonating ability than AMP, but the AMP–DEA analysis was quite ambiguous. The authors[157] succeeded to obtain almost the same kinetic parameters for all three systems involving AMP (single AMP, AMP + DEA, AMP + MEA). Reported k_2 values for AMP were found to be very close to those of Saha et al. (1995),[155] while values of $k_2k_{H_2O}/k_{-1}$, k_2k_{AM}/k_{-1}, and k_2k_{MEA}/k_{-1} were, respectively, higher, lower, and higher than those reported in the literature.[28,156,158] In Choi et al. (2007),[159] experiments were carried out to investigate the characteristics of CO_2 absorption rate in AMP solution with small additions of hexamethylenediamine (HMDA), MDEA, or piperazine. Additive concentrations of (1, 3, and 5) wt % were added for each 30 wt % AMP solution. To check the validity of the method, the authors studied the CO_2–AMP reaction and found a first-order dependence with respect to CO_2 and AMP. A value of 731 m^3·kmol^{-1}·s^{-1} for the second-order reaction rate constant (k_2) at 313 K was obtained, which was in good agreement with that reported by Messaoudi and Sada (1996)[85] (740 m^3·kmol^{-1}·s^{-1}). It should be noted that the values of Messaoudi and Sada (1996)[85] were well below any other reported k_2 values in the literature. Choi's experiments showed that the addition of HMDA, MDEA, or piperazine into AMP solutions increased the absorption rate as compared to AMP alone. Surprisingly, authors found that MDEA addition in AMP solution produced a larger or somewhat equivalent increase in the absorption rate than the Pz addition. No explanations of these results were given. The same research group also published a study concerning CO_2 absorption into aqueous AMP + MEA solutions at (293, 303, and 313) K (Choi et al., 2009).[160] The reported kinetic constants concerned the blended solutions and not AMP alone. However, they found that MEA was more reactive than AMP.

5.2. Blended AMP Systems.

The presence of a second amine in solution can enhance the deprotonation mechanism of the zwitterion. A new kinetic constant should be added: $k_2k_{AM\#2}/k_{-1}$ which represents the contribution to the deprotonation of the zwitterion by this new base in solution.

The kinetics of CO_2 in aqueous AMP + DEA solutions at (303, 308, and 313) K was studied in a wetted-wall column by Wang and Li (2004).[31] The AMP concentrations were (1.0 and 1.5) kmol·m^{-3}, with the DEA addition of (0.1, 0.2, 0.3, or 0.4) kmol·m^{-3}. A hybrid rate model was applied: a second-order reaction for AMP and zwitterion mechanism for DEA. This model succeeded to represent experimental data with 7.2 % deviation. Results of k_2 for AMP were reported by an equation. The comparison of calculated k_2 values indicated a good agreement with the values given by Saha et al. (1995)[155] and Ali (2005).[157]

The CO_2 absorption rate into aqueous solution of AMP + MEA was investigated by Xiao et al. (2000)[28] at (303, 308, and 313) K, using a wetted-wall column. Ten systems where (1.5 and 1.7) kmol·m^{-3}AMP was mixed with various MEA concentrations ((0, 0.1, 0.2, 0.3, and 0.4) kmol·m^{-3}) were studied. CO_2 absorption into 0.9 kmol·m^{-3} aqueous AMP at 313 K has been carried out to check the validity of the method; k_{ov} obtained was found to be 728 s^{-1}, which was in a good agreement with data reported by Xu et al. (1996).[156] k_{ov} values at (303 and 313) K for (1.5 and 1.7) kmol·m^{-3}AMP were also found to be in good agreement with those of Saha et al. (1995)[155] and Xu et al. (1996),[156] respectively. To represent the kinetic data, authors suggested a reaction model consisting of a first-order reaction mechanism for MEA and a zwitterion mechanism for AMP. Comparing the k_{ov} calculated using the zwitterion regression with the experimental k_{ov}, large deviations were found at 1.7 kmol·m^{-3} AMP + MEA at (308 and 313) K, and these deviations seemed to increase as the MEA concentration increased. Calculated kinetic constants for MEA and AMP were expressed as a function of temperature. The comparison between the kinetic constants for AMP and those obtained by Xu et al. (1996)[156] showed a good agreement for k_2 values only; the other kinetic constants were quite different. This may come from the fact that, in AMP + MEA systems, a new parameter (k_2k_{MEA}/k_{-1}) modified the value of the other kinetic parameters obtained by a nonlinear regression. It should be noted that the values of this new kinetic parameter involving MEA in the deprotonation of AMP zwitterion are lower at (303 and 308) K than k_2k_{AM}/k_{-1}, which seems inconsistent with the fact that MEA kinetics was well-described by a second-order overall reaction in the literature, indicating that MEA usually deprotonated its zwitterion almost instantaneously.

