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Viscosity and density measurements of aqueous amines at high pressures: MDEA-water and MEA-water mixtures for CO_2 capture

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ABSTRACT

Viscosity and density are thermophysical properties crucial to characterizing any kind of fluid such as aqueous amines. These blends are becoming more and more relevant for their CO_2 capture potential, such that having accurate viscosity and density measurements would prove useful. Densities and viscosities of these mixtures at atmospheric pressure may be found in the literature although it is more difficult to find values at high pressures, these potentially proving interesting when seeking to provide a full description of these fluids.

Viscosity and density measurements at high pressures (up to 120 MPa) and at temperatures between 293.15 K and 353.15 K of MDEA + water and MEA + water mixtures (both from 10% to 40% amine mass fraction) are presented in this work. Density measurements were performed with an Anton Paar DMA HPM densimeter with an expanded uncertainty ($k = 2$) less than ±0.7 kg·m^{-3}. A falling body technique was used to measure viscosities at high pressures due to its sturdiness in terms of corrosion. Details of this latter equipment are presented, including calibration using *n*-dodecane and uncertainty calculations, which give a relative expanded uncertainty ($k = 2$) of less than ±2.4% for the highest viscosity and ±2.9% for the lowest.

1. Introduction

Society is becoming increasingly aware of environmental issues, with the focus on problems such as the greenhouse effect. In this sense, reducing CO_2 emissions is an important goal. Although there are many substances whose Global Warming Potential (GWP) is higher than the GWP of CO_2, our current way of life, which is mainly based on fossil fuels, forces us to pay particular attention to CO_2 emissions.

There are two main actions which might help to improve this situation. Firstly, an increased use of renewable sources will reduce CO_2 emissions directly, and secondly, CO_2 may be removed from gas streams by using substances such as aqueous amines. In this regard, many initiatives have been promoted by governments over the last few years in an effort to cut CO_2 emissions.

Specifically, alkanolamine solutions are widely used in industry to remove components such as H_2S and CO_2 from natural or refinery gases, with the tertiary amine *n*-methyldiethanolamine (MDEA) an industrially important one for this purpose [1,2]. Primary amine monoethanolamine (MEA) is one of the most effective amines for CO_2 absorption, reaching efficiency rates above 90% [3] and being cataloged as one of the most promising amines for these purposes by Aaron et al. [4].

Thermophysical properties such as viscosity and density of aqueous solutions are required for two main reasons. Firstly, they are crucial for designing treatment equipment [5], and secondly, knowledge of these properties, even at high pressures, will enable a full characterization of these fluids.

In this work, viscosity and density measurements of MDEA + H_2O and MEA + H_2O mixtures (10%, 20%, 30% and 40% amine mass fraction) at pressures from 0.1 MPa to 120 MPa and temperatures of 293.15 K, 313.15 K, 333.15 K and 353.15 K are presented. Density measurements were carried out with an Anton Paar DMA HPM densimeter, already introduced [6], and density measurements were extended up to $p = 140$ MPa and $T = 393.15$ K. Viscosity measurements were performed with a falling body viscometer recently developed at the TERMOCAL laboratory [7]. Both techniques are able to resist any corrosion effects which might be caused by amines.

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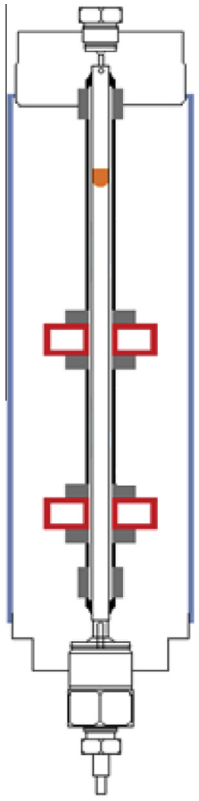

Fig. 1. Measuring cell with two operating coils.

2. Experimental procedure

2.1. Densimeter

An Anton Paar DMA HPM densimeter was employed to perform the density measurements using water and vacuum for its calibration and following the method shown in [6]. Uncertainty calculations were carried out following the procedure described in JCGM 100:2008 [8] and explained in [6], obtaining an expanded uncertainty ($k = 2$) of below ±0.7 kg·m^{-3}.

