Density, Viscosity, Refractive Index, and Electrical Conductivity of Degraded Monoethanolamine Solutions at Standard Temperatures

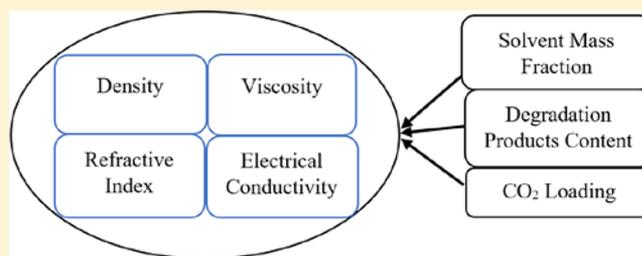Huitian Ju,[†] Walid ElMoudir,[‡] Ahmed Aboudheir,[§] and Nader Mahinpey*,[†] [iD]

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S *Supporting Information*

ABSTRACT: Densities, viscosities, refractive indices, and electrical conductivities of both artificially degraded and industrially degraded monoethanolamine (MEA) solutions are measured at a standard temperature of 293.15 or 298.15 K. These physical property measurement data are not currently available for the degraded MEA solutions, and the reported values are particularly important for monitoring solvent quality and plant performance. The data can be used to provide an estimation of the total degradation products' build-up level in the solvent with a simple measurement by the CO_2 plant operators, which would avoid using complex equipment and lengthy laboratory techniques. The data could also be useful for the CO_2 capture plant designers to consider the impact of the degradation products on the physical properties of the solvent.

1. INTRODUCTION

In a typical postcombustion CO_2 capture system, alkanolamine solvents such as monoethanolamine (MEA) are used to remove CO_2 from a flue gas stream. Exposed to impurities in the flue gas stream such as O_2, NO_x, and SO_x in the absorber and high temperature in the reboiler, alkanolamine solvents can experience chemical and thermal degradations.[1,2]

The major kinds of degradation products which draw wide attention are heat-stable salts (HSSs) due to their impact on the plant performance, equipment, and operation.[3,4] These salts cannot be thermally broken down and thus fail to release the solvent back like amine−CO_2 salts (carbamates), directly leading to a reduced CO_2 absorption capacity of the solvent. The buildup of HSSs and other degradation products would change the solvent characteristics and physical properties such as density, viscosity, refractive index, and electrical conductivity, which could further lead to plant operational challenges, plant shutdown for repairs, and increased utilities consumption. It could also increase the solvent loss and solvent makeup to maintain the required solvent concentration.

Furthermore, solvent density and viscosity are major parameters when it comes to equipment design in the CO_2 capture plant. They are closely related to the column diameter, velocity, and pressure drop within the column as well as the mass transfer prediction correlations.[5,6] They are also involved in the designing of piping, liquid pumps, and heat transfer equipment.[7]

Measurements of these physical properties are of significant importance in the field for monitoring the solvent quality and plant performance. The data could be used to roughly estimate the degradation level with a simple property measurement

without any complex chemical analysis with extra costs. Furthermore, the availability of real and accurate data for the physical properties of degraded solvent, even at one temperature (i.e., 293.15 or 298.15 K), may help the CO_2 plant designers to account for possible deviation in the physical properties, as many process simulators are not capable of considering the degradation products and their behaviors.

Although many papers discuss the physical properties of the aqueous amine solutions either CO_2-loaded or unloaded,[8−16] there is, surprisingly, very little published information about the physical properties of the degraded "real world" solvents in the literature. A few of the physical properties of the artificially degraded alkanolamine solvents, including density and refractive index, were recently reported.[17] In this study, the artificially degraded and industrially degraded MEA solvents were explored and analyzed to understand the impact of the MEA mass fraction, degradation products mass fraction, and CO_2 loading on the physical properties of MEA solvent at standard temperatures. For the artificially degraded MEA solvents, each sample was prepared by adding certain amounts of the degradation products and CO_2 gas to the MEA and water mixture, which has a specific MEA mass fraction. However, for the industrially degraded MEA solvents obtained from Canadian CO_2 capture plants, the MEA mass fractions, the degradation products mass fractions, and the CO_2 loadings are totally random as they were obtained after the treatment of different flue gas streams. For density and viscosity, the

standard temperature is 298.15 K as these two physical properties were normally measured at this temperature, which is found in most open literature articles. On the other hand, the physical properties of the refractive index and electrical conductivity were typically measured at a temperature of 293.15 K.

2. EXPERIMENTAL SECTION

2.1. Materials. Information about the reagents employed in this work is included in Table 1. Organic acids of acetic and

Table 1. Reagent Description Table

chemical name	source	CAS number	mole fraction/ weight percent purity
monoethanolamine (MEA)	Huntsman	141-43-5	>99.5% (weight percent)
carbon dioxide (CO_2)	Praxair	124-38-9	99.99% (mole fraction)
acetic acid	Sigma-Aldrich	64-19-7	>99.7% (weight percent)
formic acid	Fisher Scientific	64-18-6	>98% (weight percent)
N-acetylethanolamine	Sigma-Aldrich	142-26-7	90% (weight percent)
0.5 mol·L⁻¹ hydrochloric acid (HCl)	BDH Chemicals, VWR	7647-01-0	±0.01
0.5 mol·L⁻¹ sodium hydroxide (NaOH)	BDH Chemicals, VWR	1310-73-2	±0.01
hydranal-composite 5	Honeywell	111-90-0	<70% (weight percent)
hydranal-solver (crude) oil	Honeywell	95-47-6	<60% (weight percent)

formic acids were used to create HSSs in the artificially degraded solvents. N-Acetylethanolamine is one of the major degradation products of MEA solvent, which is a type of amide. The standard solutions of 0.5 mol·L⁻¹ hydrochloric acid (HCl) and 0.5 mol·L⁻¹ sodium hydroxide (NaOH) were used for volumetric titration. Hydranal-composite 5 and Hydranal-solver (crude) oil were used for water content determination.

2.2. Sample Preparation. By using deionized distillated water,[18] concentrated MEA was diluted to different desired amine mass fraction $(M_{amine}/(M_{amine} + M_{water}))$, $w_{amine} = (0.20$ to $0.40)$ where M represents mass. The exact concentration of each diluted MEA solution was determined by volumetric titration with a standard solution of 0.5 mol·L⁻¹ HCl to the end point determined by both a methyl orange indicator and a pH meter. The maximum MEA mass fraction is limited to 0.40 as CO_2-loaded MEA solvent at a higher mass fraction can have a negative effect on CO_2 capture due to high viscosity and the increased potential of corrosion problems.

