

A comparative study of thermophysical properties of amine aqueous solutions for CO₂ mitigation

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Abstract:

Research on carbon capture is increasing interest due to its impact in the search of net-zero carbon economy. In this sense, amine solutions play an important role in the post-combustion CO₂ capture, using them as chemical absorbents. There are different amines or mixed amines that are studied to substitute MEA, which is the best well-known despite some drawbacks such as its high energy demand or its low potential of CO₂ absorption. On the other hand, key properties such as density, viscosity or heat capacity are necessary for the design and optimization of the separation plant; the accuracy of the calculations is directly related to the accuracy of the properties. In this work, these properties, which were determined by means of experimental techniques of low uncertainty, are presented and compared for three tertiary amines: Triethanolamine (TEA), N-Methyldiethanolamine (MDEA) and 2-Dimethylaminoethanol (DMAE). Densities were measured using a commercial vibrating tube densimeter that was completed with different devices allowing the determination of density with a standard uncertainty of 0.35 kg/m³. A falling body viscometer was used for viscosity measurements with a standard uncertainty of 1.6%. Finally, a flow calorimeter, developed in our laboratory, measured isobaric heat capacities with a standard uncertainty of 0.5%. The comparison is done in a temperature range from 293.15 K to 353.15 K and pressures up to 25 MPa. In addition, different mass fractions of amine in the mixture (amine +water) are studied ($w_{\text{amine}} = 0.1$ to 0.4).

Keywords:

Density; Viscosity; Heat capacity; 2-Dimethylaminoethanol (DMAE); N-Methyldiethanolamine (MDEA); Triethanolamine (TEA).

1. Introduction

The objective of a net-zero carbon economy is fostering the research on carbon capture as a measure to promote the energy transition. In this context, alkanolamine solutions play an important role as chemical absorbents for CO₂ capture in the post-combustion. Although this technology is industrially mature, there are some key points to address to reduce the associated cost such as the search for solvents with less energy requirements, better stability, and less harmful emissions, in addition to the process optimization, and integration with the CO₂-emitting plant [1].

There are different amines or mixed amines that are studied to substitute MEA, which is the best well-known despite some drawbacks such as its high energy demand or its low potential of CO₂ absorption. However, the design and optimization of the separation plant require the knowledge of key properties such as density, viscosity or heat capacity of these new potential absorbents. Moreover, the accuracy of the calculations is directly related to the accuracy of the properties.

Our research group has been involved during the last decade in the accurate measurement of these properties as can be seen in previous papers. Density and viscosity of different aqueous solutions of alkanolamines were already measured at wide ranges of temperature and pressure: Ethanolamine (MEA) and N-Methyldiethanolamine (MDEA) in [2]; Diethanolamine (DEA), Triethanolamine (TEA) and 2-Dimethylaminoethanol (DMAE) in [3]; Piperazine (PZ) in [4] and blended amines (PZ+ DMAE) in [4] and (MDEA+DEA) in [5]. Heat capacities of 30% weight of amine up to 25 MPa for aqueous solutions of MEA, DEA and TEA were presented in [6], and heat capacities of aqueous solutions of six different amines are reported in [7].

In this work, a comparison of the behaviour of the three tertiary amines: Triethanolamine (TEA), N-Methyldiethanolamine (MDEA) and 2-Dimethylaminoethanol (DMAE) in terms of density, viscosity and heat capacity is presented and discussed. The comparison is done in a temperature range from 293.15 K to 353.15 K and pressures up to 25 MPa. In addition, different mass fractions of amine in the mixture (amine +water) are studied ($w_{\text{amine}} = 0.1$ to 0.4).

2. Experimental section

2.1. Materials

The materials used in the measurements were purchased from Sigma-Aldrich of the highest purity available and used without further purification. Their purities in mass fraction (as stated by the supplier) were: Triethanolamine (TEA) ≥ 0.99 , N-Methyldiethanolamine (MDEA) ≥ 0.99 , and 2-Dimethylaminoethanol (DMAE) ≥ 0.995 .

A precision balance (RADWAG PS750/C/2) was used to make the mixtures by weighting, estimating an expanded uncertainty ($k=2$) of 0.0002 in mass fraction.

2.2. Equipment

Three accurate techniques are used to perform the measurements: densities are determined using a commercial vibrating tube densimeter, viscosities by means of a falling body viscometer and heat capacities using a flow calorimeter. All the techniques are calibrated and checked regularly. A brief description of the main features of these techniques is explained below.

An Anton Paar DMA HPM densimeter is employed to carry out the density measurements, the technique is completed with an automatization system in such a way that, through the computer program, ramps of pressures and temperatures can be programmed, and the frequency measurements are recorded for the sample. The technique can measure density in a temperature range from 240 K to 420 K and up to 140 MPa with a relative standard uncertainty of 0.35 kg/m³. Details of the technique and the uncertainty budget are published in [8].

Density, ρ , of a fluid is related to the vibration period, τ , through (1):

$$\rho(T, p) = A(T)\tau^2(T, p) - B(T, p) \quad (1)$$

where $A(T)$ and $B(T, p)$ are two characteristic parameters of the apparatus which can be determined by a calibration procedure, in this case, water and vacuum were used for calibration.

