# Heat capacities of different amine aqueous solutions at pressures up to 25 MPa for $CO_2$ capture

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## ABSTRACT

A high-pressure flow calorimeter is used to determine isobaric heat capacities for aqueous solutions of some amines such as MEA, DEA TEA, DMAE, MDEA, PZ from $T$ = (293.15 to 353.15) K and up to 25 MPa. The experimental device can measure heat capacities with an estimated total uncertainty better than 1% for a coverage factor $k$ = 2. The isobaric heat capacity values are analysed in conjunction with their temperature and pressure dependencies. Furthermore, empirical equations are proposed to fit isobaric heat capacities as functions of temperature and pressure for given conditions, for this kind of mixtures, obtaining standard deviations within the uncertainty of the measurements. Finally, DMAE shows the highest value of heat capacity and TEA the lowest value, when they are compared at the same conditions of temperature, pressure and composition.

## 1. Introduction

The use of fossil fuels during the last century led to an increase in the concentration of $CO_2$ in the atmosphere. Carbon dioxide ($CO_2$) is primarily considered a greenhouse gas, causing environmental problems, especially global warming, and climate change. This gas is emitted by many critical industries, particularly the natural gas processing, coal gasification, synthetic, and oil refinery industries [1]. Concern about the increase in $CO_2$ in the atmosphere and its impact on the global climate resulted in an increase in efforts to develop technologies that allow the capture of $CO_2$ that is released into the atmosphere as a result of industrial processes [2]. Alkanolamine solutions are compounds used in the natural gas industry, oil refineries, oil chemical plants, and synthetic ammonia plants for the removal of acidic components such as $CO_2$ and $H_2S$ from gas streams. Among the most used are monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), N-methyldiethanolamine (MDEA), dimethylaminoethanol (DMAE), and piperazine (PZ) [3]. Although there is an important development in the absorption technique, it is necessary to address certain problems such as the associated heat of regeneration due to $CO_2$ emissions, corrosion, solvent degradation, and the high cost of absorption/stripping columns. The knowledge of the heat capacity allows the calculation of changes in enthalpy, entropy and Gibbs energy, needed in energy and entropy balances. In addition, these data are key data for the design of absorbers, regenerators, condensers and heat exchangers [4].

Density and viscosity of different aqueous solutions of alkanolamines were already measured, at wide ranges of temperature and pressure, and reported in previous papers: MEA and MDEA [5], DEA, TEA and DMAE [6], and PZ [7] and the ternary mixtures (PZ + DMAE + $H_2O$) [7] and (MDEA + DEA + $H_2O$) [8]. The main aim of this work is to measure isobaric heat capacity, for six aqueous solutions of these alkanolamines. Measuring heat capacities is relevant since the key information of the behaviour of these mixtures is completed. Accurate values of heat capacities are important not only from a thermodynamic point of view, as said above to calculate other thermodynamic properties, but, from a molecular point of view, giving information on the effects of interactions. Additionally, isobaric heat capacity data at different pressures can be used to validate equations of state [9,10].

There are in the literature a limited number of papers which contain heat capacity data of amine aqueous solutions, and all of them are at $p$ = 0.1 MPa. The most studied amines are MEA [11–16] and MDEA [12–13,17–19], the temperature range of these studies is extended from 283.15 K to 353.15 K for MEA and 278.15 K to 353.15 K for MDEA. The first measurements of heat

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capacities of MEA are reported by Pagé et al. [11] using a flow microcalorimeter. Later, Weiland et al [12] reported measurements for MEA, DEA and MDEA aqueous solutions and $CO_2$ loaded. Data for aqueous solutions of MEA, DEA and TEA are reported by Chiu et al. [13], however, their data are at mass fractions of amine higher than 0.4. This paper is the only one we have found that contains data of TEA solutions. In the case of DMAE solutions, we have only found the paper of Mundhwa et al. [20]; they measured heat capacities of different amines using a commercial flow calorimeter at temperatures between 303.15 and 353.15 K and DMAE mass fraction from 0.35 up to 0.97. Finally, two works [16,21] deal with piperazine solutions.

The present study aims to contribute to the availability of new accurate data of heat capacities. The measurements are carried out at the amine mass fraction from 0.1 to 0.4, which is the range usually used for $CO_2$ absorption, the temperature range from 293.15 to 353.15 K (20 K step) and pressures up to 25 MPa. Finally, the experimental heat capacities will be correlated as a function of temperature and pressure using empirical equations.

## 2. Experimental

### 2.1. Materials

The sources and chemical purities of the compounds used in this work are detailed in Table 1; purities are the specified by the supplier, and no further purification was carried out. The liquid mixtures were prepared by weighting with an expanded uncertainty ($k = 2$) in mass fraction $<2 \cdot 10^{-4}$.

### 2.2. Apparatus and procedure

The isobaric heat capacity is studied using a flow calorimeter developed by Segovia et al. [9]. The technique is based on the simultaneous heating and cooling of the calorimetric cell to maintain a fixed difference of temperature of $\Delta T = 0.5$ K, between the inlet and outlet temperatures of the circulating fluid, at a constant flow rate. The heat capacity is calculated by determining the net power exchanged [22].

The fluid is driven into the system by a positive displacement isocratic pump (Agilent, 1100 series), which generates a constant and programmable flow to the measuring cell. The flow rate, that was verified using water, is measured with an expanded relative uncertainty of 0.15%. The pump has a resistance thermometer associated with an Agilent 34980A thermometer, which allows to determine the temperature of the liquid in the pump and the mass and molar flow rates are evaluated using volumetric readings. Measurements are undertaken at five different flows between 1.5 and 2 ml·min$^{-1}$ based on a previous study carried out by Vega-Maza [23]. The cell operates through the joint action of a constant cooling power provided by a thermoelectric cooler element type

Peltier fed with a DC source (Agilent E3640A) which is located at the top of the cell to establish a temperature gradient in the copper block minimizing heat losses throughout the cell and avoiding the need of insulating the coil in the cell. Variable heating power is provided by an electrical resistance located in the outlet zone of the cell powered by a function generator Agilent 33220A. The cell is immersed in a thermostatic bath, model Hart Scientific 7040. The sensors used to register the inlet and outlet temperatures are calibrated by means of the calibrated PRT-25 assuring a temperature expanded uncertainty ($k = 2$) of 20 mK.

The cell pressure is controlled by a back pressure valve, model Mity-Mite 91, located at the outlet of the cell. The equipment is pressurized automatically by means of a variable volume driven by a stepper motor and the pressure is measured by a Druck DPI 145 with a relative expanded uncertainty ($k = 2$) of 0.0005.

The experimental procedure remains unchanged and is thoroughly described in [9]. The measurement starts with a non-flow (baseline) experiment: the cooling power is set and held constant, and the power input to maintain the gradient temperature is recorded, $\dot{Q}_{base}$, to assess the energy losses in the system. Then, a run is performed with one flow and, once again, the new power input is recorded, $\dot{Q}_{measure}$, and, later, a second baseline is determined. The value of the net power $\dot{Q}_{net}$ is directly related to the isobaric heat capacity by the following equation (see details in Refs [9,22,24]):

$$c_p = \frac{\dot{Q}_{net}}{\dot{m} \cdot \Delta T} = \frac{\dot{Q}_{net}}{\dot{V} \cdot \rho \cdot \Delta T} = \frac{a + b(\dot{Q}_{base} - \dot{Q}_{measure})}{\dot{V} \cdot \rho \cdot \Delta T} \tag{1}$$

where the mass flow ($\dot{m}$) is calculated from the volumetric flow rate ($\dot{V}$) established in the pump and the density ($\rho$) of the fluid at the temperature $T$ and the pressure, $p$, measured experimentally, $\Delta T$ is the temperature difference established between the inlet and outlet of the fluid and $a$ and $b$ are obtained by electric calibration of the device as explained in [9].

The uncertainty calculation was carried out following the procedure described by Segovia et al. [9] and according to the document JCGM 100:2008 (Evaluation of measurement data-Guide to the expression of uncertainty in measurement) [25]. The estimated relative expanded uncertainty ($k = 2$) in the heat capacity obtained for this work is <1%. The details of the estimation of the uncertainty associated with the measurement of heat capacity are reported in Table 2.

### 2.3. Technique validation.

Before measuring the amine mixtures, the calorimetric technique was verified by measuring the heat capacity of water at temperatures: 293.15 K, 313.15 K, 333.15 K and 353.15 K, in the pressure range from 0.1 to 25 MPa. The experimental data obtained were compared with those provided by the IAPWS (The Interna-

**Table 1**
Material description.

| Compound | Source | CAS number | Mass fraction purity[a] | Mass water content / % | Purification method |
|---|---|---|---|---|---|
| MEA | Sigma-Aldrich | 141-43-5 | ≥0.998 | <0.14 | None |
| DEA | Sigma-Aldrich | 11-42-2 | ≥0.995 | ≤0.002[b] | None |
| TEA | Sigma-Aldrich | 102-71-6 | ≥0.99 | ≤0.006[b] | None |
| MDEA | Aldrich Chemistry | 105-59-9 | ≥0.99 | ≤0.1 | None |
| DMAE | Sigma-Aldrich | 108-01-0 | ≥0.995 | <0.01[b] | None |
| PZ | Sigma-Aldrich | 110-85-0 | ≥0.99 | <0.1[b] | None |
| Water | Sigma-Aldrich | 7732-11-5 | conductivity ≤2·10$^{-6}$ ohm$^{-1}$·cm$^{-1}$ | | None |

[a] As stated by the supplier by gas chromatography.
[b] Measured by Karl Fisher titration (Mitsubishi CA-200).