The highly CO_2-loaded solutions were prepared by gently bubbling CO_2 gas into the solvent to achieve the required mass fraction. Solvents with different CO_2 loadings were prepared by diluting an aqueous amine solution of the selected mass fraction and high CO_2 loading (>0.5) with an unloaded amine solution of the same mass fraction to get the required CO_2 loading value (α), $(n(CO_2)/n(MEA))$, $\alpha = (0$ to $0.50)$ where n represents moles. CO_2-loading verification was performed by volumetric titration with a standard solution of 0.5 mol·L⁻¹ NaOH to the end point determined by a pH meter.

The artificially degraded solvents were prepared by adding certain amounts of formic acid, acetic acid, and N-acetylethanolamine at an equivalent percentage of 1/3 each to simulate the degraded MEA solvents. The range of the total degradation products' mass fraction $(M_{DP}/(M_{amine} + M_{water} + M_{DP}))$, $w_{DP} = (0$ to $0.020)$, was selected based on the maximum expected level of HSS contamination found in a typical CO_2 capture plant where DP represents the degradation products.[2]

2.3. Sample Analysis. For each industrially degraded MEA solvent, solvent concentration (mass fraction) w'_{amine}, given as $(M_{amine}/(M_{amine} + M_{water} + M_{CO_2} + M_{DP}))$, and CO_2 loading α were determined by volumetric titration. Solvent concentration w'_{amine} is totally different from amine mass fraction w_{amine}. The same titration method of CO_2 loading was employed to determine heat-stable salts (HSSs) content (mass fraction) w'_{HSS}, $(M_{HSS}/(M_{amine} + M_{water} + M_{CO_2} + M_{DP}))$, where $M_{DP} = M'_{DP} + M_{HSS}$ in each solvent sample after a full reflux distillation to strip all CO_2 out of the sample. M'_{DP} represents the mass of other degradation products that are not HSSs. There were other degradation products that could not be determined by any titration method. Water content (mass fraction) w'_{water} $(M_{water}/(M_{amine} + M_{water} + M_{CO_2} + M_{DP}))$ of each sample was determined by a Karl Fischer titrator. Amine mass fraction w_{amine} and total degradation products mass fraction w_{DP} can be calculated by the following two equations (eqs 1 and 2) in which MW_{amine} and MW_{CO_2} are the molecular weights of amine and CO_2

$$w_{amine} = \frac{w'_{amine}}{w'_{amine} + w'_{water}} \tag{1}$$

$$w_{DP} = 1 - \frac{MW_{amine}(w'_{water} + w'_{amine})}{MW_{amine} - MW_{CO_2}\alpha w'_{amine}} \tag{2}$$

2.4. Apparatus and Procedure. *2.4.1. Density Measurements.* The densities of artificially and industrially degraded MEA solvents were measured using an Anton Paar density meter (DMA 4500) at a temperature of 298.15 K. The specified repeatability of the density value and the integrated temperature measurement are ±0.01 kg·m⁻³ and ±0.01 K, respectively. The calibration was conducted using nitrogen and degassed water every time before the use of the machine. The accuracy in the density measurement is estimated to be ±0.05 kg·m⁻³. The density measurements for all of the solvents were made in triplicate, and the average values were reported for further analysis.

2.4.2. Viscosity Measurements. Viscosity measurements were performed with a rotational viscometer (model SMART, Fungilab S.A.). The specified repeatability of the viscosity value is ±0.2%, and the temperature precision is ±0.1 K. The instrument contains a measuring cell, which is connected to a thermostatic bath that allows it to maintain the samples at a standard temperature of 298.15 K. The rotational viscometer used a spring to measure the torque needed to rotate a spindle immersed in the cell, which contained the sample. The instrument converted the measured torque to viscosity and recorded it. The rotational speed of the spindle was adjusted to better measure the value of kinetic viscosity. All of the measurements were made in triplicate, and the average values were considered for further analysis.

2.4.3. Refractive Index Measurements. The refractive indices of the degraded MEA solvents were measured using a

digital refractometer (model PA203X, MISCO refractometer) at a temperature of 293.15 K. This automatic digital refractometer had two-point level I certified calibration and was in compliance with the manufacturer's specifications to a stated uncertainty of ±0.0001 of the refractive index. The refractive index measurements were made in triplicate, and the average values were recorded.

2.4.4. Electrical Conductivity Measurements. Regarding the electrical conductivity, the measurements were conducted with the traceable expanded-range conductivity meter (model A12, Fisher Scientific) at 293.15 K. Its specified accuracy is ±0.5%. The calibration was done using the traceable conductivity calibration standards. In the experimental procedure, about 5 mL of the solution and the electrode were sealed in a 10 mL glass tube and placed in the bath. The measurements of electrical conductivity were made in triplicate, and the average values were considered.

2.4.5. Water Content Measurements. The water content of each industrially degraded MEA solvent was determined by a Karl Fischer titrator (870 KF Titrino Plus, Metrohm). This titrator was calibrated with a standard solution of sodium tartrate. It can reliably and precisely be used for volumetric water determinations with water contents from a few parts per million to 100%. Hydranal-composite 5 and hydranal-solver (crude) oil were used as the titrating agent and medium, respectively. Each water content measurement was made in triplicate, and the average value was considered.

3. Results and Discussion. 3.1. Measurements of Pure Monoethanolamine and Pure Water.
A comparison between the experimental data of density, viscosity, refractive index, and electrical conductivity of pure components and data obtained by other researchers was performed and is summarized in Table 2.[9,10,15,16,19−27] Good agreement between

Table 2. Comparison between Measured and Literature Data of Density (ρ), Viscosity (η), Refractive Index (n_D), and Electrical Conductivity (k) for Pure Components at Standard Temperature T = 298.15 or 293.15 K[a]

| property/unit | T/K | MEA | | water | |
		exptl	lit	exptl	lit
ρ/kg·m^{-3}	298.15	1012.0	1011.9[9]	997.0	997.0[10]
			1012.3[16]		997.0[21]
			1011.8[10]		997.1[22]
			1012.0[19]		997.1[23]
			1012.1[20]		
η/mPa·s	298.15	18.75	18.74[23]	0.89	0.89[23]
			18.98[24]		0.89[22]
n_D	293.15	1.456	1.456[25]	1.333	1.333[15]
			1.454[26]		
k/mS·cm^{-1}	293.15	0.00	0.00[27]		

[a]Standard uncertainty u is $u(T)$ = 0.01 K, and combined expanded uncertainties U_c are $U_c(\rho)$ = 3.8 kg·m^{-3}, $U_r(\eta)$ = 0.16, $U_c(n_D)$ = 0.002, and $U_c(k)$ = 0.10 mS·cm^{-1} (level of confidence = 0.95).

the experimental data and those from the literature is observed, which validates the experimental procedures and apparatus used in this work. The electrical conductivity of pure MEA by other authors has not been found in the literature.

