Surface Tension of Aqueous Binary Mixtures of 2-(Methylamino)ethanol and 2-(Ethylamino)ethanol and Aqueous Ternary Mixtures of These Amines with Triethanolamine or *N*-Methyldiethanolamine from (293.15 to 323.15) K

Estrella Álvarez,[†] Diego Gómez-Díaz,[‡] M. Dolores La Rubia,[§] and José M. Navaza*[,‡]

Department of Chemical Engineering, ETSEI, University of Vigo, Rúa Maxwell s/n, E-36310, Vigo, Spain, Department of Chemical Engineering, ETSE, University of Santiago de Compostela, Rúa Lope Gómez de Marzoa s/n, E-15706, Santiago de Compostela, Spain, and Department of Chemical, Environmental and Materials Engineering, EPS, University of Jaén, Paraje Las Lagunillas s/n, E-23071, Jaén, Spain

The surface tension of aqueous solutions of MAE (2-(methylamino)ethanol) and EAE (2-(ethylamino)ethanol) were determined at (293.15 to 323.15) K over the entire range of concentrations of binary mixtures with water. Also, ternary mixtures of previous systems with two amines commonly employed in carbon dioxide capture processes (TEA, triethanolamine, and MDEA, *N*-methyldiethanolamine) were studied. Equations were used to fit the experimental data at different compositions and temperatures.

Introduction

Surface tension has great importance[1] regarding the behavior and hydrodynamics in gas–liquid systems, and due to aqueous solutions of amines that are employed in carbon dioxide capture, the value of surface tension of these liquid phases could play an important role in this kind of operation. The influence of surface tension upon bubble size has been widely studied in the literature,[2] and in different research works, surface tension of the liquid phase was modified by the addition of surfactants producing modifications upon the bubble's diameter when surface tension decreases.[3] Similar behaviors have also been observed when different solutes that produce a decrease in surface tension were employed.[4]

Nowadays, a great part of research regards characterization of aqueous solutions of amines for their use in carbon dioxide capture and is centered on the use of new amines[5] that contribute interesting characteristics such as suitable physical properties, high reaction rate, or low degradation in regeneration processes.

Also, a mixture of amines in aqueous solutions has been considered as a new alternative to increase the capture rate of acid gases by chemical absorption with the aim of a second amine in aqueous solutions that produces an enhancement effect.[6] For this reason, the knowledge of surface tension for these ternary mixtures could be important to understand the behavior of the liquid phases on absorption processes.

Experimental Section

All amines have been supplied by Merck, with a purity of >98 % for 2-(methylamino)ethanol (CAS Registry No. 109-83-1), 2-(ethylamino)ethanol (CAS Registry No. 110-73-6), and *N*-methyldiethanolamine (CAS Registry No. 105-59-9). The purity for triethanolamine (CAS Registry No. 102-71-6) was >99 %.

Table 1. Comparison of Results with Literature Data for the Pure Water Surface Tension

	σ/mN·m^{-1}	
T/K	this work	lit. (ref)
293.15	72.75	72.75[7]
298.15	72.01	71.95[8]
		72.01[9]
		71.98[10]
303.15	71.21	71.20[10]
308.15	70.42	70.40[10]
		70.41[9]
313.15	69.52	69.60[10]
318.15	68.84	68.77[10]
		68.79[9]
323.15	67.92	67.94[10]

All liquid mixtures were prepared by mass using an analytical balance (Kern 770) with a precision of $\pm 10^{-4}$ g. The maximum uncertainty of the sample preparation in mole fraction was ± 0.0006.

Surface tension was determined by a Krüss K-11 tensiometer using the Wilhelmy plate method. The plate employed was a commercial platinum plate supplied by Krüss. The platinum plate was cleaned with water and acetone and flame-dried before each measurement. The uncertainty of the measurement was ± 0.04 mN·m^{-1}. In general, each surface tension value reported was an average of ten measurements. Before surface tension measurements were made, the samples were stirred in a thermostatted vessel that was closed to prevent evaporation. Surface tension measurements were carried out in the range of (293.15 to 323.15) K with 5 K steps. The measurement vessel was connected to a thermostat-cryostat bath (Selecta Frigiterm) controlled to ± 0.1 K.

Table 1 shows the surface tension values for pure water obtained in the present work and the comparison with literature values to ensure that the experimental procedure for surface tension determination contributes suitable values.