**Table 2**

Uncertainty budget for the isobaric heat capacity using JCGM [25].

|  | Units | Estimate | Sensitivity coefficient | Divisor | $u(x)$ | $u(x)^2$ |
|---|---|---|---|---|---|---|
| Repeatability $u(c_p)$ | kJ kg$^{-1}$·K$^{-1}$ | 0.010 | 1 | 1 | 0.0102 | $1.1 \cdot 10^{-4}$ |
| Resolution $u(\dot{Q})$ | W | $4 \cdot 10^{-6}$ | 73.50 | $2\sqrt{3}$ | $8.5 \cdot 10^{-5}$ | $7.2 \cdot 10^{-9}$ |
| Repeatability $u(\dot{Q})$ | W | $2.0 \cdot 10^{-7}$ | 73.50 | 1 | $1.5 \cdot 10^{-5}$ | $2.1 \cdot 10^{-10}$ |
| Non-linearity $u(\dot{Q})$ | W | $1.0 \cdot 10^{-5}$ | 73.50 | 1 | $7.35 \cdot 10^{-4}$ | $5.4 \cdot 10^{-7}$ |
| Accuracy $u(\dot{V})$ | ml s$^{-1}$ | $2.5 \cdot 10^{-5}$ | 140.40 | 2 | $1.76 \cdot 10^{-3}$ | $3.1 \cdot 10^{-6}$ |
| Resolution $u(\dot{V})$ | ml s$^{-1}$ | $1.7 \cdot 10^{-5}$ | 140.40 | $2\sqrt{3}$ | $6.8 \cdot 10^{-4}$ | $4.5 \cdot 10^{-7}$ |
| Resolution $u(\Delta T)$ | K | $1 \cdot 10^{-3}$ | 7.88 | $2\sqrt{3}$ | $2.27 \cdot 10^{-3}$ | $5.2 \cdot 10^{-6}$ |
| Stability (inlet) $u(\Delta T)$ | K | $1 \cdot 10^{-3}$ | 7.88 | $\sqrt{3}$ | $4.55 \cdot 10^{-3}$ | $2.0 \cdot 10^{-5}$ |
| Stability (outlet) $u(\Delta T)$ | K | $1 \cdot 10^{-3}$ | 7.88 | $\sqrt{3}$ | $4.55 \cdot 10^{-3}$ | $2.0 \cdot 10^{-5}$ |
| $u(c_p)$ | kJ kg$^{-1}$·K$^{-1}$ |  |  |  |  | 0.012 |
|  |  |  |  | $U(c_p)$ | $(k = 2)$ | 0.025 |
|  |  |  |  | $(c_p = 3.787$ kJ kg$^{-1}$·K$^{-1}$) |  | 1% |
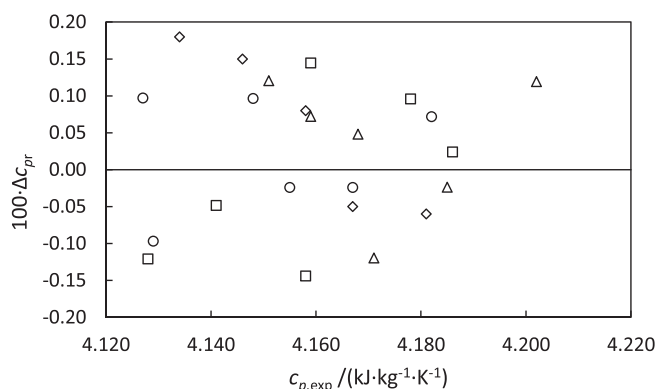


**Fig. 1.** Relative deviations between experimental heat capacities of water and the values of reference [26] ($\Delta c_{p,r} = (c_{p,\exp} - c_{p,\text{lit}})/c_{p,\text{lit}}$), as a function of the experimental values at isotherms: ($\diamond$) 293.15 K ($\circ$) 313.15 K, ($\square$) 333.15 K and ($\triangle$) 353.15 K.

tional Association for the Properties of Water and Steam) collected in the document published by Wagner and Pruss [26]. The heat capacities of water and the relative deviations with respect to the literature data [26] are shown in Fig. 1.

In addition, it is important to note that the uncertainty of the heat capacity collected in the IAPWS document [26] is 0.2%. Our experimental heat capacity data for water shows a maximum absolute relative deviation of 0.18%. Therefore, these deviations between the measured data and the literature data [26] are lower than the uncertainties of both our data and reference data at the temperature and pressure ranges used in this work, proving the correct operation of the calorimeter.

## 3. Results and discussion

Once the technique has been checked with water, the objective is the experimental determination of isobaric heat capacities of different amine aqueous solutions in a temperature range from 293.15 K to 353.15 K and pressure up to 25 MPa. Specifically, the isobaric heat capacities of twenty-one aqueous solutions of amines at four temperatures, six pressures and four amine weight fractions have been determined. The systems measured are aqueous solutions of monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), N-methyldiethanolamine (MDEA) and 2-dimethylaminoethanol (DMAE), at amine weight fractions of $w_{\text{amine}}$ = 0.1, 0.2, 0.3 and 0.4; in the case of piperazine (PZ), only the mixture $w_{\text{amine}}$ = 0.1 was determined. The experimental data for these systems are reported in Tables 3-8.

The analysis of the experimental isobaric heat capacities demonstrates that the solutions with DMAE show the highest val-

**Table 3**

Experimental isobaric heat capacities, $c_p$, of aqueous solutions of monoethanolamine {MEA (1) + H$_2$O (2)} at different temperatures ($T$), pressures ($p$) and amine weight fractions ($w_1$).[a]

| $c_p$ / (kJ·kg$^{-1}$·K$^{-1}$) |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
|  | $p$ / MPa |  |  |  |  |  |
| $T$ / K | 0.100 | 5.00 | 10.00 | 15.00 | 20.00 | 25.00 |
|  | MEA (1) + H$_2$O (2) $w_1$ = 0.1001 |  |  |  |  |  |
| 293.15 | 4.104 | 4.095 | 4.086 | 4.072 | 4.065 | 4.054 |
| 313.15 | 4.031 | 4.023 | 4.009 | 4.001 | 3.991 | 3.982 |
| 333.15 | 4.086 | 4.078 | 4.065 | 4.055 | 4.037 | 4.029 |
| 353.15 | 4.095 | 4.086 | 4.078 | 4.070 | 4.067 | 4.062 |
|  | MEA (1) + H$_2$O (2) $w_1$ = 0.2002 |  |  |  |  |  |
| 293.15 | 3.934 | 3.915 | 3.897 | 3.885 | 3.875 | 3.852 |
| 313.15 | 3.979 | 3.957 | 3.943 | 3.928 | 3.919 | 3.900 |
| 333.15 | 4.022 | 4.012 | 3.994 | 3.988 | 3.972 | 3.966 |
| 353.15 | 4.088 | 4.080 | 4.062 | 4.054 | 4.041 | 4.037 |
|  | MEA (1) + H$_2$O (2) $w_1$ = 0.2997 |  |  |  |  |  |
| 313.15 | 3.871 | 3.862 | 3.848 | 3.835 | 3.827 | 3.809 |
| 333.15 | 3.957 | 3.931 | 3.912 | 3.890 | 3.874 | 3.857 |
| 353.15 | 4.040 | 4.028 | 4.014 | 4.009 | 3.992 | 3.985 |
|  | MEA (1) + H$_2$O (2) $w_1$ = 0.4002 |  |  |  |  |  |
| 293.15 | 3.626 | 3.614 | 3.593 | 3.589 | 3.568 | 3.549 |
| 313.15 | 3.698 | 3.680 | 3.667 | 3.655 | 3.641 | 3.634 |
| 333.15 | 3.818 | 3.803 | 3.794 | 3.786 | 3.776 | 3.764 |
| 353.15 | 3.861 | 3.851 | 3.846 | 3.840 | 3.832 | 3.823 |

[a] Expanded uncertainties ($k$ = 2): $U_r(c_p)$ = 0.010; $U(T)$ = 0.02 K; $U_r(p)$ = 0.0005; $U(w)$ = 0.0002.

**Table 4**

Experimental isobaric heat capacities, $c_p$, of amine aqueous solutions of diethanolamine {DEA (1) + H$_2$O (2)} at different temperatures ($T$), pressures ($p$) and amine weight fractions ($w_1$).[a]

| $c_p$ / (kJ·kg$^{-1}$·K$^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|
| | $p$ / MPa | | | | | |
| $T$ / K | 0.100 | 5.00 | 10.00 | 15.00 | 20.00 | 25.00 |
| | DEA (1) + H$_2$O (2) $w_1$ = 0.1003 | | | | | |
| 293.15 | 4.078 | 4.068 | 4.059 | 4.046 | 4.035 | 4.027 |
| 313.15 | 4.037 | 4.025 | 4.018 | 4.007 | 4.001 | 3.989 |
| 333.15 | 4.104 | 4.098 | 4.087 | 4.081 | 4.075 | 4.065 |
| | DEA (1) + H$_2$O (2) $w_1$ = 0.2008 | | | | | |
| 293.15 | 3.842 | 3.836 | 3.824 | 3.818 | 3.809 | 3.798 |
| 313.15 | 3.924 | 3.917 | 3.907 | 3.900 | 3.898 | 3.891 |
| 333.15 | 4.003 | 3.997 | 3.982 | 3.971 | 3.962 | 3.955 |
| 353.15 | 4.061 | 4.053 | 4.041 | 4.028 | 4.021 | 4.009 |
| | DEA (1) + H$_2$O (2) $w_1$ = 0.3002 | | | | | |
| 313.15 | 3.844 | 3.837 | 3.829 | 3.822 | 3.813 | 3.799 |
| 333.15 | 3.910 | 3.906 | 3.894 | 3.882 | 3.875 | 3.862 |
| 353.15 | 3.941 | 3.931 | 3.924 | 3.916 | 3.904 | 3.900 |
| | DEA (1) + H$_2$O (2) $w_1$ = 0.4000 | | | | | |
| 293.15 | 3.633 | 3.614 | 3.601 | 3.592 | 3.578 | 3.578 |
| 313.15 | 3.676 | 3.657 | 3.640 | 3.631 | 3.618 | 3.602 |
| 333.15 | 3.744 | 3.731 | 3.720 | 3.703 | 3.681 | 3.660 |
| 353.15 | 3.824 | 3.808 | 3.789 | 3.767 | 3.752 | 3.725 |

[a] Expanded uncertainties ($k$ = 2): $U_r(c_p)$ = 0.010; $U(T)$ = 0.02 K; $U_r(p)$ = 0.0005; $U(w)$ = 0.0002.