3.2. Measurements of Monoethanolamine and Water Mixtures.
The densities, viscosities, refractive indices, and electrical conductivities of MEA−water mixtures were measured at each standard temperature and are reported in Table 3.

Table 3. Density (ρ), Viscosity (η), Refractive Index (n_D), and Electrical Conductivity (k) Changing with Amine Mass Fraction[a] w_{amine} from (0.00 to 1.00) for the MEA + Water Binary Mixture, at Standard Temperature T = 298.15 or 293.15 K and Pressure P = 0.1 MPa[b]

| | 298.15 K | | 293.15 K | |
w_{amine}	ρ/kg·m^{-3}	η/mPa·s	n_D	k/mS·cm^{-1}
0.00	997.0	0.89	1.333	
0.20	1007.1	1.70	1.358	1.02
0.30	1012.9	2.60	1.372	0.72
0.40	1018.3	3.50	1.386	0.46
0.50	1022.1	5.40	1.398	0.29
0.60	1025.1	9.67	1.412	0.11
0.70	1026.5	12.26	1.423	0.09
0.80	1024.7	20.39	1.439	0.03
0.90	1020.4	19.45	1.444	0.03
1.00	1012.0	18.75	1.456	0.03

[a]$M_{amine}/(M_{amine} + M_{water})$. [b]Standard uncertainties u are $u(T)$ = 0.01 K, $u(P)$ = 0.2 kPa, and $u(w_{amine})$ = 0.01, and the combined expanded uncertainties U_c are $U_c(\rho)$ = 3.8 kg·m^{-3}, $U_r(\eta)$ = 0.16, $U_c(n_D)$ = 0.002, and $U_c(k)$ = 0.10 mS·cm^{-1} (level of confidence = 0.95).

The presented data of density, viscosity, and refractive index were compared with those in the available literature at standard temperatures. Good agreement was found as illustrated in Figures 1−3.
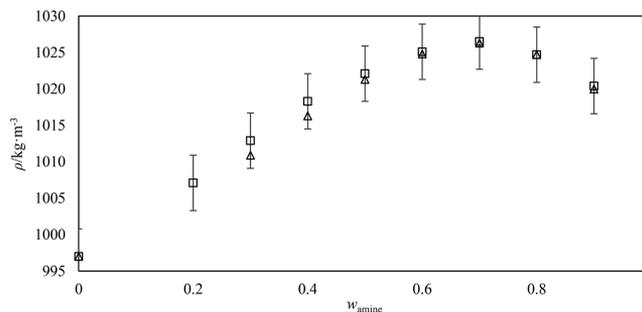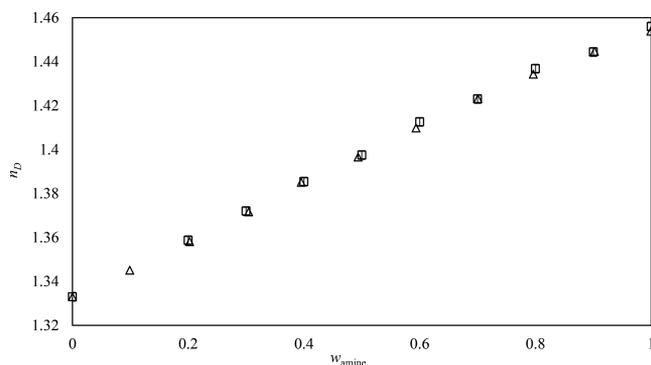

Figure 1. Comparison of measured density ρ data for the MEA + water system with published data as a function of MEA mass fraction w_{amine} at 298.15 K: □, this work; Δ, Han et al.[9]

Unlike density, viscosity, and refractive index, there are very few publications about the electrical conductivity of MEA solutions. The electrical conductivity of MEA solutions with very low solvent concentration (lower than 0.5 mol·L^{-1}) was
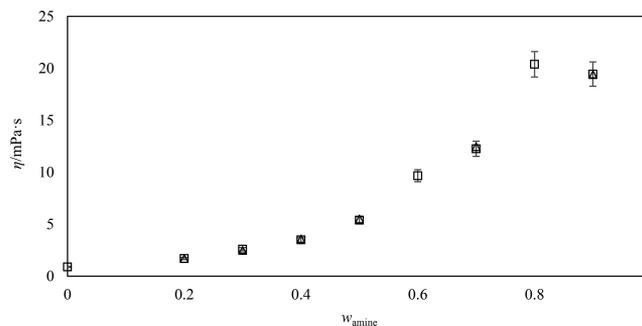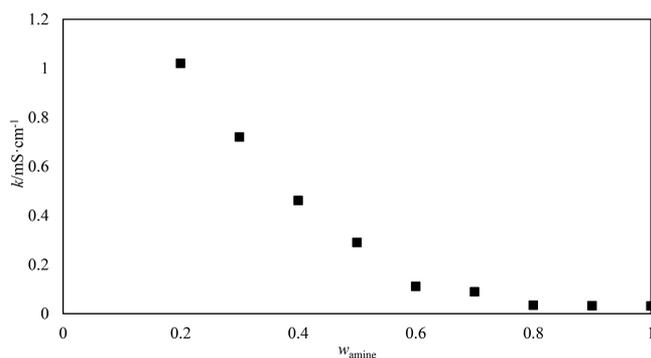

Figure 2. Comparison of measured viscosity η data for the MEA + water system with published data as a function of MEA mass fraction w_{amine} at 298.15 K: □, this work; Δ, Amundsen et al.[16]

Figure 3. Comparison of measured refractive index n_D data for the MEA + water system with published data as a function of MEA mass fraction w_{amine} at 293.15 K: $\square$, this work; $\triangle$, Tseng and Thompson.[15]

reported.[28,29] Figure 4 shows that the electrical conductivity increases slightly when the solvent is diluted from a very high concentration to a relatively low concentration. However, a huge increase can be witnessed when the MEA mass fraction is much lower, and a steep increase can be predicted when solvent reaches infinite dilution.