Results and Discussion

The experimental values obtained for surface tension of aqueous binary mixtures of MAE and EAE over the entire

* To whom correspondence should be addressed. Department of Chemical Engineering, University of Santiago de Compostela, Santiago de Compostela, E-15782, Galicia, Spain. E-mail: eqnavaza@usc.es.
[†] University of Vigo.
[‡] University of Santiago de Compostela.
[§] University of Jaén.

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Table 2. Surface Tension σ for 2-(Methylamino)ethanol (1) + Water (2) Mixtures from T = (293.15 to 323.15) K

	σ/mN·m^{-1}						
x_1	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15
0.0000	72.75	72.01	71.21	70.42	69.52	68.84	67.92
0.0125	67.99	67.18	66.21	65.44	64.58	63.71	62.80
0.0260	64.31	63.36	62.48	61.60	60.70	59.79	58.91
0.0587	58.79	57.87	56.96	56.04	55.13	54.11	53.19
0.0931	55.12	54.16	53.21	52.28	51.35	50.42	49.47
0.1379	51.96	51.14	50.21	49.29	48.38	47.55	46.65
0.1932	49.16	48.42	47.60	46.76	45.94	45.11	44.29
0.2643	46.29	45.57	44.86	44.15	43.46	42.76	42.06
0.3586	43.85	43.23	42.61	41.99	41.36	40.73	40.12
0.4730	41.66	41.13	40.59	40.04	39.51	38.97	38.43
0.6769	38.98	38.46	37.94	37.43	36.91	36.41	35.92
0.8169	37.46	37.01	36.56	36.12	35.67	35.24	34.79
0.9206	36.39	35.96	35.56	35.14	34.72	34.31	33.91
1.0000	35.68	35.28	34.90	34.54	34.15	33.75	33.37

Table 3. Surface Tension σ for 2-(Ethylamino)ethanol + Water (2) Mixtures from T = (293.15 to 323.15) K

	σ/mN·m^{-1}						
x_1	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15
0.0000	72.75	72.01	71.21	70.42	69.52	68.84	67.92
0.0104	60.69	59.57	58.47	57.37	56.29	55.19	54.05
0.0220	54.61	53.58	52.54	51.51	50.45	49.34	48.34
0.0482	48.75	47.89	46.91	46.07	45.16	44.30	43.34
0.0795	45.73	44.95	44.15	43.42	42.64	41.84	41.01
0.1189	43.72	42.97	42.25	41.47	40.71	40.03	39.32
0.1679	42.16	41.51	40.88	40.30	39.62	39.05	38.44
0.2292	40.88	40.34	39.78	39.26	38.70	38.20	37.60
0.3064	39.68	39.19	38.68	38.22	37.62	37.16	36.65
0.4252	38.28	37.75	37.28	36.78	36.26	35.75	35.28
0.6476	36.06	35.58	35.09	34.52	34.01	33.46	32.93
0.7929	34.64	34.13	33.62	33.05	32.53	32.02	31.41
0.8852	33.79	33.23	32.71	32.18	31.64	31.10	30.51
1.0000	32.75	32.21	31.67	31.10	30.54	29.98	29.41

concentration range and at different temperatures included between (293.15 and 323.15) K are summarized in Tables 2 and 3. The influence of mixture composition and the effect of temperature upon surface tension value for these systems can be observed in Figure 1. This figure shows that an increase in temperature, versus surface tension determination, produces a decrease in this property with a linear trend.

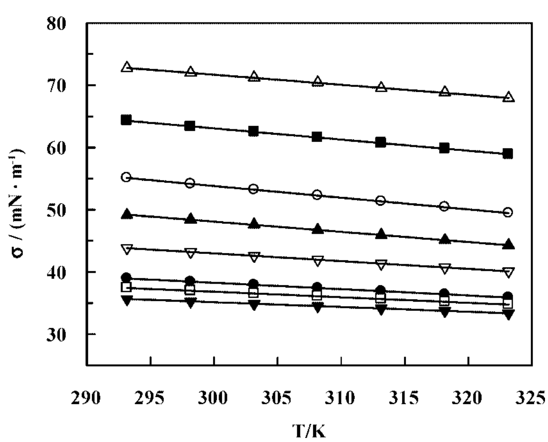

Figure 1. Surface tension, σ, of 2-(methylamino)ethanol (1) + water (2) as a function of temperature at different mole fractions of amine: △, x_1 = 0.0000; ■, x_1 = 0.0260; ○, x_1 = 0.0931; ▲, x_1 = 0.1932; ▽, x_1 = 0.3586; ●, x_1 = 0.6769; □, x_1 = 0.8169; ▼, x_1 = 1.0000; —, calculated from eq 1.