**Table 5**

Experimental isobaric heat capacities, $c_p$, of amine aqueous solutions of triethanolamine {TEA (1) + H$_2$O (2)} at different temperatures ($T$), pressures ($p$) and amine weight fractions ($w_1$).[a]

| $c_p$ / (kJ·kg$^{-1}$·K$^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|
| | $p$ / MPa | | | | | |
| $T$ / K | 0.100 | 5.00 | 10.00 | 15.00 | 20.00 | 25.00 |
| | TEA (1) + H$_2$O (2) $w_1$ = 0.1001 | | | | | |
| 293.15 | 4.064 | 4.055 | 4.041 | 4.029 | 4.016 | 4.004 |
| 313.15 | 4.041 | 4.030 | 4.023 | 4.010 | 3.998 | 3.992 |
| 333.15 | 4.054 | 4.046 | 4.038 | 4.030 | 4.019 | 4.010 |
| 353.15 | 4.071 | 4.064 | 4.055 | 4.049 | 4.035 | 4.032 |
| | TEA (1) + H$_2$O (2) $w_1$ = 0.2000 | | | | | |
| 293.15 | 3.784 | 3.774 | 3.764 | 3.760 | 3.758 | 3.756 |
| 313.15 | 3.907 | 3.883 | 3.880 | 3.876 | 3.868 | 3.866 |
| 333.15 | 3.961 | 3.961 | 3.954 | 3.942 | 3.934 | 3.933 |
| 353.15 | 3.983 | 3.975 | 3.965 | 3.963 | 3.961 | 3.949 |
| | TEA (1) + H$_2$O (2) $w_1$ = 0.2991 | | | | | |
| 313.15 | 3.803 | 3.787 | 3.775 | 3.757 | 3.749 | 3.732 |
| 333.15 | 3.871 | 3.861 | 3.854 | 3.847 | 3.834 | 3.831 |
| 353.15 | 3.934 | 3.928 | 3.925 | 3.922 | 3.917 | 3.914 |
| | TEA (1) + H$_2$O (2) $w_1$ = 0.4000 | | | | | |
| 293.15 | 3.492 | 3.416 | 3.352 | 3.293 | 3.238 | 3.199 |
| 313.15 | 3.554 | 3.484 | 3.404 | 3.355 | 3.297 | 3.260 |
| 333.15 | 3.611 | 3.533 | 3.457 | 3.403 | 3.362 | 3.318 |
| 353.15 | 3.646 | 3.563 | 3.502 | 3.451 | 3.400 | 3.354 |

[a] Expanded uncertainties ($k$ = 2): $U_r(c_p)$ = 0.010; $U(T)$ = 0.02 K; $U_r(p)$ = 0.0005; $U(w)$ = 0.0002.

ues of $c_p$ when these are compared at the same composition, temperature and pressure conditions. In general, $c_p$(MEA) > $c_p$(DEA) > $c_p$(TEA) at the same conditions, in the cases that this behaviour is not observed, the differences are below the uncertainty of the measurements.

The isobaric heat capacity decreases with pressure, this effect, when the pressure is increased from 0.1 MPa to 25 MPa, ranges from 0.6% to 3.0% with an average of 1.2% for MDEA solutions, from 0.8% to 2.6% with an average of 1.4% for DEA solutions, from 0.0% to 2% with an average of 0.9% for DMAE solutions, from 0.8% to 2.5% with an average of 1.5% for MEA solutions, from 0.5% to 8.4% with an average of 3.0% for TEA solutions, and from 2.2% to 3.5% with an average of 3.0% for PZ solutions. It is worth noting, the reduction around 8% observed for the mixture ($w_{TEA}$ = 0.4) at all the isotherms.

As regards the effect of temperature, first of all, a minimum in $c_p$ is obtained for all solutions of $w_{amine}$ = 0.1 except for piperazine. This minimum occurs at 313.15 K for MEA; DEA and TEA and at 333.15 K for MDEA and DMAE. For the rest of compositions, the isobaric heat capacities increase with increasing temperature. In order to compare this effect, the increase of $c_p$ is quantified when temperature is increased from 313.15 K to 353.15 K, obtained the following average values for $w_{amine}$ = 0.2, 0.3 and 0.4, respectively: 3.1%, 4.4% and 4.9% for MEA solutions; 3.3%, 2.5% and 3.9% for DEA solutions; 2.2%, 4.1% and 2.8% for TEA solutions; 3.1%, 5.0% and 4.5% for MDEA solutions and 3.2%, 5.0% and 4.0% for DMAE solutions. In the case of piperazine solution, which was only measured at $w_{PZ}$ = 0.1, the average increase is 2.5%.

With the purpose of visualized the behaviour described above, the Figs. 2-4 depict the experimental isobaric heat capacities as a

**Table 6**

Experimental isobaric heat capacities, $c_p$, of amine aqueous solutions of N-methyldiethanolamine {MDEA (1) + $H_2O$ (2)} at different temperatures ($T$), pressures ($p$) and amine weight fractions ($w_1$).[a]

| $c_p$ / (kJ·kg$^{-1}$·K$^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|
| | $p$ / MPa | | | | | |
| $T$ / K | 0.100 | 5.00 | 10.00 | 15.00 | 20.00 | 25.00 |
| | MDEA (1) + $H_2O$ (2) $w_1$ = 0.1001 | | | | | |
| 293.15 | 4.065 | 4.060 | 4.050 | 4.049 | 4.046 | 4.041 |
| 313.15 | 4.126 | 4.113 | 4.108 | 4.094 | 4.090 | 4.077 |
| 333.15 | 4.096 | 4.080 | 4.077 | 4.069 | 4.068 | 4.065 |
| 353.15 | 4.179 | 4.169 | 4.157 | 4.144 | 4.137 | 4.127 |
| | MDEA (1) + $H_2O$ (2) $w_1$ = 0.2001 | | | | | |
| 293.15 | 3.880 | 3.867 | 3.861 | 3.855 | 3.836 | 3.847 |
| 313.15 | 3.987 | 3.965 | 3.964 | 3.949 | 3.943 | 3.934 |
| 333.15 | 4.051 | 4.050 | 4.043 | 4.034 | 4.033 | 4.026 |
| 353.15 | 4.098 | 4.085 | 4.084 | 4.074 | 4.070 | 4.066 |
| | MDEA (1) + $H_2O$ (2) $w_1$ = 0.2998 | | | | | |
| 313.15 | 3.890 | 3.857 | 3.836 | 3.814 | 3.782 | 3.775 |
| 333.15 | 3.965 | 3.946 | 3.930 | 3.920 | 3.908 | 3.900 |
| 353.15 | 4.057 | 4.040 | 4.028 | 4.010 | 4.000 | 3.977 |
| | MDEA (1) + $H_2O$ (2) $w_1$ = 0.4001 | | | | | |
| 293.15 | 3.601 | 3.591 | 3.577 | 3.566 | 3.554 | 3.549 |
| 313.15 | 3.727 | 3.722 | 3.718 | 3.713 | 3.706 | 3.701 |
| 333.15 | 3.810 | 3.797 | 3.784 | 3.780 | 3.777 | 3.773 |
| 353.15 | 3.897 | 3.886 | 3.881 | 3.882 | 3.879 | 3.875 |

[a] Expanded uncertainties ($k$ = 2): $U_r(c_p)$ = 0.010; $U(T)$ = 0.02 K; $U_r(p)$ = 0.0005; $U(w)$ = 0.0002.

**Table 7**

Experimental isobaric heat capacities, $c_p$, of amine aqueous solutions of 2-dimethylaminoethanol {DMAE (1) + $H_2O$ (2)} at different temperatures ($T$), pressures ($p$) and amine weight fractions ($w_1$).[a]

| $c_p$ / (kJ·kg$^{-1}$·K$^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|
| | $p$ / MPa | | | | | |
| $T$ / K | 0.100 | 5.00 | 10.00 | 15.00 | 20.00 | 25.00 |
| | DMAE (1) + $H_2O$ (2) $w_1$ = 0.1000 | | | | | |
| 293.15 | 4.187 | 4.180 | 4.168 | 4.161 | 4.152 | 4.143 |
| 313.15 | 4.228 | 4.218 | 4.209 | 4.202 | 4.192 | 4.184 |
| 333.15 | 4.172 | 4.166 | 4.155 | 4.150 | 4.140 | 4.131 |
| 353.15 | 4.253 | 4.244 | 4.234 | 4.227 | 4.220 | 4.214 |
| | DMAE (1) + $H_2O$ (2) $w_1$ = 0.2005 | | | | | |
| 293.15 | 4.017 | 4.010 | 4.006 | 4.000 | 3.993 | 3.989 |
| 313.15 | 4.101 | 4.095 | 4.087 | 4.086 | 4.085 | 4.079 |
| 333.15 | 4.179 | 4.177 | 4.171 | 4.167 | 4.163 | 4.161 |
| 353.15 | 4.229 | 4.223 | 4.222 | 4.222 | 4.216 | 4.211 |
| | DMAE (1) + $H_2O$ (2) $w_1$ = 0.3005 | | | | | |
| 313.15 | 4.072 | 4.059 | 4.043 | 4.028 | 4.012 | 3.997 |
| 333.15 | 4.123 | 4.116 | 4.090 | 4.072 | 4.054 | 4.039 |
| 353.15 | 4.272 | 4.257 | 4.242 | 4.232 | 4.220 | 4.205 |
| | DMAE (1) + $H_2O$ (2) $w_1$ = 0.4000 | | | | | |
| 293.15 | 3.812 | 3.811 | 3.813 | 3.814 | 3.815 | 3.812 |
| 313.15 | 3.931 | 3.929 | 3.922 | 3.917 | 3.914 | 3.910 |
| 333.15 | 3.948 | 3.945 | 3.941 | 3.939 | 3.931 | 3.927 |
| 353.15 | 4.093 | 4.091 | 4.085 | 4.079 | 4.068 | 4.057 |

[a] Expanded uncertainties ($k$ = 2): $U_r(c_p)$ = 0.010; $U(T)$ = 0.02 K; $U_r(p)$ = 0.0005; $U(w)$ = 0.0002.