Viscosity measurements are undertaken in a falling body viscometer whose principle of measure is based on the fall time of a body in a vertical tube filled with the sample [3,9]. The apparatus can perform measurements between 240 K to 475 K and up to 140 MPa, with a relative expanded uncertainty ($k = 2$) of 3%.

The model used for this viscometer is given by (2):

$$\eta = a + b\Delta\rho\Delta t \quad (2)$$

Where viscosity (η) is related to fall time (Δt) and the difference of density between the falling body and the liquid ($\Delta\rho$) and the parameters a and b are obtained by calibration using water and dodecane.

Finally, an automated flow calorimeter, fully developed in our laboratory, is used for isobaric heat capacity measurements. Its working principle lies in balancing the heating and cooling power of the calorimetric cell to maintain a fixed difference between the inlet and exit temperatures of the circulating fluid. at constant flow rate and, heat capacity is calculated by the determination of the net power exchanged.

The value of net power (\dot{Q}_{net}) is directly related to the isobaric heat capacity as shown in equation (3):

$$C_p = \dot{Q}_{net}/(\dot{V} \times \rho \times \Delta T) = [a + b(\dot{Q}_{base} - \dot{Q}_{measured})]/(\dot{V} \times \rho \times \Delta T) \quad (3)$$

where \dot{V} is the volumetric flow of the fluid, ρ is the density of the fluid at the pump temperature, ΔT is the temperature decrease and, a and b are the calibration constants calculated by an electric calibration. The relative expanded uncertainty of the heat capacity obtained with this technique is 1%. This equipment works in the temperature range from 240 K to 420 K and up to 25 MPa, the details are described in [6, 10].

3. Results and discussion

This work is focus on the thermophysical behaviour of aqueous solutions of three ternary amines (TEA, MDEA, DMAE), based on the experimental data of densities, viscosities, and isobaric heat capacities. These properties will be compared in the range of temperatures from 293.15 K to 353.15 K, pressures from 0.1 MPa to 30 MPa and mass fractions from 0.1 to 0.4.

Experimental values of density and viscosity for (TEA+ water) and (DMAE+ water) are published in [3] at mass fractions from 0.1 to 0.4, in the range of temperatures from 293.15 K to 393.15 K and pressures up to 140 MPa for density and up to 100 MPa for viscosity. On the other hand, data for (MDEA + water) mixtures ($w_{\text{amine}} = 0.1$ to 0.4) can be found in [2] where densities from 293.15 K to 393.15 K and pressures up to 140 MPa and viscosities from 293.15 K to 353.15 K and pressures up to 120 MPa are reported.

Data of isobaric heat capacities of the aqueous solutions of the three ternary amines of this study ($W_{\text{amine}} = 0.3$) from 313.15 K to 353.15 K and up to 25 MPa are given in [6].

Although the experimental values can be found in different papers [2,3,6,7], to report the complete information, Tables 1-3 contains the experimental values of heat capacities, viscosities and densities of the amine solutions under study.

Table 1. Isobaric heat capacities for amine + water mixtures [6,7].