This phenomenon can be explained by the Debye–Huckel theory.[30] The dissociation constant of concentrated MEA at 298.15 K is 9.50. Hence, unlike strong bases, MEA is a weak base which can have only a very small dissociation in the water solution, shown in eq 3. Adding water can contribute to a higher level of dissociation. Larger amounts of $HOCH_2CH_2NH_3^+$ and OH^- can contribute to higher electrical conductivity value.

$$HOCH_2CH_2NH_2 + H_2O \rightleftharpoons HOCH_2CH_2NH_3^+ + OH^-$$
(3)
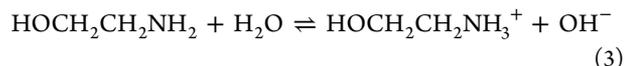
3.3. Measurements of Artificially and Industrially Degraded Monoethanolamine Solutions. The measurements of density, viscosity, refractive index, and electrical conductivity of artificially degraded and industrially degraded MEA solutions under standard temperatures are given in Tables 4 and 5, respectively. For the artificially degraded MEA solutions, they have an amine mass fraction (w_{amine}) from 0.2 to 0.4, a CO_2 loading (α) from 0 to 0.5, and a total degradation products mass fraction (w_{DP}) from 0 to 0.02.

The density, viscosity, refractive index, and electrical conductivity of the artificially degraded MEA solutions with the same MEA mass fraction show an increase with increasing degradation products mass fraction or CO_2 loading. Both the increasing degradation products mass fraction and CO_2 loading can increase the molecular interactions, which can increase the density, viscosity, refractive index, and electrical conductivity. In the case of viscosity, the increasing molecular weight of solutes is another contributor to the increased viscosity value. From Figures 5 to 12, the linear increases in density, viscosity, refractive index, and electrical conductivity in artificially

Figure 4. Measured electrical conductivity k data for the MEA + water system as a function of MEA mass fraction w_{amine} at 293.15 K.

Table 4. Density (ρ) and Viscosity (η) at 298.15 K and Refractive Index (n_D) and Electrical Conductivity (k) at 293.15 K of Artificially Degraded MEA Solutions Changing with MEA Mass Fraction[a] w_{amine} from (0.20 to 0.40), Total Degradation Products Mass Fraction[b] w_{DP} from (0 to 0.020), and CO_2 Loading[c] α from (0 to 0.50) at Pressure P = 0.1 MPa[d]

| α	ρ/kg·m^{-3}	η/mPa·s	n_D	k/mS·cm^{-1}	ρ/kg·m^{-3}	η/mPa·s	n_D	k/mS·cm^{-1}	ρ/kg·m^{-3}	η/mPa·s	n_D	k/mS·cm^{-1}
	w_{DP} = 0 (w_{amine} = 0.20)				w_{DP} = 0.010 (w_{amine} = 0.20)				w_{DP} = 0.020 (w_{amine} = 0.20)			
0	1007.1	1.70	1.359	1.02	1011.1	1.70	1.360	5.72	1014.9	1.80	1.362	9.85
0.15	1029.0	1.80	1.364	11.90	1032.5	1.80	1.366	15.82	1035.5	1.90	1.367	19.44
0.25	1045.9	1.90	1.368	18.04	1049.4	2.00	1.369	21.59	1052.0	2.00	1.370	24.59
0.35	1059.0	2.10	1.371	23.54	1062.7	2.10	1.372	26.77	1065.4	2.20	1.374	29.92
0.50	1081.0	2.20	1.375	30.80	1084.5	2.30	1.376	33.30	1086.3	2.40	1.378	35.90
	w_{DP} = 0 (w_{amine} = 0.30)				w_{DP} = 0.010 (w_{amine} = 0.30)				w_{DP} = 0.020 (w_{amine} = 0.30)			
0	1012.9	2.60	1.372	0.72	1016.8	2.70	1.374	3.69	1020.0	2.90	1.375	7.31
0.15	1044.2	2.90	1.381	11.75	1047.3	3.00	1.382	15.68	1050.0	3.20	1.384	17.29
0.25	1065.0	3.10	1.386	17.71	1067.4	3.20	1.387	21.72	1069.6	3.30	1.388	22.34
0.35	1085.1	3.30	1.391	21.93	1086.6	3.50	1.392	26.35	1088.2	3.70	1.393	27.76
0.50	1105.0	3.90	1.398	27.40	1106.2	4.10	1.399	32.30	1107.1	4.20	1.400	33.30
	w_{DP} = 0 (w_{amine} = 0.40)				w_{DP} = 0.010 (w_{amine} = 0.40)				w_{DP} = 0.020 (w_{amine} = 0.40)			
0	1018.3	3.50	1.385	0.46	1024.2	3.70	1.386	2.92	1026.6	3.80	1.388	5.31
0.15	1058.9	4.20	1.396	11.71	1061.8	4.50	1.397	13.27	1064.5	4.80	1.398	14.84
0.25	1086.6	4.70	1.403	16.80	1088.4	5.00	1.404	17.75	1090.2	5.20	1.405	19.04
0.35	1112.3	5.70	1.410	20.24	1114.0	6.00	1.411	21.07	1115.1	6.20	1.412	23.71
0.50	1138.2	6.70	1.418	23.33	1139.8	6.90	1.419	23.76	1140.7	7.10	1.420	27.79

[a]$M_{amine}/(M_{amine} + M_{water})$. [b]$M_{DP}/(M_{amine} + M_{water} + M_{DP})$. [c]$n(CO_2)/n(MEA)$. [d]Standard uncertainties u are $u(T)$ = 0.01 K, $u(P)$ = 0.2 kPa, $u(w_{amine})$ = 0.01, $u(w_{DP})$ = 0.002, and $u(\alpha)$ = 0.01, and the combined expanded uncertainties U_c are $U_c(\rho)$ = 3.8 kg·m^{-3}, $U_r(\eta)$ = 0.16, $U_c(n_D)$ = 0.002, and $U_c(k)$ = 0.10 mS·cm^{-1} (level of confidence = 0.95).

Table 5. Density (ρ) and Viscosity (η) at 298.15 K, Refractive Index (n_D) and Electrical Conductivity (k) at 293.15 K, Solvent Mass Fraction (w'_{amine}), HSSs Mass Fraction (w'_{HSS}), Water Mass Fraction (w'_{water}), CO_2 Loading (α), MEA Mass Fraction (w_{amine}), and Total Degradation Products Mass Fraction (w_{DP}) of Industrially Degraded MEA Solutions at Pressure P = 0.1 MPa[a]