Seo and Hong (2000)[158] investigated the absorption of CO_2 into AMP + Pz solutions at (303 and 313) K using a wetted-sphere absorption apparatus. The concentration of AMP was in the range of (0.55 to 3.35) kmol·m^{-3}, and Pz additions of (0.058, 0.115, and 0.233) kmol·m^{-3} were made for each AMP solution. To validate the apparatus, the kinetics of aqueous single solutions of AMP was investigated under the same concentration and temperature ranges. The reaction orders with respect to AMP were determined, and they varied from 1.29 at 303 K to 1.32 at 313 K, which could be explained by the zwitterion mechanism. Kinetic constants were reported for single AMP aqueous systems, as well as for the AMP + Pz aqueous systems. Concerning the system AMP + H_2O, the second-order rate constant for AMP, k_2, at 313 K was found to be in good agreement with the results of Yih and Shen (1988)[14] and Xu et al. (1996).[156] Concerning the blended AMP + Pz + H_2O system, kinetic constants involving AMP were quite different from what have been found for the single AMP + H_2O system in the same work,[158] but also from the works of Xu et al. (1996)[156] and Xiao et al. (2000).[28] Relatively high CO_2 partial pressures were used in Seo and Hong (2000),[158] resulting, according to Bishnoi and Rochelle (2000),[161] in substantial depletion of Pz at the gas−liquid interface that could have altered kinetic results. It could be seen however that the kinetic constants k_2k_{Pz}/k_{-1} were very high, indicating that Pz facilitated AMP zwitterion deprotonation that may have promoted the overall CO_2 absorption rate. The Pz promoting effect in AMP solutions was also later reported by Samanta and Bandyopadhyay (2009).[91]

In Sun et al. (2005),[35] the reaction kinetics of the absorption of CO_2 into mixed aqueous solutions of AMP and PZ were investigated using a wetted-wall column at (303, 308, and 313) K. The aqueous blends chosen for this kinetic study were (1.0 and 1.5) kmol·m^{-3} AMP with various Pz concentrations ((0.1, 0.2, 0.3, and 0.4) kmol·m^{-3}). A second-order reaction for the reaction of CO_2 with Pz and a zwitterion mechanism for the reaction of CO_2 with AMP were considered to model the kinetic data. Arrhenius type equations were given for each calculated kinetic parameter. Reported k_2 values were higher than literature values[28,32,155−157] but similar to k_2 values obtained by Seo and Hong (2000)[158] for the blended system AMP + Pz. All of the other kinetic parameters related to the deprotonation of AMP zwitterion given by Sun et al. (2005)[35] were in disagreement with what have been presented so far. The equation for the kinetic parameter k_2k_{Pz}/k_{-1} even seems to be misprinted because the calculations give odd values.

Following the analysis of all these works concerning AMP, it seems that no clear consensus was found concerning reliable kinetic constants. Selecting the right kinetic constant and mechanism becomes even more ambiguous because two different sets of kinetic parameters, taken either from Saha et al. (1995)[155] (second-order reaction) or Xu et al. (1996)[156] (zwitterion mechanism), have successfully been applied in simulation/modeling.[30,162,163]

The zwitterion mechanism could explain the order deviation for AMP found in several works, as well as an apparent first order, but kinetic constants can take various values as they are obtained simultaneously (see, for example, refs 15, 28, 35, 156, and 158). Utilization of the same kinetic parameters for various systems (single and blended aqueous AMP solutions) was successfully made by Ali (2005),[157] but it would be interesting to extend that study using higher AMP concentrations.

Another parameter that can influence the scattering of k_2 values found for AMP or any other amine may be the thermal effect associated with CO_2 absorption (see Section 2.2.5). Camacho et al. (2005)[164] studied the kinetics of CO_2 absorption in AMP solutions by considering this thermal effect at the gas−liquid interface. All experiments were performed using a stirred gas−liquid contactor. The variables considered were the AMP concentration ((0.1 to 3.0) kmol·m^{-3}) and temperature ((288 to 313) K). An iterative process has been used to determine the interface temperature that was found significantly higher than the bulk temperature. At 313 K, they obtained a kinetic constant k_2 of 161.0 m^3·kmol^{-1}·s^{-1}. This value was of the same order as that reported by Chakraborty et al. (1986)[101] but lower than what have been presented elsewhere in the literature. The authors mentioned that these different research groups that have worked in CO_2 absorption in AMP solutions did not consider thermal effects which caused these deviations. In the future, it should then be interesting to see more kinetic publications taking into account or addressing this thermal effect.