P , MPa	c_p , kJ/kgK							
	293.15 K	313.15 K	333.15 K	353.15 K	293.15 K	313.15 K	333.15 K	353.15 K
	$W_{\text{TEA}} = 0.1001$				$W_{\text{TEA}} = 0.2000$			
0.10	4.064	4.041	4.054	4.071	3.784	3.907	3.961	3.983
5.0	4.055	4.03	4.046	4.064	3.774	3.883	3.961	3.975
10.0	4.041	4.023	4.038	4.055	3.764	3.880	3.954	3.965
15.0	4.029	4.010	4.030	4.049	3.760	3.876	3.942	3.963
20.0	4.016	3.998	4.019	4.035	3.758	3.868	3.934	3.961
25.0	4.004	3.992	4.010	4.032	3.756	3.866	3.933	3.949
	$W_{\text{TEA}} = 0.2991$				$W_{\text{TEA}} = 0.4000$			
0.10		3.803	3.871	3.934	3.492	3.554	3.611	3.646
5.0		3.787	3.861	3.928	3.416	3.484	3.533	3.563
10.0		3.775	3.854	3.925	3.352	3.404	3.457	3.502
15.0		3.757	3.847	3.922	3.293	3.355	3.403	3.451
20.0		3.749	3.834	3.917	3.238	3.297	3.362	3.400
25.0		3.732	3.831	3.914	3.199	3.260	3.318	3.354
	$W_{\text{MDEA}} = 0.1001$				$W_{\text{MDEA}} = 0.2001$			
0.10	4.065	4.126	4.096	4.179	3.880	3.987	4.051	4.098
5.0	4.060	4.113	4.080	4.169	3.867	3.965	4.050	4.085
10.0	4.050	4.108	4.077	4.157	3.861	3.964	4.043	4.084
15.0	4.049	4.094	4.069	4.144	3.855	3.949	4.034	4.074
20.0	4.046	4.090	4.068	4.137	3.836	3.943	4.033	4.070
25.0	4.041	4.077	4.065	4.127	3.847	3.934	4.026	4.066
	$W_{\text{MDEA}} = 0.2998$				$W_{\text{MDEA}} = 0.4001$			
0.10		3.890	3.965	4.057	3.601	3.727	3.810	3.897
5.0		3.857	3.946	4.040	3.591	3.722	3.797	3.886
10.0		3.836	3.930	4.028	3.577	3.718	3.784	3.881
15.0		3.814	3.920	4.010	3.566	3.713	3.780	3.882
20.0		3.782	3.908	4.000	3.554	3.706	3.777	3.879
25.0		3.775	3.900	3.977	3.549	3.701	3.773	3.875
	$W_{\text{DMAE}} = 0.1000$				$W_{\text{DMAE}} = 0.2005$			
0.10	4.187	4.228	4.172	4.253	4.017	4.101	4.179	4.229
5.0	4.180	4.218	4.166	4.244	4.010	4.095	4.177	4.223
10.0	4.168	4.209	4.155	4.234	4.006	4.087	4.171	4.222
15.0	4.161	4.202	4.150	4.227	4.000	4.086	4.167	4.222
20.0	4.152	4.192	4.140	4.220	3.993	4.085	4.163	4.216
25.0	4.143	4.184	4.131	4.214	3.989	4.079	4.161	4.211
	$W_{\text{DMAE}} = 0.3005$				$W_{\text{DMAE}} = 0.4000$			
0.10		4.072	4.123	4.272	3.812	3.931	3.948	4.093
5.0		4.059	4.116	4.257	3.811	3.929	3.945	4.091
10.0		4.043	4.090	4.242	3.813	3.922	3.941	4.085
15.0		4.028	4.072	4.232	3.814	3.917	3.939	4.079
20.0		4.012	4.054	4.220	3.815	3.914	3.931	4.068
25.0		3.997	4.039	4.205	3.812	3.910	3.927	4.057

Table 2. Viscosities for amine + water mixtures [2,3].

η , mPa·s								
P , MPa	293.15 K	313.15 K	333.15 K	353.15 K	293.15 K	313.15 K	333.15 K	353.15 K
$w_{TEA} = 0.0992$								
				$w_{TEA} = 0.2000$				
0.10	1.429	0.909	0.612		2.038	1.203	0.808	0.581
5.0	1.459	0.894	0.611		2.036	1.208	0.808	0.583
10.0	1.455	0.896	0.615		2.035	1.210	0.813	0.588
20.0	1.450	0.897	0.618		2.042	1.220	0.820	0.594
30.0	1.446	0.899	0.622		2.046	1.228	0.828	0.601
$w_{TEA} = 0.2991$								
				$w_{TEA} = 0.4000$				
0.10	3.208	1.786	1.147	0.805	5.317	2.788	1.670	1.124
5.0	3.213	1.797	1.155	0.799	5.311	2.794	1.680	1.125
10.0	3.229	1.808	1.164	0.805	5.331	2.797	1.698	1.136
20.0	3.234	1.832	1.178	0.814	5.417	2.852	1.720	1.154
30.0	3.245	1.846	1.189	0.827	5.500	2.889	1.748	1.174
$w_{MDEA} = 0.1000$								
				$w_{MDEA} = 0.2000$				
0.10	1.476	0.912	0.624		2.350	1.345	0.872	0.617
5.0	1.475	0.914	0.627		2.353	1.347	0.876	0.620
10.0	1.475	0.915	0.630		2.357	1.349	0.881	0.625
20.0	1.471	0.920	0.634		2.364	1.358	0.890	0.633
30.0	1.472	0.923	0.638		2.372	1.367	0.898	0.640
$w_{MDEA} = 0.3000$								
				$w_{MDEA} = 0.4000$				
0.10	3.999	2.095	1.271	0.854		3.238	1.843	1.181
5.0	4.018	2.106	1.278	0.862		3.270	1.861	1.193
10.0	4.038	2.118	1.286	0.869		3.302	1.880	1.204
20.0	4.077	2.144	1.302	0.881		3.365	1.921	1.229
30.0	4.114	2.168	1.316	0.894		3.428	1.956	1.253
$w_{DMAE} = 0.1005$								
				$w_{DMAE} = 0.2020$				
0.10	1.559	0.940	0.634	0.462	2.533	1.368	0.873	0.606
5.0	1.564	0.942	0.634	0.464	2.547	1.374	0.877	0.606
10.0	1.564	0.944	0.637	0.467	2.557	1.382	0.886	0.614
20.0	1.562	0.948	0.643	0.472	2.574	1.395	0.897	0.623
30.0	1.564	0.953	0.648	0.477	2.589	1.412	0.906	0.634
$w_{DMAE} = 0.3005$								
0.10	4.211	2.042	1.217	0.806				
5.0	4.223	2.063	1.223	0.812				
10.0	4.258	2.084	1.239	0.821				
20.0	4.330	2.121	1.260	0.841				
30.0	4.405	2.161	1.283	0.856				

Table 4. Densities for amine + water mixtures [2,3].