w'_{amine}	w'_{HSS}	w'_{water}	α	w_{amine}	w_{DP}	ρ/kg·m^{-3}	η/mPa·s	n_D	k/mS·cm^{-1}
0.15	0.0038	0.786	0.52	0.16	0.007	1062.6	2.00	1.370	28.98
0.14	0.0048	0.849	0.06	0.14	0.005	1016.3	0.30	1.356	7.99
0.16	0.0047	0.807	0.24	0.16	0.007	1037.9	1.10	1.364	18.59
0.16	0.0029	0.807	0.21	0.17	0.005	1033.4	1.10	1.362	17.56
0.16	0.0050	0.807	0.24	0.16	0.005	1037.9	1.20	1.364	18.97
0.15	0.0042	0.776	0.60	0.16	0.008	1082.9	2.30	1.373	35.70
0.15	0.0053	0.794	0.45	0.16	0.007	1057.1	1.80	1.368	28.24
0.15	0.0047	0.769	0.68	0.16	0.007	1083.1	2.50	1.373	35.40
0.15	0.0037	0.820	0.24	0.15	0.005	1032.4	1.00	1.360	18.41
0.16	0.0049	0.804	0.25	0.17	0.005	1039.7	1.20	1.365	19.91
0.15	0.0028	0.820	0.19	0.16	0.005	1030.3	1.00	1.361	15.80
0.13	0.0043	0.808	0.68	0.14	0.005	1080.8	2.10	1.366	34.40
0.15	0.0049	0.769	0.68	0.16	0.006	1083.0	2.50	1.373	35.40
0.16	0.0051	0.806	0.24	0.16	0.008	1038.0	1.20	1.364	18.73
0.15	0.0052	0.772	0.69	0.16	0.007	1083.1	2.50	1.373	35.40
0.16	0.0051	0.805	0.24	0.16	0.008	1039.8	1.20	1.365	19.80
0.15	0.0041	0.817	0.24	0.16	0.005	1032.3	1.00	1.360	18.15
0.14	0.0046	0.842	0.07	0.14	0.007	1016.1	0.40	1.356	8.24
0.17	0.0038	0.801	0.19	0.18	0.004	1033.3	1.20	1.362	17.76

[a]Solvent mass fraction defined as $w'_{amine} = M_{amine}/(M_{amine} + M_{water} + M_{CO2} + M_{DP})$. HSS mass fraction defined as $w'_{HSS} = M_{HSS}/(M_{amine} + M_{water} + M_{CO_2} + M_{DP})$ where $M_{DP} = M'_{DP} + M_{HSS}$ in each solvent sample and M'_{DP} stands for the mass of other degradation products which are not HSSs. Water mass fraction defined as $w'_{water} = M_{water}/(M_{amine} + M_{water} + M_{CO2} + M_{DP})$. CO_2 loading defined as $\alpha = n(CO_2)/n(MEA)$. MEA mass fraction defined as $w_{amine} = M_{amine}/(M_{amine} + M_{water})$. Total degradation products mass fraction defined as $w_{DP} = M_{DP}/(M_{amine} + M_{water} + M_{DP})$. [b]Standard uncertainties u are $u(T)$ = 0.01 K, $u(P)$ = 0.2 kPa, $u(w'_{amine})$ = 0.01, $u(w'_{HSS})$ = 0.0005, $u(w'_{water})$ = 0.001, $u(w_{amine})$ = 0.01, $u(w_{DP})$ = 0.002, and $u(\alpha)$ = 0.01, and the combined expanded uncertainties U_c are $U_c(\rho)$ = 3.8 kg·m^{-3}, $U_r(\eta)$ = 0.16, $U_c(n_D)$ = 0.002, and $U_c(k)$ = 0.10 mS·cm^{-1} (level of confidence = 0.95).
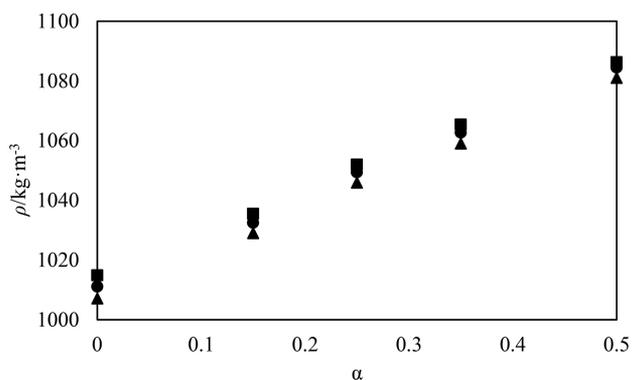
Figure 5. Measured density ρ of artificially degraded MEA solutions as a function of CO_2 loading α at 298.15 K and mass fraction w_{amine} of 0.2: ▲, w_{DP} = 0.00; ●, w_{DP} = 0.01; and ■, w_{DP} = 0.02.
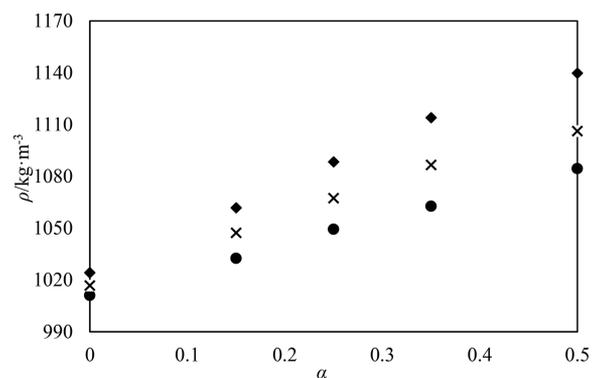
Figure 6. Measured density ρ of artificially degraded MEA solutions as a function of CO_2 loading α at 298.15 K and w_{DP} = 0.01: ●, mass fraction w_{amine} of 0.2; ×, 0.3; and ◆, 0.4.

degraded solvents can be witnessed with increasing MEA mass fraction, degradation products mass fraction, and CO_2 loading.

Hence, to roughly estimate the degradation level with a simple density, viscosity, refractive index, or electrical conductivity measurement without any complex chemical analysis or extra costs, a linear polynomial of the following form was developed to correlate the density, viscosity, refractive index, or electrical conductivity with the MEA mass fraction, degradation products mass fraction, and CO_2 loading at standard temperature based on the data of both artificially and industrially degraded solvents

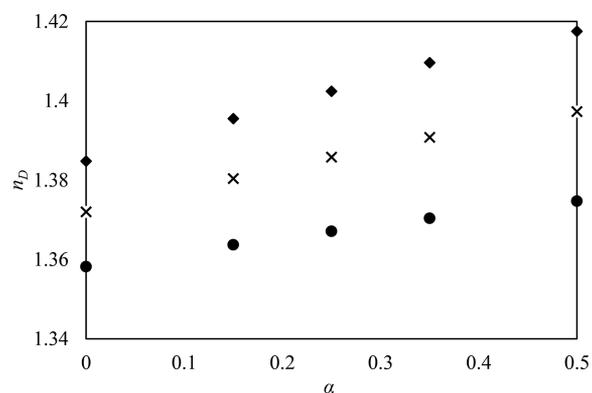$$\text{physical property} = A_0 + A_1 w_{amine} + A_2 w_{DP} + A_3 \alpha \quad (4)$$