5.3. Other SHA Systems.

5.3.1. 2-PE Systems. Shen et al. (1991),[40] Xu et al. (1993),[92] and Paul et al. (2009)[165] studied the kinetics between CO_2 and aqueous 2-PE solutions at 313 K, (283 to 313), K and (303 to 323) K, respectively. Xu et al. (1993)[92] performed experiments in a stirred cell, while Shen et al. (1991)[40] and Paul et al. (2009)[165] used a wetted-wall column.

Shen et al. (1991)[40] found the reaction to be first order with respect to both CO_2 and 2-PE. The second-order forward rate constant at 313 K had a value of 195 m^3·kmol^{-1}·s^{-1} and was extracted for amine concentration range of (0.218 to 1.0) kmol·m^{-3}. Such a low concentration range may not be sufficient for a reliable industrial-applicable kinetics study. The result was much lower than that of Xu et al. (1993)[92] (k_2 of 1468 m^3·kmol^{-1}·s^{-1} at 313 K). These values, however, do not have the same meaning, although their units are the same, since Xu et al. (1993)[92] applied the zwitterion mechanism to treat their data. If the second-order rate constant of Xu et al. (1993)[92] at 313 K was correlated using the method of Shen et al. (1991),[40] its value would become 1207 m^3·kmol^{-1}·s^{-1} with an absolute error as high as ± 13 %, which would be still larger than the value of Shen et al. (1991).[40]

In the study of Xu et al. (1993),[92] the authors made a comparison of the kinetics of 2-PE versus AMP at (293 and 313) K. They showed that the apparent kinetic rate constants of 2-PE were dramatically lower than those of AMP. This signifies that the reaction of CO_2 with 2-PE was not as fast as that with AMP. A similar observation was revealed under other experimental conditions.[5] However, the k_2 value of 1468 m^3·kmol^{-1}·s^{-1} at 313 K reported by Xu et al. (1993)[92] was above the second-order rate constant for AMP at the same temperature reported in the literature.[14,32,85,156,159,158]

Paul et al. (2009)[165] studied the kinetics of CO_2 absorption in 2-PE solutions of (0.14 to 1.13) kmol·m^{-3}. The reaction order was found to be between 1.10 and 1.12 with respect to amine, which could be explained by the zwitterion mechanism, but the authors treated their results by considering a second-order reaction. The second-order rate constants, k_2, were (696, 1147, and 2047) m^3·kmol^{-1}·s^{-1} at (303, 313, and 323) K, respectively, with an activation energy of 45.2 kJ·mol^{-1}. The results at (303 and 313) K were lower to those reported by Xu et al. (1993)[92] and may therefore reconcile the fact that 2-PE reacts slower than AMP. However, the results reported by Paul et al. (2009)[165] should be considered with care as almost all their Hatta numbers were higher than the calculated instantaneous enhancement factor (E_∞). An intermediate regime should have been presented instead of the desired fast pseudofirst-order regime, even if the extraction of reliable kinetics results would have been much more difficult.[166]

Considering these three studies, the zwitterion mechanism seems to describe well the absorption of CO_2 in 2-PE solutions, but more studies would be necessary to obtain reliable kinetic constants (k_2 and zwitterion deprotonation kinetic constants).

5.3.2. AEPD Systems. Only the publication of Yoon et al. (2002)[45] was found in the open literature concerning the kinetics of reaction between aqueous AEPD and CO_2. The study was performed at (305.15, 313.15, and 318.15) K for aqueous solutions from (5 to 25) wt % AEPD, using a wetted-wall column absorber. As commonly observed in kinetic studies between CO_2 and alkanolamines,[167] a first-order rate dependence in respect to CO_2 was found. The zwitterion mechanism was used to treat the experimental data. Three reaction rate parameters, k_2, $k_2k_{H_2O}/k_{-1}$, and k_2k_{AM}/k_{-1}, were determined simultaneously by a nonlinear regression method, and values were reported at each temperature. The parameter $k_2k_{OH^-}/k_{-1}$ was neglected because the contribution of the hydroxyl ion was considered negligible. Arrhenius type equations have been used here to correlate the kinetic parameters:

$$k_2/\mathrm{m^3 \cdot kmol^{-1} \cdot s^{-1}} = \exp\left(31.730 - \frac{7820}{T/\mathrm{K}}\right) \tag{29}$$

$$\frac{k_2k_{H_2O}}{k_{-1}}/\mathrm{m^6 \cdot kmol^{-2} \cdot s^{-1}} = \exp\left(72.316 - \frac{22843}{T/\mathrm{K}}\right) \tag{30}$$

$$\frac{k_2k_{AM}}{k_{-1}}/\mathrm{m^6 \cdot kmol^{-2} \cdot s^{-1}} = \exp\left(21.902 - \frac{4809}{T/\mathrm{K}}\right) \tag{31}$$

The activation energy (based on k_2) was found to be 65.0 kJ·mol^{-1} with an absolute error of 2 %. It was observed that the overall absorption rate constant (k_{ov}) indicated in Table 1 given in Yoon et al. (2002)[45] differed from those reported in Tables 2 to 4 of the same paper. Because this is the single work found in the literature concerning AEPD kinetics, more studies would be compulsory to shed a light upon those discrepancies.

5.3.3. AHPD Systems. Two kinetic studies were found in the literature concerning CO_2 absorption in AHPD solutions. Both works by Bougie and Iliuta (2009)[93] and Paul et al. (2009)[168] used a wetted-wall column absorber and studied the reaction kinetics at (303.15, 313.15, and 323.15) K.

In Bougie and Iliuta (2009),[93] the AHPD concentration was varied between (0.5 and 2.4) kmol·m^{-3}, and the chemical absorption was described using the zwitterion mechanism. The fast pseudofirst-order regime was verified by analyzing gas and amine concentration profiles in the liquid film. Three reaction rate parameters, k_2, $k_2k_{H_2O}/k_{-1}$, and k_2k_{AM}/k_{-1}, were determined using a nonlinear regression method for each studied temperature and correlated using Arrhenius type equations. The calculated activation energy for k_2 was found to be 53.7 kJ·mol^{-1}. The authors analyzed the overall absorption rate constants of various SHA and observed that the amines reactivity varied in the following ascending order AEPD, AHPD, AMPD, and AMP, which represents the opposite order of the amines bulkiness (steric hindrance). This seemed to confirm the assumption that a reduced steric hindrance leads to a more pronounced reaction rate constant (more reactivity).

Paul et al. (2009)[168] used AHPD concentrations of (0.179 to 1.789) kmol·m^{-3}. The reaction order was found to be in between 1.0 and 1.1 with respect to amine for the above-mentioned concentration range. Kinetic rate parameters were calculated and presented at each experimental condition assuming an overall second-order reaction. Second-order rate constants, k_2, were found to be (532.7, 1096, and 2380) m^3·kmol^{-1}·s^{-1} at (303, 313, and 323) K, respectively, with an activation energy of 65.2 kJ·mol^{-1}. These results were significantly higher than those of Bougie and Iliuta (2009),[93] but it should be recalled that these values were not obtained on the basis of the same reaction mechanism. Paul et al. (2009)[168] performed a parametric sensitivity analysis and found that Henry's law constant values for CO_2 in solution had a huge impact on the calculated CO_2 absorption rates.

5.3.4. AMPD Systems. As for AHPD, only two kinetic studies were found in the literature concerning CO_2 absorption in AMPD solutions.

Bouhamra et al. (1999)[169] studied the mechanism and the kinetics of CO_2 absorption in AMPD solutions by a stopped-flow technique between (278 and 303) K. Concentrations were varied between (0.025 and 1.600) kmol·m^{-3} AMPD. They found that the partial order related to the amine varied between 1.26 and 1.33 which could be explained by the zwitterion mechanism. Based on this mechanism, they extracted corresponding kinetic constants for each temperature and correlated them following an Arrhenius law. The activation energies for k_2, k_2k_{AM}/k_{-1}, and $k_2k_{H_2O}/k_{-1}$ are respectively (33.7, 44.7, and 62.05) kJ·mol^{-1}.

Comparisons were made by the authors with AMP values from the literature,[153,156] and as expected, the observed reaction rate for AMPD were smaller than that of AMP which was caused by added hindrance and charge effect of an hydroxyl group which replaced one hydrogen in AMP.