ρ , kg/m ³								
P , MPa	293.15 K	313.15 K	333.15 K	353.15 K	293.15 K	313.15 K	333.15 K	353.15 K
$w_{TEA} = 0.0992$								
				$w_{TEA} = 0.2000$				
0.1	1013.3	1006.9	997.2	985.7	1029.5	1021.9	1011.6	999.5
0.5	1013.5	1007.0	997.5	985.7	1029.5	1022.1	1011.8	999.6
1	1013.7	1007.2	997.7	985.9	1029.7	1022.3	1012	999.8
2	1014.2	1007.6	998.1	986.4	1030.2	1022.7	1012.4	1000.1
5	1015.5	1008.9	999.3	987.7	1031.4	1023.9	1013.6	1001.5
10	1017.6	1010.9	1001.4	989.9	1033.4	1025.9	1015.7	1003.7

Table 4. (cont.) Densities for amine + water mixtures [2,3].

		ρ , kg/m ³							
		293.15 K	313.15 K	333.15 K	353.15 K	293.15 K	313.15 K	333.15 K	353.15 K
<i>P</i> , MPa		<i>W</i> _{TEA} = 0.0992				<i>W</i> _{TEA} = 0.2000			
15		1019.6	1013.0	1003.5	992.1	1035.4	1027.8	1017.7	1005.8
20		1021.8	1015.0	1005.5	994.1	1037.4	1029.7	1019.7	1007.8
30		1026.0	1019.1	1009.6	998.2	1041.4	1033.7	1023.6	1011.9
		<i>W</i> _{TEA} = 0.2991				<i>W</i> _{TEA} = 0.4000			
0.1		1046.1	1037.4	1026.3	1013.6	1065.2	1055.1	1043.1	1029.7
0.5		1046.2	1037.5	1026.5	1013.7	1065.3	1055.3	1043.3	1029.8
1		1046.4	1037.7	1026.7	1013.9	1065.4	1055.4	1043.5	1030
2		1046.8	1038.1	1027.2	1014.3	1065.8	1055.8	1043.9	1030.4
5		1047.9	1039.3	1028.3	1015.6	1066.9	1056.9	1045.1	1031.7
10		1049.8	1041.2	1030.4	1017.8	1068.7	1058.8	1047.1	1033.9
15		1051.7	1043.1	1032.4	1019.9	1070.5	1060.6	1049	1035.8
20		1053.7	1045	1034.3	1021.9	1072.3	1062.4	1050.9	1037.9
30		1057.4	1048.8	1038.2	1025.9	1075.8	1066	1054.7	1041.9
		<i>W</i> _{MDEA} = 0.1000				<i>W</i> _{MDEA} = 0.2002			
0.1		1007.0	1000.2	990.5	978.6	1016.5	1008.5	997.8	985.3
0.5		1007.2	1000.4	990.6	978.7	1016.6	1008.6	998.0	985.3
1		1007.4	1000.6	990.8	978.9	1016.8	1008.8	998.2	985.5
2		1007.8	1001.0	991.3	979.3	1017.2	1009.2	998.6	985.9
5		1009.0	1002.2	992.5	980.6	1018.4	1010.4	999.8	987.2
10		1011.1	1004.3	994.6	982.8	1020.3	1012.3	1001.8	989.4
15		1013.2	1006.3	996.6	984.9	1022.2	1014.2	1003.8	991.5
20		1015.3	1008.2	998.6	987.0	1024.2	1016.1	1005.7	993.5
30		1019.4	1012.3	1002.6	991.2	1028.0	1019.9	1009.7	997.6
		<i>W</i> _{MDEA} = 0.3000				<i>W</i> _{MDEA} = 0.4000			
0.1		1026.7	1017.2	1005.4	992.0	1036.6	1025.5	1012.4	998.1
0.5		1026.9	1017.4	1005.6	992.0	1036.8	1025.6	1012.7	998.2
1		1027.1	1017.5	1005.7	992.2	1036.9	1025.8	1012.8	998.4
2		1027.4	1017.9	1006.2	992.7	1037.3	1026.2	1013.2	998.8
5		1028.6	1019.1	1007.3	993.9	1038.3	1027.3	1014.4	1000.1
10		1030.4	1020.9	1009.3	996.1	1040.1	1029.2	1016.4	1002.3
15		1032.2	1022.8	1011.3	998.2	1041.9	1031.0	1018.4	1004.4
20		1034.1	1024.6	1013.2	1000.3	1043.6	1032.8	1020.3	1006.5
30		1037.7	1028.4	1017.0	1004.3	1047.1	1036.3	1024.1	1010.5
		<i>W</i> _{DMAE} = 0.1005				<i>W</i> _{DMAE} = 0.2020			
0.1		994.5	987.4	977.4	965.2	992.6	983.2	971.5	958.1
0.5		994.7	987.6	977.6	965.3	992.7	983.4	971.8	958.1
1		994.8	987.8	977.8	965.6	992.9	983.6	972.0	958.4
2		995.3	988.3	978.2	966.0	993.3	984.0	972.4	958.8
5		996.5	989.5	979.5	967.3	994.4	985.2	973.7	960.1
10		998.5	991.5	981.5	969.5	996.3	987.2	975.7	962.4
15		1000.5	993.4	983.6	971.6	998.2	989.1	977.7	964.5
20		1002.6	995.4	985.6	973.8	1000.0	990.9	979.7	966.7
30		1006.6	999.4	989.7	978.0	1003.7	994.8	983.7	971.0

Table 4. (cont.) Densities for amine + water mixtures [2,3].