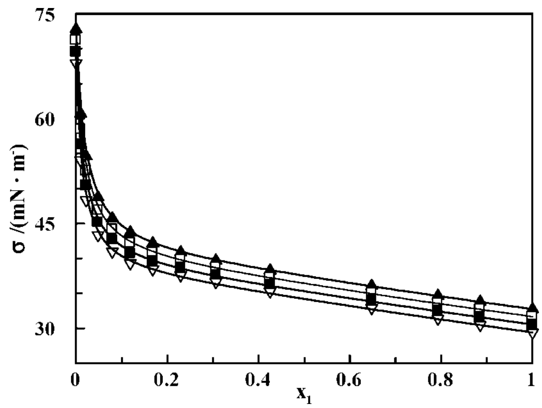

Figure 2. Experimental and calculated surface tensions, σ, for 2-(ethylamino)ethanol (1) + water (2): ▲, 293.15 K; □, 303.15 K; ■, 313.15 K; ▽, 323.15 K; —, calculated from eq 2.

Table 4. Surface Tension σ of Aqueous Ternary Solutions of 2-(Methylamino)ethanol and TEA or MDEA from T = (293.15 to 323.15) K

	σ/mN·m^{-1}						
$\%_{\text{mass}}/\%_{\text{mass}}$	x_1	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15
2-(Methylamino)ethanol/Triethanolamine							
0/50	53.72	52.88	52.08	51.29	50.37	49.68	48.76
10/40	53.07	52.18	51.36	50.55	49.64	48.82	48.02
20/30	52.40	51.54	50.65	49.79	48.94	48.04	47.27
30/20	51.49	50.51	49.73	48.95	48.00	47.25	46.32
40/10	50.39	49.51	48.68	47.84	46.96	46.14	45.36
50/0	49.16	48.42	47.60	46.76	45.94	45.11	44.29
2-(Methylamino)ethanol/*N*-Methyldiethanolamine							
0/50	50.61	49.79	49.06	48.24	47.50	46.70	45.80
10/40	50.35	49.50	48.69	47.89	47.04	46.23	45.42
20/30	50.10	49.28	48.45	47.61	46.78	45.93	45.10
30/20	49.81	48.97	48.14	47.30	46.46	45.64	44.84
40/10	49.52	48.68	47.91	47.06	46.24	45.40	44.55
50/0	49.16	48.42	47.60	46.76	45.94	45.11	44.29

Table 5. Surface Tension σ of Aqueous Ternary Solutions of 2-(Ethylamino)ethanol and TEA or MDEA from T = (293.15 to 323.15) K

	σ/mN·m^{-1}						
$\%_{\text{mass}}/\%_{\text{mass}}$	x_1	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15
2-(Ethylamino)ethanol/Triethanolamine							
0/50	53.72	52.88	52.08	51.29	50.37	49.68	48.76
10/40	51.60	50.79	49.96	49.20	48.33	47.62	46.74
20/30	49.27	48.42	47.64	46.90	46.15	45.31	44.58
30/20	46.67	45.89	45.11	44.42	43.67	42.91	42.18
40/10	44.50	43.86	43.10	42.40	41.79	41.08	40.40
50/0	42.16	41.51	40.83	40.30	39.72	39.09	38.48
2-(Ethylamino)ethanol/*N*-Methyldiethanolamine							
0/50	50.61	49.79	49.06	48.24	47.50	46.70	45.80
10/40	49.50	48.81	48.06	47.22	46.46	45.67	44.89
20/30	47.94	47.18	46.30	45.60	44.86	44.11	43.36
30/20	45.75	45.04	44.31	43.65	42.94	42.24	41.61
40/10	43.86	43.23	42.52	41.93	41.27	40.54	39.89
50/0	42.16	41.51	40.83	40.30	39.72	39.09	38.48

This linear trend observed in Figure 1 allows the use of eq 1 that has been employed in previous works[11] to fit experimental data of surface tension and the effect of temperature

$$\sigma = K_1 - K_2 \cdot T \qquad (1)$$

where σ is the surface tension; T is temperature; and K_1 and K_2 are fitting parameters.

The obtained fittings, shown in Figure 1, have been suitable with low standard deviations.