**Table 8**

Experimental isobaric heat capacities, $c_p$, of amine aqueous solutions of piperazine {PZ (1) + $H_2O$ (2)} at different temperatures ($T$), pressures ($p$) and amine weight fractions ($w_1$).[a]

| $c_p$ / (kJ·kg$^{-1}$·K$^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|
| $T$ / K | $p$ / MPa | | | | | |
| | 0.100 | 5.00 | 10.00 | 15.00 | 20.00 | 25.00 |
| | PZ (1) + $H_2O$ (2) $w_1$ = 0.1001 | | | | | |
| 313.15 | 4.066 | 4.055 | 4.037 | 4.019 | 3.992 | 3.977 |
| 333.15 | 4.167 | 4.130 | 4.103 | 4.080 | 4.061 | 4.021 |
| 353.15 | 4.205 | 4.164 | 4.126 | 4.104 | 4.082 | 4.061 |

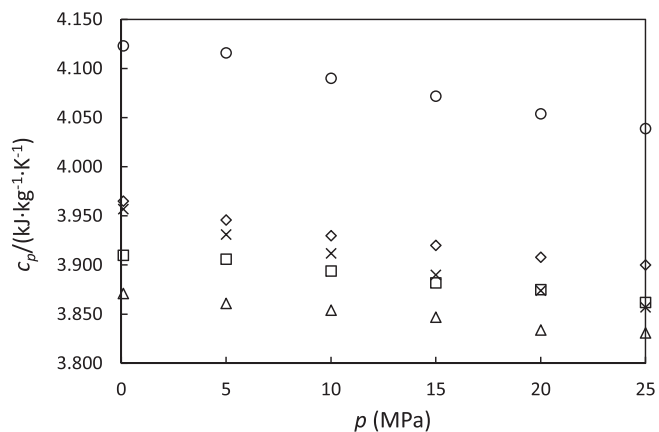[a] Expanded uncertainties ($k$ = 2): $U_r(c_p)$ = 0.010; $U(T)$ = 0.02 K; $U_r(p)$ = 0.0005; $U(w)$ = 0.0002.

**Fig. 2.** Experimental isobaric heat capacities of different aqueous amine solutions ($w_{amine}$ = 0.3) as a function of pressure at $T$ = 333.15 K: (○) DMAE, (◇) MDEA, (×) MEA, (□) DEA and (△) TEA.

function pressure and temperature for some of the mixture studied which are representative of the general observed trends.

Finally, regarding the influence of composition, the heat capacity values decrease when the solution is enriched in amine, specifically the average decrement of $c_p$, when the composition is changed from $w_{amine}$ = 0.1 to 0.4, ranges from 5.7% to 12.0% for MEA; 9.3 % to 11.2% for DEA; 14.0% to 17.4% for TEA; 6.5% to 11.8 % for MDEA and 3.6% to 8.5% for DMAE being always the highest decrease at the lowest temperature.

As an example and a summary, in Fig. 5 can be seen the effect of composition for TEA, as well as temperature and pressure; the specific isobaric heat capacity is represented as a function of amine mass fraction at two temperatures and two pressures (lowest and highest).

An empirical equation is presented to correlate heat capacities with temperature and pressure. The equation used, in its fundamental form, was advanced by Nakagawa et al. [27–28], Yomo et al. [29] and Tanaka et al. [30]. These models were adopted for the study of the isobaric heat capacity in refrigerants and, it is nec-
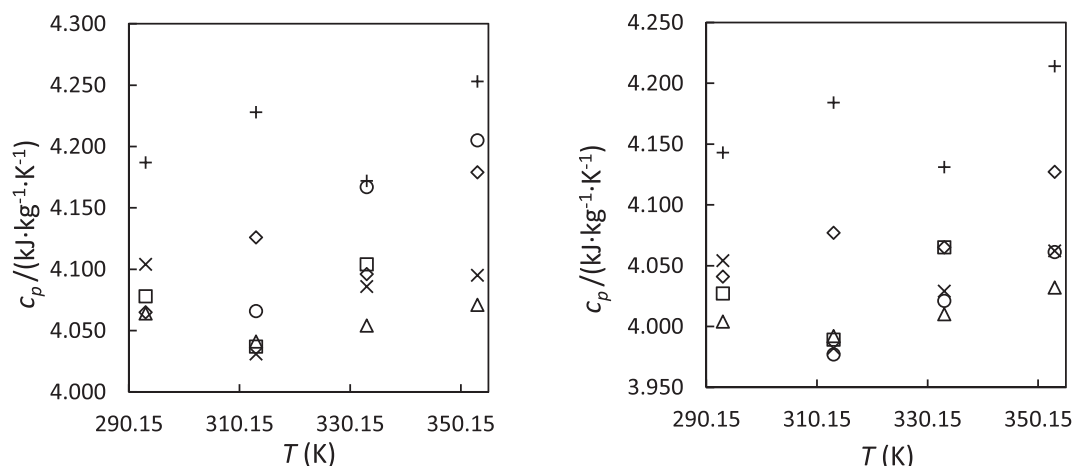


**Fig. 3.** Experimental isobaric heat capacities of different aqueous amine solutions ($w_{amine}$ = 0.1) as a function of temperature at $p$ = 0.1 MPa (left) and $p$ = 25 MPa (right): (+) DMAE, (◇) MDEA, (×) MEA, (□) DEA, (△) TEA and (○) PZ.
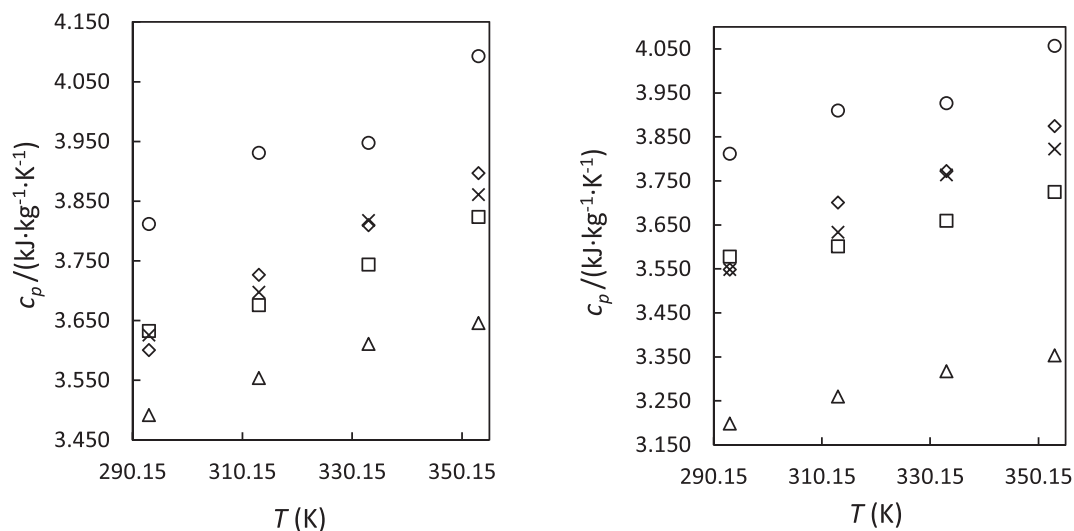


**Fig. 4.** Experimental isobaric heat capacities of different aqueous amine solutions ($w_{amine}$ = 0.4) as a function of temperature at $p$ = 0.1 MPa (left) and $p$ = 25 MPa (right): (○) DMAE, (◇) MDEA, (×) MEA, (□) DEA and (△) TEA.
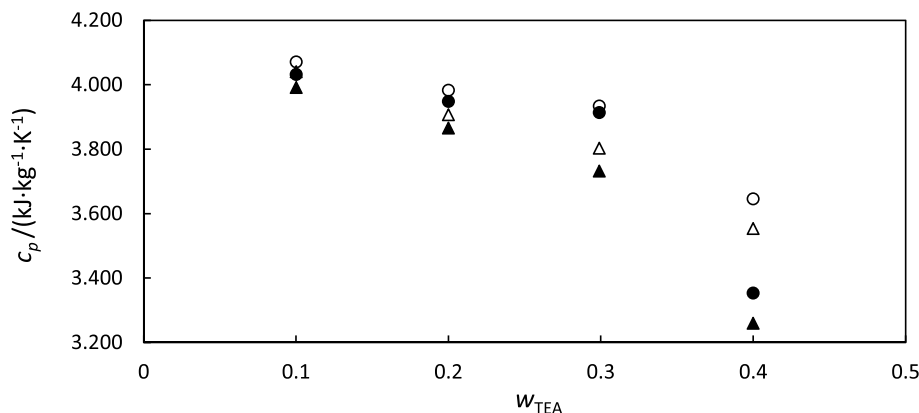
**Fig. 5.** Experimental isobaric heat capacities of different aqueous solutions of TEA as a function of composition (mass fraction) at $p$ = 0.1 MPa (empty symbols) and $p$ = 25 MPa (filled symbols): ($\triangle$, $\blacktriangle$) $T$ = 313.15 K; ($\bigcirc$, $\bullet$) $T$ = 353.15 K.

essary, for their application, to know the critical parameters of the studied compounds [31]. Lugo et al. [22] and Jovanovic et al. [31] have successfully used variations of the models presented by [28–30], applied to different types of fluids. Since the critical parameters for all viscous fluids analysed in this work are not available, the following pure empirical equation is proposed:

$$\frac{c_p(p,T)}{(\text{kJ/kgK})} = a_0 + a_1\left(\frac{p}{\text{MPa}}\right) + a_2\left(\frac{T}{\text{K}}\right) + a_3\left(\frac{p}{\text{MPa}}\right)^2 + a_4\left(\frac{T}{\text{K}}\right)^2 + a_5\left(\frac{p}{\text{MPa}}\right)\left(\frac{T}{\text{K}}\right) \quad (2)$$

where $a_0$, $a_1$, $a_2$, $a_3$, $a_4$, $a_5$ are the fitting parameters obtained by least squares using the MATLAB software [32] and the goodness of fit was determined using the standard deviation ($\sigma$). These fitting parameters and the corresponding standard deviations are summarized in Tables 9–14.