P, MPa	ρ , kg/m ³							
	293.15 K	313.15 K	333.15 K	353.15 K	293.15 K	313.15 K	333.15 K	353.15 K
	$w_{\text{DMAE}} = 0.3005$				$w_{\text{DMAE}} = 0.3995$			
0.1	990.6	978.8	965.2	950.2	986.6	972.7	957.4	941.1
0.5	990.7	979.0	965.4	950.3	986.7	972.9	957.6	941.2
1	990.9	979.2	965.6	950.6	986.9	973.1	957.9	941.4
2	991.3	979.6	966.1	951.0	987.3	973.5	958.3	941.9
5	992.4	980.8	967.3	952.4	988.4	974.7	959.6	943.3
10	994.2	982.7	969.5	954.7	990.3	976.7	961.8	945.8
15	996.0	984.6	971.5	956.9	992.1	978.6	963.9	948.1
20	997.8	986.5	973.5	959.1	994.0	980.6	966.0	950.5
30	1001.4	990.3	977.5	963.4	997.5	984.4	970.2	954.9

To better illustrate the comparison in the behaviour of the mixtures under study, some experimental results are presented graphically. Figure 1 presents the density as a function of pressure at different temperatures for the aqueous solutions of MDEA, DMAE and TEA at mass fractions of 0.2 and 0.4 as an example.

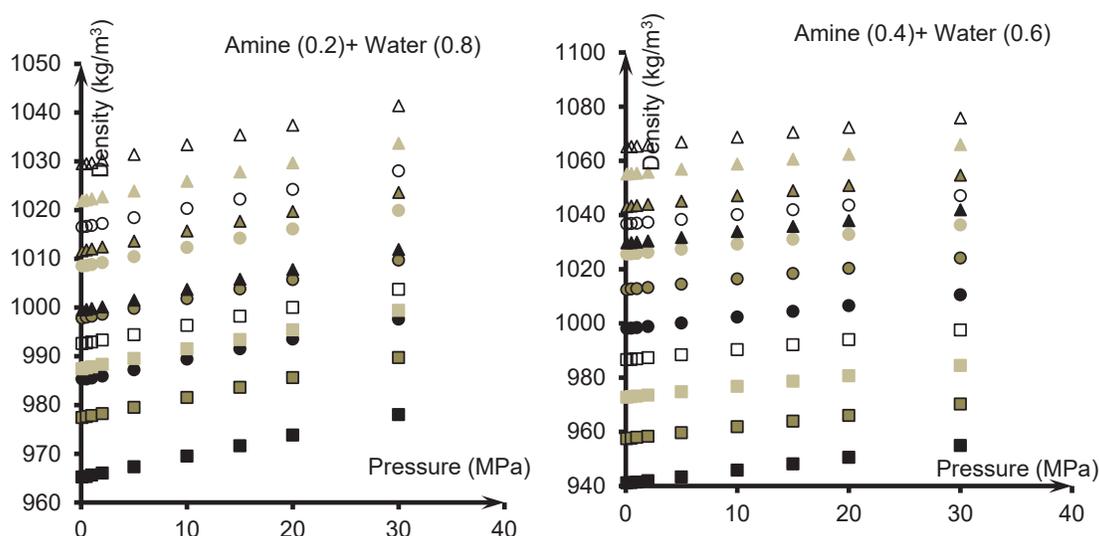


Figure 1. Densities of the amine + water mixtures, TEA (triangle), MDEA (circle) and DMAE (square), as a function of pressure at different temperatures: (empty symbol) 293.15 K, (clear grey) 313.15 K, (dark grey) 333.15 K and (black) 353.15 K.

As can be seen in Figure 1, whether the aqueous solutions of amines are compared at the same conditions of temperature, pressure and compositions, densities follow the following sequence $\rho(\text{TEA}) > \rho(\text{MDEA}) > \rho(\text{DMAE})$ which is the same as the pure amines. TEA and MDEA have densities higher than water whereas DMAE density is lower than water, therefore, when the mixture is enriched in amine the density is enhanced for TEA and MDEA solutions and is decreased for DMAE mixtures. When the mass fraction of the amine is changed from 0.1 to 0.4, the increase of density ranges from 1.9% up to 2.9% for MDEA solutions and from 4.4% up to 5.1% for TEA solutions, the maximum effect is obtained at 293.15 K. In the case of DMAE solutions, the decrease of density varies from 0.8% up to 2.5%, and the maximum decrease is found at 353.15 K.