2.2. Viscometer

A falling body viscometer was used for the measurements. It is based on the falling time measurement of a body (a cylinder in our case) when it falls through a vertical pipe containing the fluid whose viscosity we wish to know. The apparatus is able to measure in wide pressure ranges, from 0.1 MPa to 140 MPa, and temperature, from 253.15 K to 523.15 K.

The cell, where measurements take place, was designed by the Groupe de Haute Pression, Laboratoire des Fluides Complexes of the University of Pau [9], and its full experimental setup was developed and improved at the TERMOCAL laboratory.

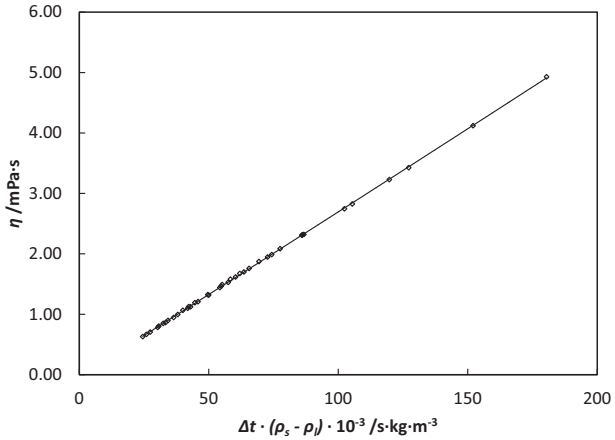

Fig. 2. Falling body viscometer calibration fitting using *n*-dodecane as reference fluid.

Table 2
Coefficients of Eq. (2) obtained for the falling body viscometer calibration with *n*-dodecane.

	Parameters	Standard deviation
a/mPa·s	$-4.49383\cdot10^{-2}$	$8.7\cdot10^{-3}$
b/mPa·m^3·kg^{-1}	$2.77769\cdot10^{-5}$	$1.1\cdot10^{-7}$

Considering that the body reaches its terminal velocity without eccentricity and laminar flow, Eq. (1) could theoretically describe the behavior of this sort of viscometers. This expression is based on the Stokes' law and Newton's second law:

$$\eta = K \cdot \Delta\rho \cdot \Delta t \quad (1)$$

The terms of the expression (1) are: η the viscosity, K a calibration constant which depends on the apparatus and the falling body, $\Delta\rho$ the difference between the density of the body material and the liquid density, and Δt the time registered between two coils.

In an ideal case, K could be determined without any calibration from the dimensions of the instrument, the mass of the falling cylinder and its density using a mathematical expression. However, in practice, this is not advisable because real operation of this instrument differs from the simplified model given by that mathematical expression in several factors [10,11], which is why a calibration procedure is always performed in this kind of viscometer. Several ways of calibration based on Eq. (1) have been successfully performed [12]: from the use of a single calibration constant modified by thermal expansion coefficients to using several calibration constants for each temperature and pressure set.

In our case, the model described by Eq. (1) fits the range of viscosities considering in this work (up to 5 mPa·s approximately) quite well. However, adding an independent term (intercept) to the expression (1) has allowed us to achieve a better approach to the behavior of our viscometer. Expression (2) is therefore used in this work:

Table 1
Material description.

Compound	Source	Mass fraction purity[a]	Water content (%)	Purification method
n-Dodecane	Sigma–Aldrich	⩾0.99	Máx. 0.01	None
1-Butanol	Sigma–Aldrich	⩾0.995	Máx. 0.1 (157.5 ppm)	None
MDEA	Aldrich Chemistry	⩾0.999	Máx. 0.1	None
MEA	Sigma–Aldrich	⩾0.998	Máx. 0.14	None
Water	Sigma–Aldrich	Conductivity ⩽ $2\cdot10^{-6}$ ohm^{-1} cm^{-1}		None

[a] As stated by the supplier and checked by gas chromatography.