In addition, the experimental data were fitted to the equations presented by Lugo et al. [22] (Eq. 3) and Jovanovic et al. [31] (Eq. 4), which also do not include dependence on critical parameters.

$$\frac{c_p(p,T)}{(\text{kJ/kgK})} = \sum_{i=0}^{1} a_i (p/p_0)^i + \sum_{j=1}^{2} b_j (T/T_0)^{-j} \quad (3)$$

$$\frac{(\text{kJ/kgK})}{c_p(T,p)} = A + \frac{B}{(T/K)} + \frac{C}{(T/K)^2} + D \cdot (T/K) \cdot (p/\text{MPa}) \quad (4)$$

Where, for Eq. (3): $a_i$, $b_j$ are adjustment parameters, where $p_0$ = 0.1 MPa and $T_0$ is set to reference value and for Eq. (4), A, B, C, and D, are adjustment parameters. Tables 9–14 also summarize the fitting parameters and the standard deviations obtained for both equations.

**Table 9**
Fitting parameters and standard deviations $\sigma$ for the isobaric heat capacities for the system MEA (1) + H$_2$O (2) for the different mass fractions of MEA ($w_1$).

| MEA (1) + H$_2$O (2) | | | | |
|---|---|---|---|---|
| | $w_1$ = 0.1001 | $w_1$ = 0.2002 | $w_1$ = 0.2997 | $w_1$ = 0.4002 |
| | New correlation Eq. (2) | | | |
| $a_0$ | 9.5744 | 4.6795 | 8.9823 | 1.0664 |
| $a_1$ | $-8.7141\ 10^{-3}$ | $-8.8391\ 10^{-3}$ | $-5.1182\ 10^{-3}$ | $-1.0752\ 10^{-2}$ |
| $a_2$ | $-3.4154\ 10^{-2}$ | $-6.7790\ 10^{-3}$ | $-3.4428\ 10^{-2}$ | $1.2551\ 10^{-2}$ |
| $a_3$ | $9.9658\ 10^{-6}$ | $2.2421\ 10^{-5}$ | $1.2796\ 10^{-5}$ | $2.7869\ 10^{-6}$ |
| $a_4$ | $5.2848\ 10^{-5}$ | $1.4460\ 10^{-5}$ | $5.7916\ 10^{-5}$ | $-1.3078\ 10^{-5}$ |
| $a_5$ | $1.9959\ 10^{-5}$ | $1.7398\ 10^{-5}$ | $5.7480\ 10^{-6}$ | $2.6016\ 10^{-5}$ |
| $\sigma$ / kJ·kg$^{-1}$·K$^{-1}$ | 0.021 | 0.003 | 0.008 | 0.017 |
| | Lugo et al. [22], Eq. (3) | | | |
| $a_0$ | 10.081 | 7.2844 | 13.212 | 5.4281 |
| $a_1$ | $-2.0143\ 10^{-4}$ | $-2.6543\ 10^{-4}$ | $-2.8822\ 10^{-4}$ | $-2.0562\ 10^{-4}$ |
| $b_1$ | $-13.096$ | $-6.2224$ | $-18.173$ | $-2.1277$ |
| $b_2$ | 7.1127 | 2.8646 | 8.8397 | 0.3099 |
| $T_0$ / K | 293.15 | 293.15 | 313.15 | 293.15 |
| $\sigma$ / kJ·kg$^{-1}$·K$^{-1}$ | 0.018 | 0.005 | 0.008 | 0.017 |
| | Jovanovic et al. [31], Eq. (4) | | | |
| A | $-0.1215$ | $5.0356\ 10^{-2}$ | $-0.3183$ | 0.1896 |
| B | 234.12 | 109.58 | 348.96 | 16.114 |
| C | $-37207.15$ | $-14537.34$ | $-52752.31$ | 2817.35 |
| D | $3.7087\ 10^{-7}$ | $5.0718\ 10^{-7}$ | $5.5580\ 10^{-7}$ | $4.3803\ 10^{-7}$ |
| $\sigma$ / kJ·kg$^{-1}$·K$^{-1}$ | 0.018 | 0.007 | 0.009 | 0.018 |

**Table 10**

Fitting parameters and standard deviations $\sigma$ for the isobaric heat capacities for the system DEA (1) + H$_2$O (2) for the different mass fractions of DEA ($w_1$).

| DEA (1) + H$_2$O (2) | | | | |
|---|---|---|---|---|
| | $w_1$ = 0.1003 | $w_1$ = 0.2008 | $w_1$ = 0.3002 | $w_1$ = 0.4000 |
| | New correlation Eq. (2) | | | |
| $a_0$ | 17.447 | 0.9489 | −1.5277 | 4.6504 |
| $a_1$ | −6.0978 $10^{-3}$ | 9.6509 $10^{-4}$ | −2.0648 $10^{-3}$ | 4.6013 $10^{-3}$ |
| $a_2$ | −8.6307 $10^{-2}$ | 1.4991 $10^{-2}$ | 3.0281 $10^{-2}$ | −9.1666 $10^{-3}$ |
| $a_3$ | 2.8110 $10^{-6}$ | 7.5632 $10^{-6}$ | −1.3165 $10^{-5}$ | −8.4820 $10^{-6}$ |
| $a_4$ | 1.3886 $10^{-4}$ | −1.7487 $10^{-5}$ | −4.1903 $10^{-5}$ | 1.9353 $10^{-5}$ |
| $a_5$ | 1.3371 $10^{-5}$ | −9.1396 $10^{-6}$ | 1.7646 $10^{-6}$ | −2.3419 $10^{-5}$ |
| $\sigma$ / kJ·kg$^{-1}$·K$^{-1}$ | 0.001 | 0.003 | 0.002 | 0.005 |
| | Lugo et al. [22], Eq. (3) | | | |
| $a_0$ | 18.226 | 4.4571 | 0.9039 | 7.7533 |
| $a_1$ | −1.8400 $10^{-4}$ | −1.7954 $10^{-4}$ | −1.8016 $10^{-4}$ | −3.1795 $10^{-4}$ |
| $b_1$ | −29.920 | 0.1706 | 7.2103 | −7.7850 |
| $b_2$ | 15.769 | −0.7843 | −4.2677 | 3.6680 |
| $T_0$ / K | 293.15 | 293.15 | 313.15 | 293.15 |
| $\sigma$ / kJ·kg$^{-1}$·K$^{-1}$ | 0.002 | 0.003 | 0.002 | 0.006 |
| | Jovanovic et al. [31], Eq. (4) | | | |
| A | −0.6224 | 0.2395 | 0.4633 | −1.4751 $10^{-2}$ |
| B | 537.57 | −15.997 | −155.75 | 158.50 |
| C | −82999.95 | 6486.07 | 28849.57 | −21529.16 |
| D | 3.5425 $10^{-7}$ | 3.5783 $10^{-7}$ | 3.5731 $10^{-7}$ | 7.2877 $10^{-7}$ |
| $\sigma$ / kJ·kg$^{-1}$·K$^{-1}$ | 0.003 | 0.003 | 0.005 | 0.005 |

**Table 11**

Fitting parameters and standard deviations $\sigma$ for the isobaric heat capacities for the system TEA (1) + H$_2$O (2) for the different mass fractions of TEA ($w_1$).

| TEA (1) + H$_2$O (2) | | | | |
|---|---|---|---|---|
| | $w_1$ = 0.1001 | $w_1$ = 0.2000 | $w_1$ = 0.2991 | $w_1$ = 0.4000 |
| | new correlation Eq. (2) | | | |
| $a_0$ | 6.4187 | −3.3647 | 1.5555 | 1.3177 |
| $a_1$ | −6.1687 $10^{-3}$ | −1.8181 $10^{-3}$ | −1.8682 $10^{-2}$ | −1.8274 $10^{-2}$ |
| $a_2$ | −1.4848 $10^{-2}$ | 4.1855 $10^{-2}$ | 1.0632 $10^{-2}$ | 1.1509 $10^{-2}$ |
| $a_3$ | −3.9628 $10^{-6}$ | 3.1057 $10^{-5}$ | 7.5558 $10^{-6}$ | 1.8534 $10^{-4}$ |
| $a_4$ | 2.3230 $10^{-5}$ | −5.9587 $10^{-5}$ | −1.1042 $10^{-5}$ | −1.3917 $10^{-5}$ |
| $a_5$ | 1.3270 $10^{-5}$ | −7.3683 $10^{-7}$ | 5.0285 $10^{-5}$ | 5.9261 $10^{-6}$ |
| $\sigma$ / kJ·kg$^{-1}$·K$^{-1}$ | 0.005 | 0.004 | 0.002 | 0.005 |
| | Lugo et al. [22], Eq. (3) | | | |
| $a_0$ | 6.7642 | −0.1077 | 5.2429 | 3.8151 |
| $a_1$ | −1.9800 $10^{-4}$ | −1.2770 $10^{-4}$ | −1.7400 $10^{-4}$ | −1.1708 $10^{-3}$ |
| $b_1$ | −5.8296 | 10.004 | −1.5387 | 0.3595 |
| $b_2$ | 3.1236 | −6.1152 | 8.4772 $10^{-2}$ | −0.6969 |
| $T_0$ / K | 293.15 | 293.15 | 313.15 | 293.15 |
| $\sigma$ / kJ·kg$^{-1}$·K$^{-1}$ | 0.005 | 0.005 | 0.008 | 0.013 |
| | Jovanovic et al. [31], Eq. (4) | | | |
| A | 7.7473 $10^{-2}$ | 0.5398 | 0.1926 | 0.2552 |
| B | 106.28 | −206.28 | 14.229 | −10.234 |
| C | −16624.60 | 36820.09 | 2559.26 | 5911.96 |
| D | 3.7045 $10^{-7}$ | 2.5819 $10^{-7}$ | 3.3648 $10^{-7}$ | 3.0774 $10^{-6}$ |
| $\sigma$ / kJ·kg$^{-1}$·K$^{-1}$ | 0.006 | 0.005 | 0.009 | 0.016 |