where A_0, A_1, A_2, and A_3 are the optimized coefficients estimated by the least-squares method, and the values are listed in Table 6. The average absolute percentage deviation (AAD) was estimated according to the following equation

$$\text{AAD} = \frac{\sum_1^n \left| \frac{x_{exptl} - x_{calc}}{x_{exptl}} \right|}{n} 100\% \quad (5)$$
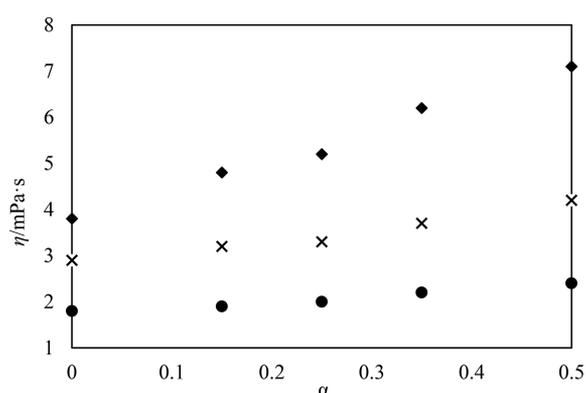
It is found that for each physical property, the AAD of industrially degraded MEA solutions is much lower than that of artificially degraded MEA solutions. It means that the physical properties of density, viscosity, refractive index, and electrical conductivity for industrially degraded MEA solutions fit better
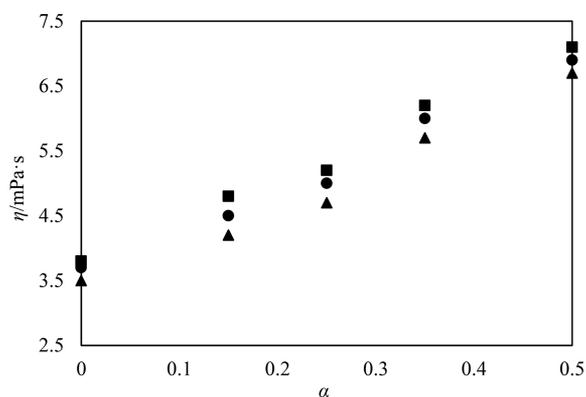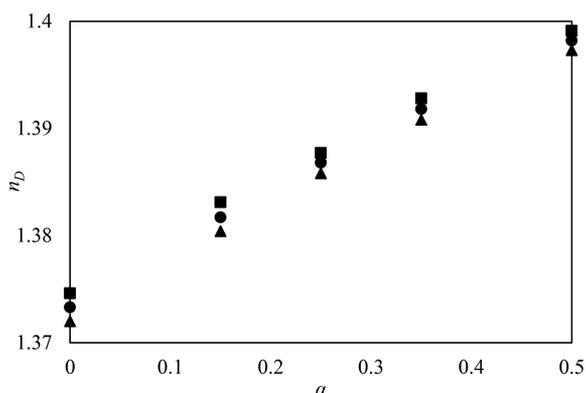
Figure 7. Measured viscosity η of artificially degraded MEA solutions as a function of CO_2 loading α at 298.15 K and mass fraction w_{amine} of 0.4: ▲, $w_{DP} = 0.00$; ●, $w_{DP} = 0.01$; and ■, $w_{DP} = 0.02$.

Figure 8. Measured viscosity η of artificially degraded MEA solutions as a function of CO_2 loading α at 298.15 K and $w_{DP} = 0.02$: ●, mass fraction w_{amine} of 0.2; ✕, 0.3; and ♦, 0.4.

Figure 9. Measured refractive index n_D of artificially degraded MEA solutions as a function of CO_2 loading α at 293.15 K and mass fraction w_{amine} of 0.3: ▲, $w_{DP} = 0.00$; ●, $w_{DP} = 0.01$; and ■, $w_{DP} = 0.02$.
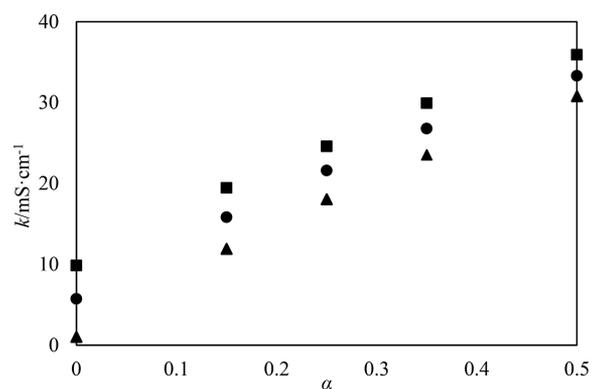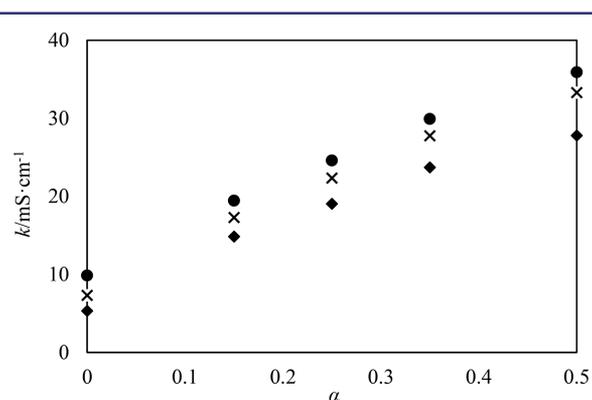

Figure 10. Measured refractive index n_D of artificially degraded MEA solutions as a function of CO_2 loading α at 293.15 K and $w_{DP} = 0.00$: ●, mass fraction w_{amine} of 0.2; ✕, 0.3; and ♦, 0.4.

Figure 11. Measured electrical conductivity k of artificially degraded MEA solutions as a function of CO_2 loading α at 293.15 K and mass fraction w_{amine} of 0.2: ▲, $w_{DP} = 0.00$; ●, $w_{DP} = 0.01$; and ■, $w_{DP} = 0.02$.

Figure 12. Measured electrical conductivity k of artificially degraded MEA solutions as a function of CO_2 loading α at 293.15 K and $w_{DP} = 0.02$: ●, mass fraction w_{amine} of 0.2; ✕, 0.3; and ♦, 0.4.

with the linear equations. One possible explanation is that compared with the artificially degraded MEA solutions, the industrially degraded MEA solutions have more narrow ranges of the MEA mass fraction and the degradation products mass fraction. The fact that industrially degraded MEA solutions have a broader diversity of degradation products could be another reason.

In addition, when there is no MEA or degradation products or CO_2 in the solution, the solution becomes pure water. As a result, the value of each A_0 should be the value of each physical property for the pure water, which was not the case in our experiments. This is due to the fact that the physical properties of pure water were not taken into consideration when the empirical correlations were developed. Therefore, the developed empirical correlations cannot be used to estimate the physical properties of the pure water.