Concerning the second study, Yoon et al. (2003)[48] with a wetted-wall column obtained the kinetics constant for AMPD solutions of concentration between (0.236 to 2.963) kmol·m^{-3} ((2.5 to 30) wt %) and for temperature ranging from (303 to 323) K. As in Bouhamra et al. (1999),[169] they used the zwitterion mechanism to interpret their data and found that the partial order for the amine was varying from 1.36 to 1.41. The activation energy for k_2 was calculated to be 38.3 kJ·mol^{-1} with an absolute error of 3 %. Kinetic constant values of each study were analyzed, and it was found that k_2 values of Yoon et al. (2003)[48] followed almost the same trend as values of Bouhamra et al. (1999).[169] Values of the kinetic parameter $k_2k_{H_2O}/k_{-1}$ were also found to follow the same trend if the value at 303 K from Bouhamra et al. (1999)[169] was not taken into account. k_2k_{AM}/k_{-1} values from both study were in disagreement. A set of kinetic parameters coming from the combination of the absorption data of both studies may correct these discrepancies, but data in Bouhamra et al. (1999)[169] were not tabulated, which limited this opportunity.

5.3.5. Other SHA Systems. Ali et al. (2002)[170] investigated the kinetics of the reaction between aqueous solutions of carbon dioxide and TBAE over a temperature range of (283 to 308) K by using a direct stopped-flow technique. Steric factors caused TBAE to react slower than its unhindered constitutional isomer (2-(*n*-butylamino)ethanol), but with the increase in temperature, the detrimental effect of these steric factors on the reaction rates was found to decrease. Authors mentioned that the reaction mechanism of TBAE was similar to that for tertiary amines, while the obtained k_2 values of TBAE are significantly higher than those corresponding to MDEA and TEA at 298 K. Sharma (1965)[152] reported values of the second-order rate constant (k_2) for the reaction of CO_2 with various SHA (AHPD, AMP, AMPD, DIBA, DIPA, TBA) for 1 kmol·m^{-3} aqueous solutions at (291 and/or 298) K. However, the errors in the reported values were estimated to be higher than 25 %. A comparison with other works[93,153,169] also revealed major deviations of k_2 values for AMP, AHPD, and AMPD solutions.

6. REGENERATION CAPABILITY

Compared to the extensive number of studies on CO_2 absorption in the open literature, there are relatively few data related to CO_2 thermal desorption processes, despite the fact that the stripping unit is usually highly energy-consuming and it is responsible for the main operational cost of the process (Tobiesen and Svendsen, 2006).[171] For that reason, amine solutions with low regeneration costs are essential for the economic viability of the absorption/desorption processes.

In comparison to conventional primary and secondary alkanolamines like MEA and DEA, sterically hindered alkanolamines (e.g., AMP) form unstable carbamates due to the hindrance of the bulky group adjacent to the amino group.[5] The presence of carbamates influences the regeneration efficiency of alkanolamine solutions. Stable carbamates are difficult to revert to fresh amines, leading therefore to a longer regeneration time and more energy consumption (Barzagli et al., 2010;[172] Sakwattanapong et al., 2005[173]). The hydrolysis of the voluminous carbamates leads to a preferential bicarbonate formation process, and it is expected that a solution containing a larger proportion of bicarbonate undergoes desorption at a higher rate (requiring less energy) and produces a lean solution containing less physically and chemically absorbed CO_2 (Hook, 1997;[174] Sartori and Savage, 1983;[5] Tontiwachwuthikul et al., 1991[107]).

In a large scale continuous process, the solvent is continuously circulating between the absorber and desorber, so that neither the regenerated amine is saturated by CO_2 nor the loaded amine solution needs to be fully regenerated. There is then a place for a high quantity of possible configurations for an optimal absorption−regeneration process depending on solution flow rate, amine concentration, lean and rich loading, and absorption and regeneration temperatures. To improve the efficiency of the carbon dioxide cycling process and to reduce the regeneration energy consumption, SHA regenerative behavior over conventional alkanolamines was investigated in some studies.