Concerning the effect of pressure, the density increases lineally with pressure, in the range of this study; this increment varies between 1% and 1.5% when the pressure is changed from 0.1 MPa to 30 MPa, being similar, regardless the amine or its amount. This effect is well quantified since the uncertainty in density is less than 0.1%.

On the other hand, density decreases with increasing temperature as expected. When temperature is increased from 293.15 K to 353.15 K, the density for the mixtures under study decreases between 2.7% up to

4.5%. In this case, a slightly different behaviour between the amines is observed. The density of TEA mixtures decreases between 2.7% up to 3.3% whereas the decrease ranges from 3% up to 3.6% for MDEA solutions and from 3.4% up to 4.5% for DMAE solutions. For the three amines, the highest effect is observed for the mixture of the highest amine content ($w_{\text{amine}} = 0.4$).

Results for viscosity are illustrated in Figure 2 in a similar way than for density. Viscosity is presented as a function of pressure at different isotherms for two mixtures of amine mass fraction of 0.2 and 0.4. It should be clarified that isotherm at 293.15 K for the system {MDEA (0.4) + water (0.6)} was not measured.

If the viscosities are compared for the different amine solutions at the same conditions (p , T , and w), TEA solutions are less viscous than MDEA solutions in the whole ranges of studied, and the same is true in comparison to DMAE solutions except at $w_{\text{amine}} = 0.4$ and $T = 353.15$ K; at these conditions, viscosity of DMAE mixture is less than TEA mixture. Moreover, the comparison of TEA and DMAE solutions at $w_{\text{amine}} = 0.4$ and $T = 333.15$ K, indicates that viscosity of DMAE mixture is less than TEA up to 10 MPa and above 15 MPa TEA solutions are less viscous but the differences in viscosity at this isotherm are below the uncertainty of the measurements.

The comparison between MDEA and DMAE solutions in terms of viscosity, let conclude that viscosity of DMAE solutions is higher than MDEA solutions for $w_{\text{amine}} = 0.1$ and 0.2 at $T = 293.15$ K, 313.15 K and 333.15 K, and $w_{\text{amine}} = 0.3$ at $T = 293.15$ K, and the whole pressure range (0.1 MPa to 30 MPa). On the contrary, viscosity of MDEA solutions is higher than DMAE solutions for $w_{\text{amine}} = 0.2$ and $T = 353.15$ K; $w_{\text{amine}} = 0.3$ and 0.4 and $T = 313.15$ K, 333.15 K and 353.15 K; and the whole pressure range (0.1 MPa to 30 MPa).

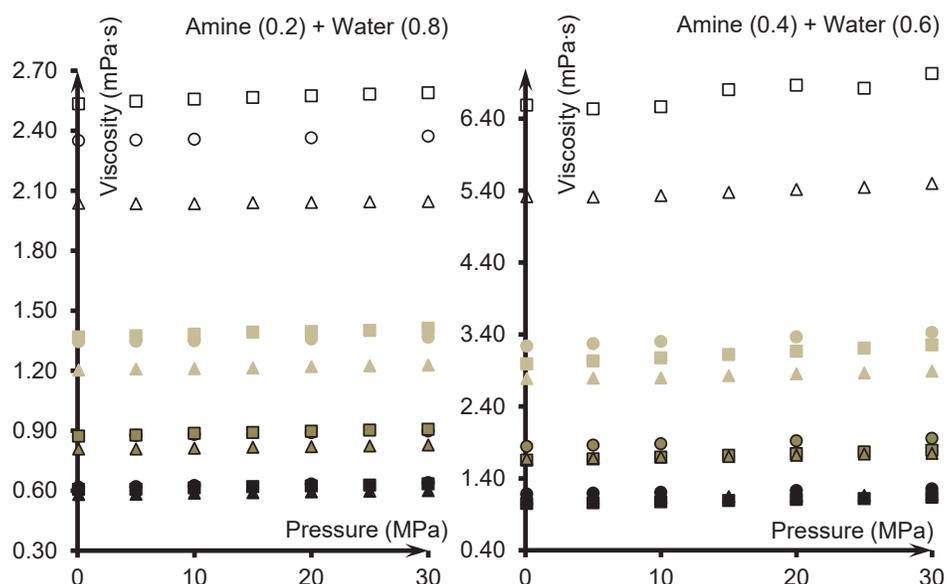


Figure 2. Viscosities of the amine + water mixtures, TEA (triangle), MDEA (circle) and DMAE (square), as a function of pressure at different temperatures: (empty symbol) 293.15 K, (clear grey) 313.15 K, (dark grey) 333.15 K and (black) 353.15 K.

If we compare the effect on viscosity of increasing the amine composition from 0.1 to 0.4, the result is a remarkable increase: from 145% (at 353.15 K and 0.1 MPa) up to 280% (293.15 K and 30 MPa) for TEA, from 195% (at 333.15 K and 0.1 MPa) up to 271% (313.15 K and 30 MPa) for DMAE and, from 127% (at 353.15 K and 0.1 MPa) up to 349% (293.15 K and 30 MPa) for MDEA.