For density, A_2 of industrially degraded MEA solutions is larger than that of artificially degraded MEA solutions. However, for viscosity, A_2 of industrially degraded MEA solutions is smaller than that of artificially degraded MEA

Table 6. Fitting Parameters (A_0, A_1, A_2, and A_3) of Equation 4 and Average Absolute Percentage Deviations (AAD) for the Empirical Correlations of Density (ρ), Viscosity (η), Refractive Index (n_D), and Electrical Conductivity (k) for Artificially and Industrially Degraded MEA Solutions

properties	units	T/K	samples	A_0	A_1	A_2	A_3	AAD
ρ	kg·m^{-3}	298.15	artificially	959.9	187.8	258.7	188.3	0.53%
			industrially	983.4	143.7	718.6	106.4	0.17%
η	mPa·s	298.15	artificially	−2.32	16.03	14.67	3.46	11.15%
			industrially	−1.89	13.73	10.10	3.08	1.87%
n_D		293.15	artificially	1.321	0.174	0.114	0.049	0.13%
			industrially	1.323	0.186	0.713	0.022	0.05%
k	mS·cm^{-1}	293.15	artificially	9.76	−22.07	270.13	51.10	28.58%
			industrially	−9.98	110.70	89.97	41.16	4.10%

solutions. Thus, the density of the real degraded MEA solutions increases more dramatically with increases in the degradation products mass fraction. The refractive index of the industrially degraded solutions also increases more dramatically with increases in the degradation products mass fraction compared with the artificially degraded solutions. However, things are a little different when it comes to electrical conductivity. The electrical conductivity of artificially degraded MEA solutions decreases with increases in the MEA mass fraction, which shows the same trend with the clean MEA solutions. On the contrary, the A_1 value of the industrially degraded MEA solutions is positive, which means that the electrical conductivity of industrially degraded MEA solutions increases when the MEA mass fraction increases. Besides, the electrical conductivity of the artificially degraded MEA solutions increases more dramatically with increases in the degradation products.

An additional 14 industrially degraded MEA solvents collected from the working CO_2 capture plant in the USA were analyzed, and the measured density data were used to determine the predictability of the two developed correlations. The result is presented in Figure 13.

The average absolute percentage deviation is 0.778% between the measured values and the calculated values from the equation developed from artificially degraded solvents. On the other hand, the average absolute percentage deviation is 0.412% between the measured values and the calculated values
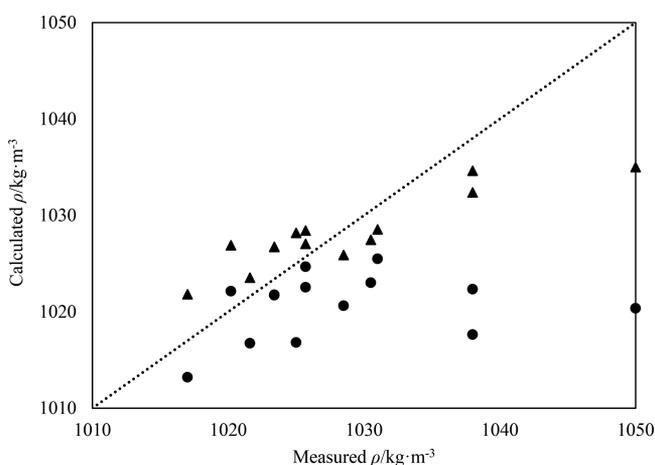
from the equation developed from industrially degraded solvents. The empirical correlation of the industrially degraded MEA solvents is more reliable in estimating the density than that of the artificially degraded solvents. The fact that the MEA mass fraction, w_{amine}, and degradation products mass fraction, w_{DP}, of industrially degraded MEA solvents have a much narrower range of results in a more accurate adjusted physical property equation.

4. CONCLUSIONS

Densities, viscosities, refractive indices, and electrical conductivities of artificially degraded and industrially degraded MEA solutions were measured at a standard temperature of 293.15 or 298.15 K. This allows for the quantification of the impact of the degradation products on the physical properties. The measured physical properties show a significant dependence on the MEA mass fraction, degradation products mass fraction, and CO_2 loading. Empirical correlations were developed to allow the degradation level to be roughly estimated with a simple property measurement without any complex chemical analyses incurring extra costs. The predictability of the developed empirical correlations was determined by additional industrially degraded solvents obtained from the working plant. The result shows that the empirical correlation of the industrially degraded MEA solvents is more reliable for estimating the density than that of the artificially degraded solvents.

■ ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.7b01101.

> Comparisons of measured data (with error bars) with the published data for density, viscosity, and refractive index of the MEA + water system are presented in Figures S1, S2, and S3, respectively. Experimental and calculated data of density, viscosity, refractive index, and electrical conductivity of artificially degraded MEA solutions are shown in Tables S1 to S3. Experimental and calculated data of density, viscosity, refractive index, and electrical conductivity of industrially degraded MEA solutions are shown in Table S4. (PDF)

Figure 13. Parity chart comparing the measured density ρ data for real degraded MEA solvents with the calculated densities from the equations developed from artificially degraded (●) and industrially degraded (▲) solvents.

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Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Strazisar, B. R.; Anderson, R. R.; White, C. M. Degradation pathways for monoethanolamine in a CO_2 capture facility. *Energy Fuels* **2003**, *17*, 1034−1039.

(2) ElMoudir, W.; Fairchild, J.; Aboudheir, A. HTC solvent reclaimer system at searles valley minerals facility in Trona, California. *Energy Procedia* **2014**, *63*, 6156−6165.

(3) Blanc, C.; Elgue, J.; Lallemand, F. MDEA process selects H_2S. *Hydrocarbon Process* **1981**, *60*, 111−116.

(4) Bacon, T. R. Amine Solution Quality Control through Design, Operation and Correction. *Proceedings of Laurance Reid Gas Conditioning Conference*; Norman, OK, USA, March 2−4, 1987.

(5) Stichlmair, J.; Bravo, J. L.; Fair, J. R. General model for prediction of pressure drop and capacity of countercurrent gas/liquid packed columns. *Gas Sep. Purif.* **1989**, *3*, 19−28.

(6) Wang, G. Q.; Yuan, X. G.; Yu, K. T. Review of mass-transfer correlations for packed columns. *Ind. Eng. Chem. Res.* **2005**, *44*, 8715−8729.

(7) Jassim, M. S.; Rochelle, G.; Eimer, D.; Ramshaw, C. Carbon dioxide absorption and desorption in aqueous monoethanolamine solutions in a rotating packed bed. *Ind. Eng. Chem. Res.* **2007**, *46*, 2823−2833.