Hook (1997)[174] studied the CO_2 absorption/desorption capacity of solutions of eight different amine compounds including MEA, AMP, and six potassium amino salts. The aim of that work was to identify the absorbent which minimizes the power consumption of the regeneration step compared to MEA solutions in non-nuclear submarines where power conservation is crucial. Carbon dioxide absorption experiments were performed using 100 % CO_2 and mixtures of 4.7 vol % and 1.1 vol % CO_2 in air. Carbon dioxide absorption was measured by following the volume changes of a CO_2 gas "reservoir" which provided the atmosphere over 10 mL of a stirred 2.5 $kmol \cdot m^{-3}$ aqueous amine solution for 5 h (equilibrium 20 h) at 295 ± 0.5 K. For desorption experiments, the volume of gas generated by the equilibrated solutions when stirred in a 393 K oil bath was measured. Desorption experiments were conducted for 1 h, well in excess of the equilibrium time. Solutions reached 363 K in 2.5 min and 372 K in 8 min and then remained at (372 to 373) K. Carbon dioxide cycling experiments were performed by incorporating at least three absorptions and two desorptions sequentially. From their results, some interesting observations appeared. It was found, as expected, that the position and the nature of the substitution around the amino group influenced the absorption rate and the absorption capacity of the studied solutions. The slow absorption of the *N*-substituted, *R*-dimethylated (secondary) amines relatively to sterically hindered primary amines indicated that the presence of three bulky groups around the reaction site caused important steric restriction, thus significantly impeding the reaction. If only desorption kinetics was considered, the calculated CO_2 released during the first 5 min of desorption led to the following order: AMP (0.69 mol of CO_2 released/mol of amine) > MEA (0.38). AMP was desorbed to a level of 0.1 mol/mol, while MEA reached only 0.2 mol/mol. The tested potassium amino salt failed to desorb to the levels reached by the alkanolamines. No polyalcohols were tested to verify if adding more hydroxyl groups increased the regeneration performances. Globally, the authors observed that potassium amino salts exhibited precipitation problems which limited their application. As a general trend, it was observed that the amines which allowed the higher CO_2 absorption, by generating the most bicarbonate, produced the fastest CO_2 stripping upon heating. Although AMP exhibited encouraging desorption characteristics, the rate of CO_2 absorption at low partial pressures versus MEA was likely to restrict its use. However, at higher CO_2 concentrations, as encountered in several industrial processes, AMP may be potentially superior to MEA.

In Sakwattanapong et al. (2005),[173] the reboiler heat duty for regeneration of loaded aqueous single and blended alkanolamines was experimentally evaluated in a bench-scale regeneration column under atmospheric pressure. Various alkanolamines, including MEA, DEA, MDEA, and the mixtures of MEA + MDEA, DEA + MDEA, and AMP + MEA were included in this study. The results indicated that the reboiler heat duty was dependent on the CO_2 loading of lean and rich solutions, alkanolamine type and concentration, as well as on the composition of blended alkanolamines. MEA required the highest reboiler heat duty, followed by DEA and MDEA. Unfortunately, single AMP aqueous solutions were not evaluated since it was reported that these solutions underwent crystallization under the tested conditions (solutions of (4, 5, and 7) $kmol \cdot m^{-3}$). In general, the use of more concentrated solutions led to the reduction of the reboiler heat duties. Similar conclusions were reported by Mejdell et al. (2010)[175] who studied different combinations of AMP + MEA and found that aqueous mixtures of 20 wt % AMP + 30 wt % MEA and 25 wt % AMP + 25 wt % MEA offered the net cyclic capacity advantage over 30 wt % MEA aqueous solutions. For aqueous blended amine solutions, the heat duties were found to be between the heat duties of their parent alkanolamines. Concerning the loading influence, the results indicated that the reboiler heat duty was in inverse relationship with the achieved lean CO_2 loading; that is, it decreased with increasing lean CO_2 loading. It was shown that the reboiler heat duty did not have a linear correlation with lean CO_2 loading; two distinct regions seemed to be present. In the first region where the lean CO_2 loading was below around 0.1, a significant amount of additional heat duty was required for a small reduction in lean CO_2 loading. In some cases, the lean CO_2 loading remained virtually unchanged regardless of the amount of energy supplied. This presented an unfavorable operating region that consumed excessive energy during solvent regeneration. In the second region, where the lean CO_2 loading was above about 0.1, only a small amount of additional heat duty was required to achieve a substantial reduction in lean CO_2 loading, thus presenting a favorable operating region. In addition, it was apparent that, at a given lean CO_2 loading, a reduction in rich CO_2 loading (from 0.5 to 0.3) caused the reboiler heat duty to increase substantially. Lowering the rich loading caused the CO_2 partial pressure in equilibrium to be reduced accordingly, increasing therefore the need of heating for producing more water vapor, which required much more energy at the reboiler.