In general, the new correlation (Eq. 2) gives similar standard deviations to those obtained with the Eqs. (3) and (4). The best results are obtained for the mixtures with DEA and TEA whose standard deviations range from (0.001 to 0.005) kJ·kg$^{-1}$·K$^{-1}$ for our empirical equation, from (0.002 to 0.013) kJ·kg$^{-1}$·K$^{-1}$ for the equation proposed by Lugo et al. [22] and from (0.003 to 0.016) kJ·kg$^{-1}$·K$^{-1}$ for the equation proposed by Jovanovic et al. [31]. On the other hand, the worst results are obtained for the mixtures $w_{MDEA}$ = 0.1 and $w_{DMAE}$ = 0.1; 0.4. Nevertheless, the relative deviations are between the uncertainty of the measurements (1%). As

examples, the relative deviations between experimental and calculated values using the new empirical correlation are shown graphically for DEA solutions (Fig. 6) and DMAE solutions (Fig. 7) being their relative deviations below 0.4% and 1%, respectively.

Finally, the comparison between our experimental data and those found in the literature was performed, however, literature data are measured at atmospheric pressure and they are scarce: Heat capacities of MEA solutions are reported by [11–16], of DEA solutions by [12–13], of TEA solutions by [13], of MDEA solutions by [12–13,17–19], of DMEA solutions by [20] and of piperazine

**Table 12**
Fitting parameters and standard deviations $\sigma$ for the isobaric heat capacities for the system MDEA (1) + $H_2O$ (2) for the different mass fractions of MDEA ($w_1$).

| MDEA (1) + $H_2O$ (2) | | | | |
|---|---|---|---|---|
| | $w_1 = 0.1001$ | $w_1 = 0.2001$ | $w_1 = 0.2998$ | $w_1 = 0.4001$ |
| | New correlation Eq. (2) | | | |
| $a_0$ | 5.3521 | −1.005 | 0.8714 | −0.7164 |
| $a_1$ | $2.4245\ 10^{-3}$ | $-4.9710\ 10^{-3}$ | $-1.7841\ 10^{-2}$ | $-8.4371\ 10^{-3}$ |
| $a_2$ | $-9.2488\ 10^{-3}$ | $2.7485\ 10^{-2}$ | $1.4311\ 10^{-2}$ | $2.3013\ 10^{-2}$ |
| $a_3$ | $2.2739\ 10^{-5}$ | $2.5053\ 10^{-5}$ | $3.3598\ 10^{-5}$ | $2.8525\ 10^{-5}$ |
| $a_4$ | $1.6706\ 10^{-5}$ | $-3.6910\ 10^{-5}$ | $-1.5001\ 10^{-5}$ | $-2.8225\ 10^{-5}$ |
| $a_5$ | $-1.3976\ 10^{-5}$ | $8.9401\ 10^{-6}$ | $4.0652\ 10^{-5}$ | $1.9734\ 10^{-5}$ |
| $\sigma$ / kJ·kg$^{-1}$·K$^{-1}$ | 0.023 | 0.006 | 0.008 | 0.013 |
| | Lugo et al. [22], Eq. (3) | | | |
| $a_0$ | 6.3037 | 2.6540 | 5.5155 | 3.8437 |
| $a_1$ | $-1.5213\ 10^{-4}$ | $-1.4534\ 10^{-4}$ | $-3.4548\ 10^{-4}$ | $-1.3445\ 10^{-4}$ |
| $b_1$ | −4.3256 | 4.2896 | −1.5818 | 1.5867 |
| $b_2$ | 2.1003 | −3.0690 | $-6.4715\ 10^{-2}$ | −1.8372 |
| $T_0$ / K | 293.15 | 293.15 | 313.15 | 293.15 |
| $\sigma$ / kJ·kg$^{-1}$·K$^{-1}$ | 0.023 | 0.007 | 0.010 | 0.012 |
| | Jovanovic et al. [31], Eq. (4) | | | |
| A | 0.1101 | 0.3574 | 0.1863 | 0.3016 |
| B | 76.825 | −94.201 | 8.2564 | −60.456 |
| C | −10898.53 | 19100.47 | 4530.38 | 15745.07 |
| D | $2.8332\ 10^{-7}$ | $2.7508\ 10^{-7}$ | $6.5570\ 10^{-7}$ | $2.7917\ 10^{-7}$ |
| $\sigma$ / kJ·kg$^{-1}$·K$^{-1}$ | 0.023 | 0.007 | 0.012 | 0.013 |

**Table 13**
Fitting parameters and standard deviations $\sigma$ for the isobaric heat capacities for the system DMAE (1) + $H_2O$ (2) for the different mass fractions of DMAE ($w_1$).

| DMAE (1) + $H_2O$ (2) | | | | |
|---|---|---|---|---|
| | $w_1 = 0.1000$ | $w_1 = 0.2005$ | $w_1 = 0.3005$ | $w_1 = 0.4000$ |
| | New correlation Eq. (2) | | | |
| $a_0$ | 6.5477 | 0.6680 | 17.529 | 4.6642 |
| $a_1$ | $-2.7689\ 10^{-3}$ | $-3.3687\ 10^{-3}$ | $-6.6559\ 10^{-3}$ | $7.0046\ 10^{-3}$ |
| $a_2$ | $-1.5246\ 10^{-2}$ | $1.7925\ 10^{-2}$ | $-8.5429\ 10^{-2}$ | $-8.8732\ 10^{-3}$ |
| $a_3$ | $4.4577\ 10^{-6}$ | $3.8409\ 10^{-6}$ | $-2.1744\ 10^{-7}$ | $-1.7182\ 10^{-5}$ |
| $a_4$ | $2.4678\ 10^{-5}$ | $-2.2198\ 10^{-5}$ | $1.3562\ 10^{-4}$ | $2.0481\ 10^{-5}$ |
| $a_5$ | $3.0223\ 10^{-6}$ | $7.5358\ 10^{-6}$ | $1.0757\ 10^{-5}$ | $-2.2746\ 10^{-5}$ |
| $\sigma$ / kJ·kg$^{-1}$·K$^{-1}$ | 0.029 | 0.004 | 0.005 | 0.027 |
| | Lugo et al. [22], Eq. (3) | | | |
| $a_0$ | 6.6973 | 4.2568 | 22.607 | 8.2695 |
| $a_1$ | $-1.6804\ 10^{-4}$ | $-8.3719\ 10^{-5}$ | $-3.0776\ 10^{-4}$ | $-7.9302\ 10^{-5}$ |
| $b_1$ | −5.2052 | 1.0257 | −37.414 | −7.5388 |
| $b_2$ | 2.7037 | −1.2707 | 18.881 | 3.1686 |
| $T_0$ / K | 293.15 | 293.15 | 313.15 | 313.15 |
| $\sigma$ / kJ·kg$^{-1}$·K$^{-1}$ | 0.029 | 0.004 | 0.005 | 0.027 |
| | Jovanovic et al. [31], Eq. (4) | | | |
| A | $9.2120\ 10^{-2}$ | 0.2547 | −0.8117 | $-4.7669\ 10^{-3}$ |
| B | 88.944 | −30.828 | 666.78 | 138.83 |
| C | −13497.89 | 8579.35 | −105107.77 | −17857.71 |
| D | $2.9343\ 10^{-7}$ | $1.4708\ 10^{-7}$ | $5.3526\ 10^{-7}$ | $1.6364\ 10^{-7}$ |
| $\sigma$ / kJ·kg$^{-1}$·K$^{-1}$ | 0.029 | 0.004 | 0.006 | 0.027 |

**Table 14**
Fitting parameters and standard deviations $\sigma$ for the isobaric heat capacities for the system PZ (1) + $H_2O$ (2) for a mass fraction of PZ ($w_1 = 0.1001$).