(8) Kohl, A. L.; Nielsen, R. B. *Gas Purification*, 5th ed.; Gulf Publishing Company: Houston, TX, 1997.

(9) Han, J.; Jin, J.; Eimer, D. A.; Melaaen, M. C. Density of Water (1) + Monoethanolamine (2) + CO_2 (3) from (298.15 to 413.15) K and Surface Tension of Water (1) + Monoethanolamine (2) from (303.15 to 333.15) K. *J. Chem. Eng. Data* **2012**, *57*, 1095−1103.

(10) Maham, Y.; Teng, T. T.; Hepler, L. G.; Mather, A. E. Densities, excess molar volumes, and partial molar volumes for binary mixtures of water with monoethanolamine, diethanolamine, and triethanolamine from 25 to 80 C. *J. Solution Chem.* **1994**, *23*, 195−205.

(11) Jayarathna, S. A.; Weerasooriya, A.; Dayarathna, S.; Eimer, D. A.; Melaaen, M. C. Densities and surface tensions of CO_2 loaded aqueous monoethanolamine solutions with r = (0.2 to 0.7) at T = (303.15 to 333.15) K. *J. Chem. Eng. Data* **2013**, *58*, 986−992.

(12) Lee, M. J.; Lin, T. K. Density and viscosity for monoethanolamine + water, + ethanol, and + 2-propanol. *J. Chem. Eng. Data* **1995**, *40*, 336−339.

(13) Lee, H. S.; Seo, M. D.; Kang, J. W.; Yang, D. R. Measurement and correlation of the solubility of carbon dioxide in the mixtures of aqueous monoethanolamine solution and benzoic acid. *J. Chem. Eng. Data* **2012**, *57*, 3744−3750.

(14) DiGuilio, R. M.; Lee, R. J.; Schaeffer, S. T.; Brasher, L. L.; Teja, A. S. Densities and Viscosities of the Ethanolamines. *J. Chem. Eng. Data* **1992**, *37*, 239−242.

(15) Tseng, Y. M.; Thompson, A. R. Densities and Refractive Indices of Aqueous Monoethanolamine, Diethanolamine, Triethanolamine. *J. Chem. Eng. Data* **1964**, *9*, 264−267.

(16) Amundsen, T. G.; Øi, L. E.; Eimer, D. A. Density and viscosity of monoethanolamine + water + carbon dioxide from (25 to 80) °C. *J. Chem. Eng. Data* **2009**, *54*, 3096−3100.

(17) ElMoudir, W. *Experimental Studies for Development of a Purification Process for Single and Mixed Amine Solvents.* Ph.D. Thesis, University of Regina, Regina, Canada, October 2012.

(18) Supap, T.; Idem, R.; Tontiwachwuthikul, P.; Saiwan, C. Analysis of monoethanolamine and its oxidative degradation products during CO_2 absorption from flue gases: A comparative study of GC-MS, HPLC-RID, and CE-DAD analytical techniques and possible optimum combinations. *Ind. Eng. Chem. Res.* **2006**, *45*, 2437−2451.

(19) Álvarez, E.; Cerdeira, F.; Gómez-Diaz, D.; Navaza, J. M. Density, speed of sound, isentropic compressibility, and excess volume of binary mixtures of 1-amino-2-propanol or 3-amino-1-propanol with 2-amino-2-methyl-1-propanol, diethanolamine, or triethanolamine from (293.15 to 323.15) K. *J. Chem. Eng. Data* **2010**, *55*, 2567−2575.

(20) Li, X. X.; Fan, G. C.; Zhang, Z. L.; Wang, Y. W.; Lu, Y. Q. Density and viscosity for binary mixtures of diethylene glycol monobutyl ether with monoethanolamine, diethanolamine, and triethanolamine from (293.15 to 333.15) K. *J. Chem. Eng. Data* **2013**, *58*, 1229−1235.

(21) Pagé, M.; Huot, J. Y.; Jolicoeur, C. A comprehensive thermodynamic investigation of water−ethanolamine mixtures at 10, 25, and 40°C. *Can. J. Chem.* **1993**, *71*, 1064−1072.

(22) González, B.; Calvar, N.; Gomez, E.; Domínguez, A. Density, dynamic viscosity, and derived properties of binary mixtures of methanol or ethanol with water, ethyl acetate, and methyl acetate at T = (293.15, 298.15, and 303.15) K. *J. Chem. Thermodyn.* **2007**, *39*, 1578−1588.

(23) García-Abuín, A.; Gómez-Díaz, D.; Navaza, J. M. Density, Speed of Sound, and Viscosity of Monoethanolamine + Water + N-Ethyl-2-pyrrolidone from T = (293.15 to 323.15) K. *J. Chem. Eng. Data* **2013**, *58*, 3387−3391.

(24) Mandal, B. P.; Kundu, M.; Bandyopadhyay, S. S. Density and viscosity of aqueous solutions of (N-methyldiethanolamine + monoethanolamine), (N-methyldiethanolamine + diethanolamine), (2-amino-2-methyl-1-propanol + monoethanolamine), and (2-amino2-methyl-1-propanol + diethanolamine). *J. Chem. Eng. Data* **2003**, *48*, 703−707.

(25) Taib, M. M.; Murugesan, T. Density, refractive index, and excess properties of 1-butyl-3-methylimidazolium tetrafluoroborate with water and monoethanolamine. *J. Chem. Eng. Data* **2012**, *57*, 120−126.

(26) Tariq, M.; Forte, P. A. S.; CostaGomez, M. F.; CanongiaLopes, J. N.; Rebelo, L. P. N. Densities and Refractive Indices of Imidazoliumand Phosphonium-Based Ionic Liquids: Effect of Temperature, Alkyl Chain Length, and Anion. *J. Chem. Thermodyn.* **2009**, *41*, 790−798.

(27) Alam, M. S.; Mandal, A.; Mandal, A. B. Effect of KCl on the micellization and clouding phenomenon of the amphiphilic phenothiazine drug promethazine hydrochloride: some thermodynamic properties. *J. Chem. Eng. Data* **2011**, *56*, 1540−1546.

(28) Han, S. J.; Wee, J. H. Correction to Estimation of Correlation between Electrical Conductivity and CO_2 Absorption in a Monoethanolamine Solvent System. *J. Chem. Eng. Data* **2014**, *59*, 3944−3946.

(29) Han, S. J.; Wee, J. H. Estimation of correlation between electrical conductivity and CO_2 absorption in a monoethanolamine solvent system. *J. Chem. Eng. Data* **2013**, *58*, 2381−2388.

(30) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*; Reinhold Publishing Corporation: New York, 1943.