Analysing the effect of increase pressure from 0.1 MPa up to 30 MPa in the viscosity, the results are as follows: There is an increase in viscosity whose value depends on the amine and its quantity in such a way that the highest increased is observed for $w_{\text{amine}} = 0.4$. For the mixtures with this composition, the increase of viscosity ranges from 3.4% to 4.6% for TEA, 5.9% to 6.1% for MDEA and 6.7% up to 8.8% for DMAE, whereas the increase ranges from 1.2% to 3.6% for TEA, 2.9% to 4.7% for MDEA and 4.6% up to 6.2% for DMAE, for the $w_{\text{amine}} = 0.3$ mixtures. In contrast with the mixtures with $w_{\text{amine}} = 0.1$, whose increments in viscosity are between -1.1% up to 3.2%, being these values within the uncertainty of the measurements.

As clearly shown in Figure 2, the higher the temperature, the lower the viscosity, being the average decrease, when temperature is increased from 293.15 K up to 353.15 K, between 68.5% and 83.8% for $w_{\text{TEA}} = 0.1$ and

$w_{DMAE} = 0.4$, respectively. Moreover, the effect is greater for solutions richer in amine, for example the average decrease is 69.9 % for $w_{DMAE} = 0.1$ and 78.7% for $w_{TEA} = 0.4$.

Finally, it can be concluded that the viscosity of DMAE solutions is the most sensitive to pressure and temperature changes. For example, the viscosity varies, at $T=353.15$ K, from 1.050 mPa/s at $p=0.1$ MPa to 1.135 mPa/s at $p= 30$ MPa, and, at $T=293.15$ K, from 6.587 mPa/s at $p=0.1$ MPa to 7.027 mPa/s at $p= 30$ MPa, for the $w_{DMAE} = 0.4$ mixture.

The last comparison refers to the isobaric heat capacity that is shown in Figure 3, where this property is represented for the three amines at different conditions.

At the same conditions of temperature, pressure and composition, the isobaric heat capacity of the amine solutions studied is ordered as follows: c_p (DMAE) > c_p (MDEA) > c_p (TEA) which is the opposite to the behaviour of density and different from viscosity, as well.

When the effect of increasing pressure from 0.1 MPa to 25 MPa is quantified, the general trend is a slight decrease which is within the uncertainty of the measurements (1%) except for the mixtures $w_{DMAE} = 0.3$, $w_{MDEA} = 0.3$; and $w_{TEA} = 0.4$. The average decrement of isobaric heat capacity is 1.8%, 2.2% and 8.2%, respectively. This remarkable effect for the $w_{TEA} = 0.4$ solution is clearly shown in Figure 3.

In relation to the variation of the heat capacity with the temperature, it should be noted that for mixtures of composition 0.1, a minimum is observed at 313.15 K for TEA and at 333.15 K for MDEA and DMEA; for the other compositions, the heat capacity increases with increasing temperatures.

In order to discuss the effect of temperature on the isobaric heat capacity values, this is computed when the temperature is changed from 313.15 K to 353.15 K: The heat capacity of TEA aqueous solutions increases an average of 2.2% ($w_{TEA} = 0.2$), 4.1% ($w_{TEA} = 0.3$) and 2.8% ($w_{TEA} = 0.4$); the effect for MDEA solutions is an average increment of 3.1% ($w_{MDEA} = 0.2$), 5% ($w_{MDEA} = 0.3$) and 4.5% ($w_{MDEA} = 0.4$); and for DMAE mixtures is 3.2% ($w_{DMAE} = 0.2$), 5% ($w_{DMAE} = 0.3$), and 4% ($w_{DMAE} = 0.4$).

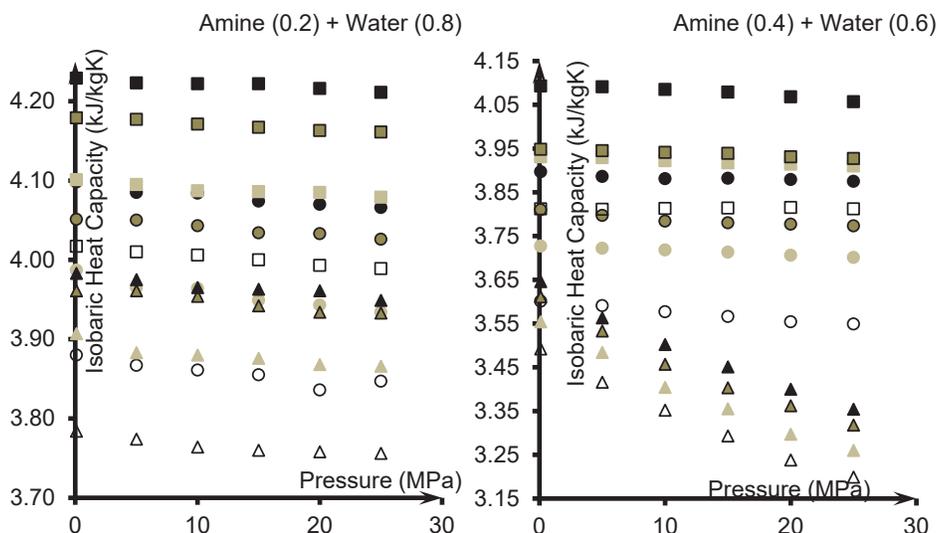


Figure 3. Isobaric heat capacities of the amine + water mixtures, TEA (triangle), MDEA (circle) and DMAE (square), as a function of pressure at different temperatures: (empty symbol) 293.15 K, (clear grey) 313.15 K, (dark grey) 333.15 K and (black) 353.15 K.