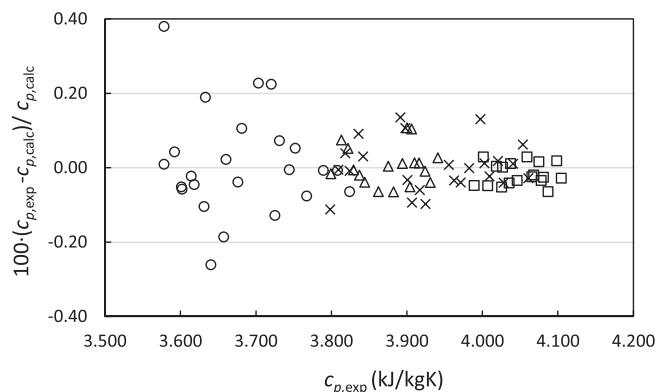| PZ (1) + $H_2O$ (2) $w_1 = 0.1001$ | | | | | |
|---|---|---|---|---|---|
| New correlation Eq. (2) | | Lugo et al. [22], Eq. (3) | | Jovanovic et al. [31], Eq. (4) | |
| $a_0$ | −2.3263 | $a_0$ | 0.3338 | A | 0.4740 |
| $a_1$ | $1.0245\ 10^{-2}$ | $a_1$ | $-4.9657\ 10^{-4}$ | B | −172.649 |
| $a_2$ | $3.5845\ 10^{-2}$ | $b_1$ | 8.9736 | C | 31610.95 |
| $a_3$ | $3.1698\ 10^{-5}$ | $b_2$ | −5.2210 | D | $9.0078\ 10^{-7}$ |
| $a_4$ | $-4.9168\ 10^{-5}$ | $T_0$ / K | 313.15 | | |
| $a_5$ | $-4.8043\ 10^{-5}$ | | | | |
| $\sigma$ / kJ·kg$^{-1}$·K$^{-1}$ | 0.008 | | 0.011 | | 0.008 |

**Fig. 6.** Relative heat capacity deviations between experimental values and those calculated by Eq. (2) as a function of the experimental heat capacities for the mixture DEA (1) + $H_2O$ (2) at different amine mass fractions: (□) $w_1 = 0.1$; (×) $w_2 = 0.2$; (△) $w_3 = 0.3$ and (○) $w_4 = 0.4$.
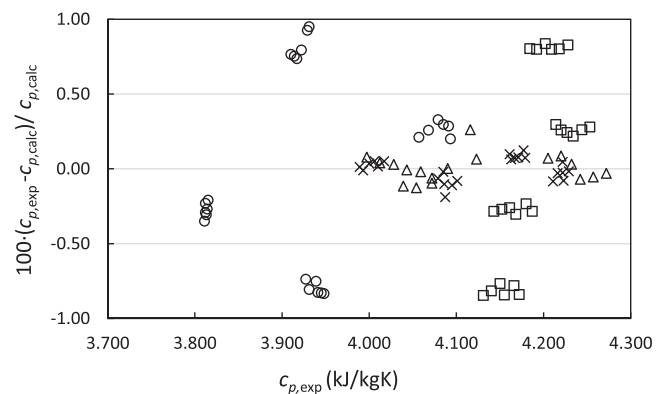


**Fig. 7.** Relative heat capacity deviations between experimental values and those calculated by Eq. (2) as a function of the experimental heat capacities for the mixture DMAE (1) + $H_2O$ (2) at different amine mass fractions: (□) $w_1 = 0.1$; (×) $w_2 = 0.2$; (△) $w_3 = 0.3$ and (○) $w_4 = 0.4$.

(PZ) [16,21]. Table 15 contains a summary of these literature data related with the mixtures studied in this paper, including the measurements conditions and, where can be seen that some literature data were measured at different conditions of temperature or compositions than this work being not possible this comparison. This table also reports the experimental points given in the literature data and the number of data included in the comparison. The average absolute relative deviation (AAD) was used to quantify the agreement between our data and literature data. The AAD is within the uncertainty of the measurements.

As an example, Fig. 8 depicts the comparison for MEA solutions: Pagé et al. [11] measured at $T = 313.15$ K and $w_1 = (0.1, 0.2)$; Abdulkadir et al. [14] measured at $w_1 = 0.3$ and $T = (313.15, 333.15, 353.15)$ K, Quang et al. [15] at $w_1 = 0.3$ and $T = (313.15, 333.15, 353.15)$ K; and Kim et al. [16] at $w_1 = 0.1$ and $T = (313, 333, 353)$ K. The average absolute relative deviations are: 0.84 %, 0.69 %, 0.47% and 1.9%, respectively. The (MDEA + $H_2O$) mixture was compared with Zhang et al. [19], their measurements at $w_{MDEA} = 0.2968$ and $T = (313.15, 333.15, 353.15)$ K were compared obtaining an AAD of 1.9%. Finally, an AAD of 0.9% from [16] was obtained for the (PZ + $H_2O$) system for data at $w_{PZ} = 0.1$ and $T = (313.15, 333.15, 353.15)$ K. No data are available at the same conditions for the other amines studied.

## 4. Conclusions

The heat capacities of different aqueous solutions of alkanolamines were measured at different temperatures and pressure up to 25 MPa. In general, the mixtures present a slight decrease in the isobaric heat capacity for increasing pressure, and a larger increase in the heat capacity for increasing temperature except at $w_{amine} = 0.1$. Furthermore, in this study, a new empirical equation is introduced to correlate the heat capacity as a function of pressure and temperature of heat capacity in the range of temperature and pressure studied. The new model is a six-parameter equation that fits the measured heat capacities within the uncertainty of the measurements. The paper report new data in ranges of pressure which are not available in the literature.

**Table 15**
Comparison between literature data and our experimental data for the amine aqueous solutions under study. Temperature and pressure ranges and number of experimental points (NP) of the literature data are included as well as the number of experimental points compared (PC) and the average absolute deviation (AAD).

| Reference | Year | $T$ / K | $p$ / MPa | $x_1$ /$w_1$ | NP | $U_r(c_p)$ | PC | AAD% |
|---|---|---|---|---|---|---|---|---|
| MEA (1) + $H_2O$ (2) | | | | | | | | |
| Pagé et al. [11] | 1993 | 283.15 –313.15 | 0.1 | $x_1 = 0 - 1$ | 54 | – | 2 $w_1 = 0.1, 0.2$ | 0.84 |
| Weiland et al. [12] | 1997 | 298.15 | 0.1 | $w_1 = 0.1 - 0.4$ | 4 | 1% | – | |
| Chiu et al. [13] | 1999 | 303.15 – 353.15 | 0.1 | $x_1 = 0.2 - 0.8$ | 44 | 3% | - $w_1 \geq 0.46$ | |
| Abdulkadir et al. [14] | 2014 | 313.15– 353.15 | 0.1 | 5 M, 3 M, 2 M | 33 | | 3 $w_1 = 0.1$ | 0.69 |
| Quang et al. [15] | 2015 | 303.15– 363.15 | 0.1 | $w_1 = 0.3$ | 13 | 3% | 3 | 0.47 |
| Kim et al. [16] | 2015 | 303 – 353 | 0.1 | $w_1 = 0.1$ | 11 | | 3 | 1.9 |
| DEA (1) + $H_2O$ (2) | | | | | | | | |
| Weiland et al. [12] | 1997 | 298.15 | 0.1 | $w_1 = 0.1 - 0.4$ | 4 | 1% | – | |
| Chiu et al. [13] | 1999 | 303.15 –353.15 | 0.1 | $x_1 = 0.2 - 0.8$ | 44 | 3% | - $w_1 \geq 0.59$ | |
| TEA (1) + $H_2O$ (2) | | | | | | | | |
| Chiu et al. [13] | 1999 | 303.15 –353.15 | 0.1 | $x_1 = 0.2 - 0.8$ | 44 | 3% | - $w_1 \geq 0.67$ | |
| MDEA (1) + $H_2O$ (2) | | | | | | | | |
| Hayden et al. [17] | 1983 | 298.15 – 348.15 | 0.1 | $w_1 = 0.23; 0.50$ | 6 | < 1% | – | |
| Weiland et al. [12] | 1997 | 298.15 | 0.1 | $w_1 = 0.3 - 0.6$ | 4 | 1% | – | |

**Table 15** (*continued*)

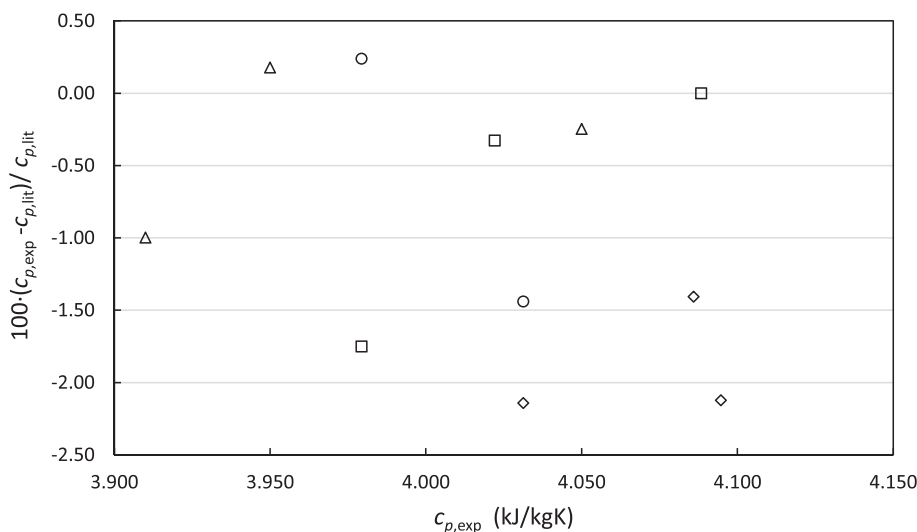| Reference | Year | $T$ / K | $p$ / MPa | $x_1$ /$w_1$ | NP | $U_r(c_p)$ | PC | AAD% |
|---|---|---|---|---|---|---|---|---|
| Chiu et al. [13] | 1999 | 303.15 – 353.15 | 0.1 | $w_1$ = 0.23; 0.50 $x_1$ = 0.2 – 0.8 | 66 | 3% | – | |
| Chen et al. [18] | 2001 | 303.15 – 353.15 | 0.1 | $x_1$ = 0.2 – 0.8 | 44 | 2% | - $w_1 \geq 0.62$ | |
| Zhang et al. [19] | 2002 | 278.15 – 303.15 | 0.1 | $x_1$ = 0.03 – 0.94 | 72 | 2% | 3 | 1.9 |
| DMAE (1) + H$_2$O (2) | | | | | | | | |
| Mundhwa et al. [20] | 2007 | 303.15 –353.15 | 0.1 | $x_1$ = 0.1 – 0.9 | 99 | | | |
| PZ (1) + H$_2$O (2) | | | | | | | | |
| Chen et al. [21] | 2010 | 303.15 – 353.15 | 0.1 | $x_1$ = 0.05 – 0.2 | 44 | 0.5% | - $w_1 \geq 0.2$ | |
| Kim et al. [16] | 2015 | 303 – 353 | 0.1 | $w_1$ = 0.1 | 11 | | 3 | 0.9 |



**Fig. 8.** Relative heat capacity deviations between experimental values and literature data as a function of the experimental heat capacities for the mixture MEA (1) + H$_2$O (2): (○) Pagé et al. [11], (□) Abdulkadir et al. [14], (△) Quang et al. [15]and (◇) Kim et al. [16].