Table 6. Surface Tension Parameters K_1 and K_2 (in Equation 1) for Aqueous Binary Mixtures of 2-(Methylamino)ethanol and 2-(Ethylamino)ethanol[a]

x_1	K_1/mN·m^{-1}	K_2/mN·m^{-1}·K^{-1}	σ_{st}	x_1	K_1/mN·m^{-1}	K_2/mN·m^{-1}·K^{-1}	σ_{st}
			2-(Methylamino)ethanol (1) + Water (2)				
0.0000	119.949	0.1609	0.056	0.2643	87.547	0.1408	0.012
0.0125	118.549	0.1724	0.043	0.3586	80.371	0.1246	0.012
0.0260	116.884	0.1794	0.021	0.4730	73.261	0.1078	0.007
0.0587	113.571	0.1868	0.035	0.6769	68.933	0.1022	0.013
0.0931	110.153	0.1878	0.013	0.8169	63.503	0.0889	0.016
0.1379	104.206	0.1781	0.036	0.9206	60.630	0.0827	0.010
0.1932	97.137	0.1635	0.029	1.0000	58.164	0.0767	0.012
			2-(Ethylamino)ethanol (1) + Water (2)				
0.0000	119.949	0.1609	0.056	0.2292	72.708	0.1086	0.023
0.0104	125.301	0.2204	0.019	0.3064	69.449	0.1015	0.030
0.0220	116.148	0.2099	0.031	0.4252	67.628	0.1001	0.023
0.0482	101.439	0.1797	0.034	0.6476	66.899	0.1051	0.030
0.0795	91.573	0.1564	0.032	0.7929	66.073	0.1071	0.033
0.1189	86.882	0.1473	0.031	0.8852	65.743	0.1089	0.032
0.1679	78.447	0.1239	0.030	1.0000	65.453	0.1115	0.013

[a] $\sigma = [\Sigma(\sigma_{calcd} - \sigma_{exptl})^2/(N - n)]^{1/2}$ where N is the number of data points and n is the number of parameters.

Table 7. Surface Tension Parameters K_1 and K_2 (in Equation 1) for Aqueous Ternary Mixtures of 2-(Methylamino)ethanol + (TEA or MDEA) and 2-(Ethylamino)ethanol + (TEA or MDEA)[a]

%$_{mass}$/%$_{mass}$	K_1/mN·m^{-1}	K_2/mN·m^{-1}·K^{-1}	σ_{st}	K_1/mN·m^{-1}	K_2/mN·m^{-1}·K^{-1}	σ_{st}
	2-(Methylamino)ethanol/Triethanolamine			2-(Ethylamino)ethanol/Triethanolamine		
0/50	97.041	0.1584	0.049	101.827	0.1642	0.056
10/40	98.455	0.1641	0.021	98.811	0.1611	0.037
20/30	99.046	0.1669	0.013	94.835	0.1556	0.036
30/20	98.483	0.1661	0.018	90.343	0.1491	0.026
40/10	97.984	0.1653	0.023	84.642	0.1369	0.036
50/0	97.137	0.1635	0.029	77.695	0.1214	0.043
	2-(Methylamino)ethanol/*N*-Methyldiethanolamine			2-(Ethylamino)ethanol/*N*-Methyldiethanolamine		
0/50	101.857	0.1642	0.047	97.041	0.1584	0.049
10/40	102.443	0.1685	0.030	95.015	0.1551	0.040
20/30	102.850	0.1721	0.035	92.548	0.1523	0.046
30/20	101.190	0.1697	0.060	86.327	0.1385	0.028
40/10	99.675	0.1682	0.031	82.713	0.1325	0.036
50/0	97.137	0.1635	0.029	77.695	0.1214	0.043

[a] $\sigma = [\Sigma(\sigma_{calcd} - \sigma_{exptl})^2/(N - n)]^{1/2}$ where N is the number of data points and n is the number of parameters.