Zhang et al. (2008)[176] studied the regeneration of loaded aqueous AMP solutions. All absorption experiments were conducted in a double stirred-cell contactor at a temperature of 303 K and with a gas mixture containing 15 % CO_2 and 85 % N_2. AMP concentration was keep at 1.0 kmol·m^{-3}. Regeneration experiments were run at (358, 368, 378, 383, 393, and 403) K. Each regeneration run lasted for (2 to 3) h. An analysis of the optimum regeneration temperature indicated that the regeneration efficiency increased from 86.2 % to 98.3 % when temperature increased from (358 to 403) K. The most suitable regeneration temperature for AMP was found to be 383 K. After six absorption/regeneration cycles, the regeneration efficiency for AMP solution sloped only from 98.3 % to 94.0 %, possibly because of the formation of heat-stable and nonregenerable salts. For similar experimental conditions (383 K and regeneration runs of 1.5 h), a comparison of the regeneration efficiency of different amine solutions was performed after three cycles of absorption/regeneration. The results indicated that the aqueous AMP solution was easier to regenerate, with less loss in the absorption capacity than the other amines. The regeneration performance were ranked in the following order: AMP > MDEA > DETA (diethylenetriamine) > DEA > MEA. However, an analysis of the absorption rate led to the following ranking: DETA > MEA > DEA > AMP > MDEA at the beginning of the reaction. All of these results led the authors to the conclusion that AMP may be more suited for application in industrial processes where CO_2 partial pressures are higher. AMP solutions could then take advantage of its higher absorption capacity and appreciable absorption rate.

Another work concerning the regeneration of SHA was recently published by Bougie and Iliuta (2010).[177] The aim of this study was to compare the regeneration capability of different single sterically hindered alkanolamines (AMP, AEPD, AMPD, AHPD) or Pz-activated aqueous solutions with that of single MEA or Pz aqueous solutions. The absorption/regeneration cycles were performed in the following conditions of solution concentrations and regeneration temperatures: (i) 1.00 kmol·m^{-3} AHPD for a regeneration temperature between (353.2 and 393.2) K and (ii) 1.00 kmol·m^{-3} (AEPD, AMPD, AMP, AHPD, or Pz), 2.00 kmol·m^{-3} MEA, and 0.90 kmol·m^{-3} AHPD + 0.10 kmol·m^{-3} Pz for a regeneration temperature of 383.2 K. The desorption rate was calculated on the basis of the CO_2 released, which was measured online using a microGC. Taken together, the results of that work revealed that the regeneration efficiency can be classified in the following order: AHPD (76.0) ≫ AMPD (62.6) ≥ AEPD (60.2) > MEA (43.9) ≥ Pz (42.3) > AMP (34.8). These results demonstrated that solutions of the three most hindered alkanolamine (AHPD, AMPD, and AEPD), and in particular AHPD, were easier to regenerate because they possibly did not form (or very few) stable carbamates in solution. However, the results obtained for AMP solutions showed that the calculated cyclic capacity and the regeneration efficiency, under the mentioned experimental conditions, were the lowest of all tested amines. MEA and Pz showed almost the same cyclic capacity and regeneration efficiency. However, Pz, with its higher kinetic constants over MEA, seemed to be the best activator. Finally, it was found that the addition of a small amount of Pz to AHPD aqueous solution allowed obtaining almost the same cyclic capacity and regeneration efficiency as nonactivated solutions but for half of the absorption time. Furthermore, based on the results and economic considerations (the prices for the three best SHA were (0.06, 0.22, and 0.57) dollars per gram, respectively, for AHPD, AEPD, and AMPD) and amine availability, the aqueous mixture AHPD + Pz seemed to be a potential new solvent for CO_2 capture.

Choi et al. (2009)[160] studied the absorption and regeneration performance of loaded aqueous blends of AMP + MEA (wt % AMP/wt % MEA: 30:0, 24:6, 18:12, 12:18, 6:24, 0:30). The absorption was performed at 313 K while the effect of the regenerator temperature on the stripping efficiency was investigated at (363, 373, and 383) K. The authors found that a regeneration temperature of 383 K gave the highest stripping efficiency, so they kept this temperature in the following experiments. The results showed that the CO_2 removal efficiency was optimal at 30 wt %. Further amine additions in the solution did not lead to significant amelioration of the removal efficiency. They mentioned that the amine degradation might have caused this behavior. In single amine solutions, AMP had a better stripping efficiency than MEA. In blended amine solutions, the stripping efficiency was influenced by the ratio between AMP and MEA. According to the reactivity and the regeneration efficiency, the optimum blend AMP + MEA was found at a concentration ratio of 18:12 wt %.