## CRediT authorship contribution statement

**Eduardo I. Concepción:** Investigation, Validation, Formal analysis. **Alejandro Moreau:** Investigation, Validation, Formal analysis. **David Vega-Maza:** Validation, Formal analysis. **Xavier Paredes:** Formal analysis, Validation. **M. Carmen Martín:** Project administration, Conceptualization, Methodology, Supervision, Writing - review & editing.

## Data availability

Data will be made available on request.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## References

[1] A. Ahmady, M.A. Hashim, M.K. Aroua, Experimental investigation on the solubility and initial rate of absorption of CO$_2$ in aqueous mixtures of methyldiethanolamine with the ionic liquid 1-Butyl-3-methylimidazolium Tetrafluoroborate, J. Chem. Eng. Data 55 (2010) 5733–5738, https://doi.org/10.1021/je1006949.

[2] R. Lindsey, Climate change: atmospheric carbon dioxide, 2022, https://www.climate.gov/news-features/understanding-climate/climate-change-atmospheric-carbon-dioxide (accessed in July 2022).

[3] L.F. Chiu, H.F. Liu, M.H. Li, Heat capacity of alkanolamines by differential scanning calorimetry, J. Chem. Eng. Data 44 (1999) 631–636, https://doi.org/10.1021/je980217x.

[4] S. Poozesh, A.V. Rayer, A. Henni, Molar heat capacity (Cp) of aqueous cyclic amine solutions from (298.15 to 353.15) K, J. Chem. Eng. Data 58 (2013) 1989–2000, https://doi.org/10.1021/je400178k.

[5] M. Sobrino, E.I. Concepción, A. Gómez-Hernández, M.C. Martín, J.J. Segovia, Viscosity and density measurements of aqueous amines at high pressures: MDEA-water and MEA-water mixtures for CO2 capture, J. Chem. Thermodyn. 98 (2016) 231–241, https://doi.org/10.1016/j.jct.2016.03.021.

[6] E.I. Concepción, A. Gómez-Hernández, M.C. Martín, J.J. Segovia, Density and viscosity measurements of aqueous amines at high pressures: DEA-water, DMAE-water and TEA-water mixtures, J. Chem. Thermodyn. 112 (2017) 227–239, https://doi.org/10.1016/j.jct.2017.05.001.

[7] E.I. Concepción, A. Moreau, M.C. Martín, M.D. Bermejo, J.J. Segovia, Density and viscosity measurements of (piperazine + water) and (piperazine + 2-

dimethylaminoethanol + water) at high pressures, J. Chem. Thermodyn. 141 (2020), https://doi.org/10.1016/j.jct. 2019.105960.

[8] E.I. Concepción, A. Moreau, M.C. Martín, D. Vega-Maza, J.J. Segovia, Density and viscosity of aqueous solutions of methyldiethanolamine (MDEA) + diethanolamine (DEA) at high pressures, J. Chem. Thermodyn. 148 (2020), https://doi.org/10.1016/j.jct. 2019.106141.

[9] J. Segovia, D. Vega-Maza, R. Chamorro, M.C. Martín, High-pressure isobaric heat capacities using a new flow calorimeter, J. Supercrit. Fluids 46 (2008) 258–264, https://doi.org/10.1016/j.supflu.2008.01.011.

[10] K.N. Marsh, P.A.G. O'Hare (Eds.), Solution Calorimetry. Experimental Thermodynamics, vol. IV, Blackwell Scientific Publications, Oxford, U.K. (1994).

[11] M. Pagé, J.Y. Huot, C. Jolicoeur, A comprehensive thermodynamic investigation of water-ethanolamine mixtures at 10, 25, and 40 °C, Can. J. Chem. 71 (1993) 1064–1072, https://doi.org/10.1139/v93-142.

[12] R.H. Weiland, J.C. Dingman, D.B. Cronin, Heat capacity of aqueous monoethanolamine, diethanolamine, N-methyldiethanolamine, and N-methyldiethanolamine-based blends with carbon dioxide, J. Chem. Eng. Data 42 (1997) 1004–1006, https://doi.org/10.1021/je960314v.

[13] L.F. Chiu, M.H. Li, Heat capacity of alkanolamine aqueous solutions, J. Chem. Eng. Data 44 (1999) 1396–1401, https://doi.org/10.1021/je990131j.

[14] D.V. Quang, A. Dindi, A.V. Rayer, N. El Hadri, A. Abdulkadir, M.R.M. Abu-Zahra, Effect of moisture on the heat capacity and the regeneration heat required for $CO_2$ capture process using PEI impregnated mesoporous precipitated silica, Greenh. Gases Sci. Technol. 5 (2015) 91–101, https://doi.org/10.1002/ghg.1427.

[15] A. Abdulkadir, A.V. Rayer, D.V. Quang, N. El-Hadri, A. Dindi, P.H.M. Feron, M.R. M. Abu-Zahra, Heat of absorption and specific heat of carbon dioxide in aqueous solutions of monoethanolamine, 3-piperidinemethanol and their blends, Energy Procedia 63 (2014) 2070–2081, https://doi.org/10.1016/j.egypro.2014.11.223.

[16] Y.E. Kim, S.H. Yun, J.H. Choi, S.C. Nam, S.Y. Park, S.K. Jeong, Y.I. Yoon, Comparison of the $CO_2$ absorption characteristics of aqueous solutions of diamines: absorption capacity, specific heat capacity, and heat of absorption, Energy Fuels 29 (2015) 2582–2590, https://doi.org/10.1021/ef500561a.

[17] T.A. Hayden, T.G.A. Smith, A.E. Mather, Heat capacity of aqueous methyldiethanolamine solutions, J. Chem. Eng. Data 28 (1983) 196–197, https://doi.org/10.1021/je00032a020.

[18] Y.J. Chen, T.W. Shih, M.H. Li, Heat capacity of aqueous mixtures of monoethanolamine with N-methyldiethanolamine, J. Chem. Eng. Data 46 (2001) 51–55, https://doi.org/10.1021/je0000367.

[19] K. Zhang, B. Hawrylak, R. Palepu, P.R. Tremaine, Thermodynamics of aqueous amines: excess molar heat capacities, volumes, and expansibilities of water + methyldiethanolamine (MDEA) and {water + 2-amino-2-methyl-1-propanol (AMP)}, J. Chem. Thermodyn. 34 (2002) 679–710, https://doi.org/10.1006/jcht.2002.0937.

[20] M. Mundhwa, A. Henni, Molar heat capacity of various aqueous alkanolamine solutions from 303.15 K to 353.15 K, J. Chem. Eng. Data 52 (2007) 491–498, https://doi.org/10.1021/je0604232.

[21] Y.R. Chen, A.R. Caparanga, A.N. Soriano, M.H. Li, Liquid heat capacity of the solvent system (piperazine + n-methyldiethanolamine + water), J. Chem. Thermodyn. 42 (2010) 54–59, https://doi.org/10.1016/j.jct.2009.07.005.

[22] L. Lugo, J.J. Segovia, M.C. Martín, J. Fernández, M.A. Villamañán, An experimental setup for isobaric heat capacities for viscous fluids at high pressure: squalane, bis(2-ethylhexyl) sebacate and bis(2-ethylhexyl) phthalate, J. Chem. Thermodyn. 49 (2012) 75–80, https://doi.org/10.1016/j.jct.2012.01.011.

[23] D. Vega-Maza, Thermodynamic Characterization of New Generation Liquid Fuels with Renewable Components using a New High Pressure Isobaric Calorimeter and Volumetric Measurements, Ph.D. Thesis, 2009, University of Valladolid, Spain.

[24] D. Vega-Maza, M.C. Martín, J.P.M. Trusler, J.J. Segovia, Heat capacities and densities of the binary mixtures containing ethanol, cyclohexane or 1-hexene at high pressures, J. Chem. Thermodyn. 57 (2013) 550–557, https://doi.org/10.1016/j.jct.2012.07.018.

[25] BIPM (2008). Evaluation of measurement data – Guide to the expression of uncertainty in measurement (JCGM 100:2008)

[26] W. Wagner, A. Pruss, I.A.P.W.S. The formulation, for the thermodynamic properties of ordinary water substance for general and scientific use, J. Phys. Chem. Ref. Data 31 (2002) 387–535, https://doi.org/10.1063/1.1461829.

[27] S. Nakagawa, H. Sato, K. Watanabe, Isobaric heat capacity data for liquid HCFC-123 (CHCl2CF3, 2,2-dichloro-1,1, 1-trifluoroethane), J. Chem. Eng. Data 36 (1991) 156–159, https://doi.org/10.1021/je00002a007.

[28] S. Nakagawa, T. Hori, H. Sato, K. Watanabe, Isobaric heat capacity for liquid 1-chloro-1,1-difluoroethane and 1,1-difluoroethane, J. Chem. Eng. Data 38 (1993) 70–74, https://doi.org/10.1021/je00009a017.

[29] M. Yomo, H. Sato, K. Watanabe, Measurements of isobaric heat capacity for liquid difluoromethane (HFC-32), High Temp. High Press. 26 (1994) 267–272.

[30] K. Tanaka, Y. Higashi, Measurements of the isobaric specific heat capacity and density for dimethyl ether in the liquid state, J. Chem. Eng. Data 55 (2010) 2658–2661, https://doi.org/10.1021/je900922x.

[31] J.D. Jovanović, A.B. Knežević-Stevanović, D.K. Grozdanić, An empirical equation for temperature and pressure dependence of liquid heat capacity, J. Taiwan Inst. Chem. Eng. 40 (2009) 105–109, https://doi.org/10.1016/j.jtice.2008.07.001.

[32] MATLAB software. The MathWorks Inc., 1995.