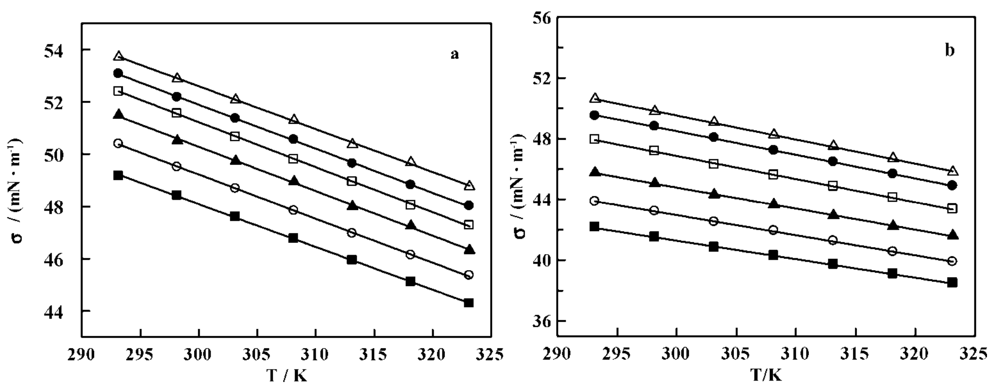

Figure 3. Surface tension dependence with temperature for aqueous ternary mixtures of (a) MAE (1) + TEA (2) and (b) EAE (1) + MDEA (2): △, 0/50; ●, 10/40; □, 20/30; ▲, 30/20; ○, 40/10; ■, 50/0; —, calculated from eq 1.

On the other hand, regarding the influence of binary mixture composition upon surface tension, Figure 1 also shows that when a mixture is enriched in amine surface tension decreases. Using the experimental data shown in Figure 1, it is possible to observe that the mentioned decrease is not linear (see Figure 2). In both cases, the presence of low concentrations of amine produces an important decrease in surface tension value. Similar behaviors were found in previous studies in systems which have analyzed aqueous solutions of different amines.[12,13]

For this kind of experimental behavior, seen in Figure 2, a theoretically derived equation[14] (see eq 2) has been employed in previous works[15] that allows fitting the experimental values of surface tension of the mixture composition

$$\frac{\sigma - \sigma_2}{\sigma_2 - \sigma_1} = -x_1\left(1 + \frac{ax_2}{1 - bx_2}\right) \qquad (2)$$

where σ is the mixture surface tension; σ_1 and σ_2 are the amine and water surface tension, respectively; x_1 and x_2 are the molar

Table 8. Surface Tension Parameters *a* and *b* (in Equation 2) for Aqueous Binary Mixtures of 2-(Methylamino)ethanol and 2-(Ethylamino)ethanol[a]

	T/K						
	293.15	298.15	303.15	308.15	313.15	318.15	323.15
	2-(Methylamino)ethanol (1) + Water (2)						
a	0.7339	0.7370	0.7424	0.7508	0.7572	0.7613	0.7684
b	0.9264	0.9296	0.9322	0.9340	0.9354	0.9389	0.9401
σ_{st}	0.257	0.258	0.238	0.201	0.167	0.157	0.125
	2-(Ethylamino)ethanol (1) + Water (2)						
a	0.7769	0.7765	0.7720	0.7686	0.7675	0.7646	0.7611
b	0.9827	0.9836	0.9849	0.9858	0.9864	0.9874	0.9882
σ_{st}	0.039	0.054	0.067	0.098	0.133	0.160	0.195

[a] $\sigma = [\sum(\sigma_{calcd} - \sigma_{exptl})^2/(N - n)]^{1/2}$ where N is the number of data points and n is the number of parameters.

fraction of amine and water; and a and b are fitting parameters (Table 8).

Figure 2 shows the good agreement of eq 2 and the experimental data under the different conditions of temperature for surface tension determination.

The last part of the present work is centered on the influence of mixture composition in a ternary system formed by the previously analyzed binary mixtures and the addition of other amines, which in this work are TEA and MDEA due to their common use in acid gas capture. Tables 4 and 5 show the experimental values for surface tension corresponding to the ternary systems previously mentioned when composition was varied.

The experimental results obtained for surface tension for these ternary systems are shown in Figure 3 and allow us to analyze the effect of mixture composition and temperature upon the value of surface tension. The influence of temperature upon surface tension in the ternary mixtures is similar to the previously observed behavior for binary ones because a decrease is observed when temperature increases. The observed trend is linear again. Equation 1 was employed, and fitting parameters are included in Tables 6 and 7.

The influence of the mixture composition upon the value of surface tension and the presence of TEA or MDEA in the ternary mixture produces an increase in the value of surface tension. This increase is higher in the ternary system that includes MAE as a component. All the experimental data show that the increase in surface tension produced by the presence of TEA and MDEA is linear with different slopes.

Conclusions

The surface tension of aqueous solutions of two amines (MAE and EAE) has been determined over the entire range of amine concentration and at different temperatures, and the experimental results show that both variables produce a decrease in the value of surface tension.

On the other hand, the influence of the presence of other amines (TEA and MDEA) to form ternary mixtures produces an increase of surface tension in all cases, with a higher effect in mixtures with MDEA.

Also, the equations employed in the present work to correlate the experimental values with regard to mixture composition and temperature show good results for all the experimental systems.

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