Recently, Barzagli et al. (2010)[172] studied experimentally the performances of CO_2 capture by aqueous solutions of single alkanolamines DEA, MDEA, and AMP ((0.667, 1.33, and 2.00) kmol·m^{-3}), as well as some alkanolamine blends (total amine content of 2.00 kmol·m^{-3}). CO_2-loaded and regenerated amine solutions were continuously circulated at the same rate of 0.60 dm^3·h^{-1} in a closed system between the absorber (set at 293 K) and the desorber (set at 363 K, 373 K, and (363 to 388) K). The gas mixture of 12 vol % CO_2 in air, simulating the flue gas, continuously flowed at the bottom of the absorber through a sintered-glass diffuser. CO_2-amine reaction equilibria have been investigated by ^{13}C NMR spectroscopy, for establishing the regeneration efficiency and the loading capacity for each single amine. It was found that AMP displayed the highest absorption efficiency, and MDEA the highest regeneration efficiency, at every given amine concentration and desorber temperature. Under the same operating conditions, blended AMP + MDEA and AMP + DEA aqueous systems (1:2 and 2:1 molar ratios for a total of 2 kmol·m^{-3}) significantly enhanced the absorption efficiency (in the range (7 to 14) %) with respect to single amines. AMP + MDEA blends displayed better performances than AMP + DEA due to the lower efficiency of DEA carbamate in both CO_2 absorption and amine regeneration. Owing to a higher thermal stability, AMP and MDEA solutions surpassed DEA, as no degradation product were detected by ^{13}C NMR analysis after heating AMP and MDEA solutions at 403 K up to 14 days, whereas a degradation rate of about 0.4 %/day for DEA solution was identified.

7. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

An update of different aspects which are essential for the design and operation of the CO_2 absorption apparatus using solutions containing sterically hindered amines, such as physical properties (density, viscosity, vapor pressure, heat capacity and heat of absorption, and CO_2 and amine diffusivity), CO_2 absorption capacity and kinetics, and regeneration capability, has been presented here. It was observed that AMP was by far the most studied SHA in the literature. Very limited information was found concerning other SHAs; new works reporting data on different aspects covered here would be saluted.

Several conclusions were made for each particular section. As it can be shown in the tables and also mentioned in the analysis of existing data, new experimental works for various systems would be useful for the elucidation of contradictory behaviors or for completing the existing database, as for example: (1) surface tension for aqueous AMP solutions, as well as for various other SHAs, to be able to compare and analyze data; (2) vapor pressure and heat capacity for aqueous solutions of various SHAs (except AMP) where data are very limited or even unavailable; (3) amine diffusivity for all SHAs; (4) CO_2 solubility in aqueous AMPD and AEPD solutions; (5) physical solubility (Henry's constants) for AMP + MEA or DEA where data are quite contradictory (cf. Figures 3 and 4); (6) new kinetic studies for all SHAs, even for AMP, where the values for kinetic parameters are broadly spread, would be very welcome. Kinetic studies for single amine solutions, using the zwitterion mechanism to treat CO_2 reaction rate in a well-defined reaction regime over large temperature and concentration ranges and taking into account the thermal effect that happened at the gas−liquid interface, may help to get reliable sets of kinetic rate constants.

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■ LIST OF SYMBOLS

C_i = concentration of species i
C_p = heat capacity
D = diffusion coefficient
E = enhancement factor
E_∞ = instantaneous enhancement factor
E_a = activation energy
H_{gas} = Henry's law constant
H_{sol} = enthalpy of solution
k_2 = second-order forward reaction rate constant
k_L = liquid-film mass transfer coefficient
k_{ov} = overall pseudofirst order reaction rate constant
P = pressure
$r_{CO_2\text{-amine}}$ = reaction rate of CO_2 with the amine in the liquid phase
R = universal gas constant
T = temperature
w = mass percentage

Greek Letters

α = CO_2 loading in solution
β = exponent in the Stokes−Einstein relation
Δ = uncertainty of specified value
μ = viscosity
ρ = density

Subscripts and Superscripts

A = gas
B = amine
Am = amine
sat = saturation

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