Therefore, no significant differences are observed for the three amines, at a given composition, in relation to the effect of temperature, however, it is the amount of amine that matters. If the mass fraction of amine is increased from 0.1 to 0.4, the heat capacity of the mixtures decreases between 4% and 9% for DMAE solutions, 6% and 9% for MDEA solutions and 10% and 20% for TEA solutions.

Besides, the experimental data are fitted to semiempirical equations. The modified Tammann-Tait equation (Eq. 1) is used for density for each composition:

$$\rho(T, p) = (A_0 + A_1T + A_2T^2)/1 - C \ln \left(\frac{B_0 + B_1T + B_2T^2 + p}{B_0 + B_1T + B_2T^2 + 0.1MPa} \right) \quad (1)$$

On the other hand, viscosity data are correlated using the modified VFT (Vogel-Fulcher-Tammann) model, Eq. (2), for each composition, that was used by other authors [11]:

$$\eta(T, p) = \exp [a + bp + (c + dp + ep^2)/(T - f)] \quad (2)$$

Regarding isobaric heat capacities, the following empirical correlation is used [7]:

$$c_p(p, T) = a_0 + a_1p + a_2T + a_3p^2 + a_4T^2 + a_5pT \quad (3)$$

The fitting parameters are reported in [2,3,7], and the standard deviations obtained for the three thermophysical properties under study are summarized in Table 5.

Table 5. Results of the standard deviations σ obtained by the different fitting equation of the experimental data: density Eq. (1), viscosity Eq. (2) and isobaric heat capacity Eq. (3).

MDEA (1) + H ₂ O (2)	$w_1 = 0.1$	$w_1 = 0.2$	$w_1 = 0.3$	$w_1 = 0.4$
Density, Eq. (1): σ (kg/m ³)	0.029	0.018	0.0046	0.026
Viscosity, Eq. (2): σ (mPa·s)	0.0042	0.0035	0.017	0.026
Heat capacity, Eq. (3): σ (kJ/kgK)	0.023	0.006	0.008	0.013
TEA (1) + H ₂ O (2)	$w_1 = 0.1$	$w_1 = 0.2$	$w_1 = 0.3$	$w_1 = 0.4$
Density, Eq. (1): σ (kg/m ³)	0.164	0.146	0.130	0.0915
Viscosity, Eq. (2): σ (mPa·s)	0.0022	0.012	0.015	0.057
Heat capacity, Eq. (3): σ (kJ/kgK)	0.005	0.004	0.002	0.005
DMAE (1) + H ₂ O (2)	$w_1 = 0.1$	$w_1 = 0.2$	$w_1 = 0.3$	$w_1 = 0.4$
Density, Eq. (1): σ (kg/m ³)	0.162	0.119	0.0849	0.0881
Viscosity, Eq. (2): σ (mPa·s)	0.0080	0.0122	0.0213	0.0190
Heat capacity, Eq. (3): σ (kJ/kgK)	0.029	0.004	0.005	0.027

Table 5 shows that the standard deviations obtained are always lower than the expanded uncertainty of the experimental measurements: 0.7 kg/m³ for density; 3% for viscosity or 1% for heat capacity, proving the goodness of these equations.

4. Conclusions

Experimental thermophysical properties, for amine aqueous solutions of MDEA, TEA and DMAE (at amine mass fractions of 10%, 20%, 30% and 40%) are reported and the behaviour is compared. Whether the aqueous solutions of amines are compared at the same conditions of temperature, pressure and compositions, the density of the mixtures follows the same behaviour than the pure amines: $\rho(\text{TEA}) > \rho(\text{MDEA}) > \rho(\text{DMAE})$ which is the same as the pure amines and wide ranges of temperature and pressure. Densities increase for richer amine solutions for MDEA and TEA but decrease for DMAE. In contrast, the heat capacity of the mixtures varies in a different order: $c_p(\text{DMAE}) > c_p(\text{MDEA}) > c_p(\text{TEA})$, and the heat capacity decreases for richer amine solutions for the three amines being TEA more sensitive. Finally, viscosity shows different tendencies and some differences observed are within the uncertainty of the measurements, however, viscosities of these mixtures increase with increasing amine weight fraction.

Finally, it should be noted the importance of having accurate data of these properties, since the results of these calculations will be as accurate as the properties involved in them. These measurements enrich data bases and allow to check the models which are used in the software for designing and optimizing industrial plants.

Acknowledgments

This work was supported by the Regional Government of Castilla y León and the EU-FEDER programs (VA280P18 and CLU-2019-04) and by European Union (EURAMET), Project Number: 21GRD06.

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