



Universidad de Valladolid

Master Thesis

Title: Density and Viscosity for the mixtures; **DMSO + choline acetate** and **DMSO + 1-ethyl-3-methyl imidazolium acetate (EMIM Ac)** between temperatures 20°C to 100°C.

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Chapter 1. Introduction

In this work density and viscosity of mixtures Dimethyl sulfoxide (DMSO) plus choline acetate (Ch Ac, 2 – Hydroxyethyl – trimethylammonium acetate) and of DMSO plus 1-ethyl-3-methyl imidazolium acetate (EMIM Ac) were determined using a viscometer with range of temperature between 10 to 100 °C within the whole possible range of composition. The drift of a high pressure densitometer was also studied.

1.1 Importance of density and viscosity measurements

For most of the articles written about moving fluids, they tend to refer back to its fundamental properties; density and viscosity of the fluid [1]. Density and viscosity measurement are important in many applications; including , fundamental research, quality control, process and research environments, industrial productions including food, petrochemical, paint, oil and more to consider. [2]

Density

Density is one of the fundamental physical property expresses as a ratio of mass to volume. Identification of density can be helpful in characterization of different substances. Knowledge of density in different temperature and pressure conditions is not only necessary to industrial application such as calculating the height of rectification towers, commercial distribution of petroleum products or optimizing the operation conditions but it is also essential for calculating other properties such as the solubility or viscosity [1]. Density is also important in assessing the capacity of solvent fluids [3]. Other relevant fundamental properties such as Isothermal compressibility or Isobaric thermal expansion coefficient can be determined from the density. [1]

Viscosity

Viscosity is the resistance of a fluid to flow due to of internal frictions. It is a key factor when fluid is transported or pumped, general involving any process in fluid flow. Understanding viscosity will help in determining the energy required, the force needed to induce movement within fluid. It also help in designing of production and transportation processes. In generally viscosity is used in indication of the magnitude of the fluidity of a fluid.

Having knowledge of density and viscosity is necessary to understand many processes, for example; for the efficiency of the calculations for power plants and internal combustion

engines. [1] For instant if there is increase in concentration there will be increases of density and the viscosity. Or if the fluid is very dense then it turns to be more viscous.

There are two type of viscosity; dynamic viscosity and kinematic viscosity. For dynamic viscosity it is the measure of torque resistance experience in the mixture or the relative shear motions. Measured units in pascal – seconds (Pa.s);

$$\eta = \frac{F/A}{\gamma} \text{ [Pa.s]}$$

In kinematic viscosity it measure how much of a fluid flow from a given force that is applied. Basically it define the ration of absolute viscosity to the density of fluid. The SI unit of ν is m^2/s ;

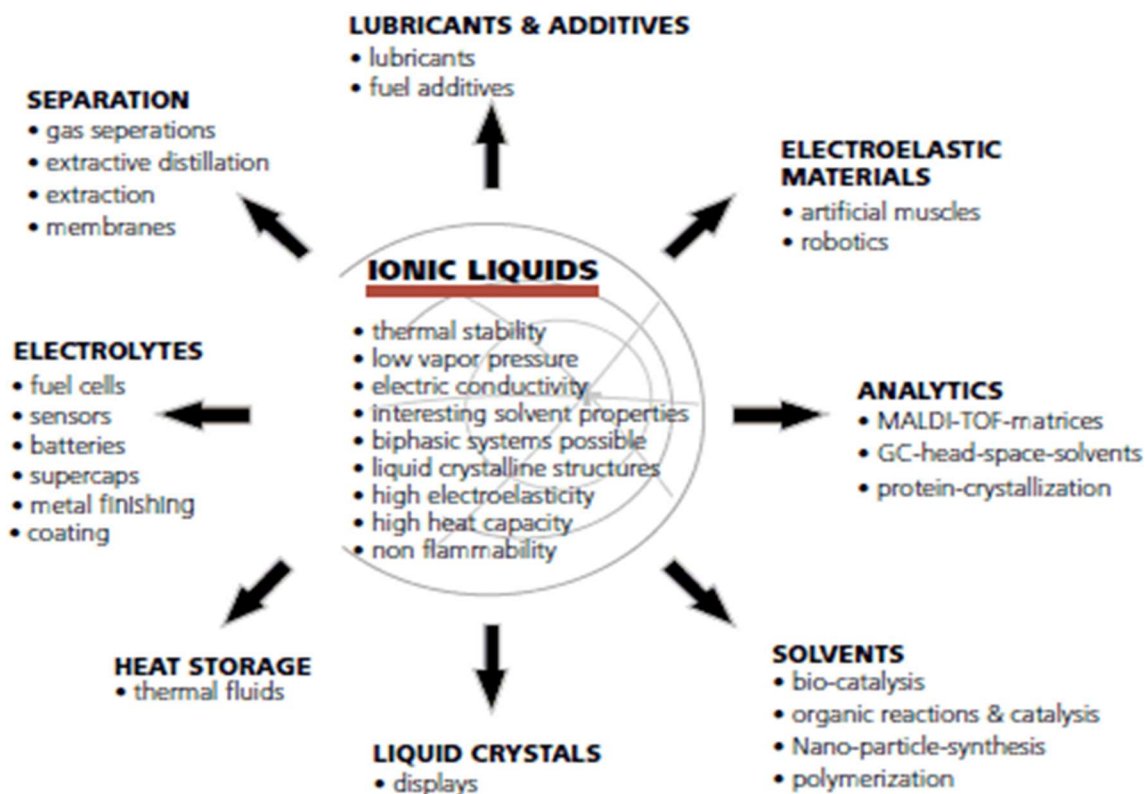
$$\nu = \frac{\eta}{\rho} \text{ [m}^2/\text{s]}$$

1.2 Ionic liquids

Ionic liquids are organic salts that remain at liquid state at room temperature. Often their melting point is below 100°C [4]. They have an ion delocalized charge preventing long chain formation or a stable crystal. [5] They are found to be green solvents or catalysts for organic reactions because of their unique characteristics. They are highly thermally, mechanically and electrochemically stable and non-flammable substances. Their standout property is its negligible vapour pressure [6] Because of this they are low volatility to any air pollution and also fully recyclable.

1.3 Use of ionic Liquids

Ionic liquids are characterised by their high densities and viscosities. They differ from the neutral small – molecule organic solvent counterparts by their low vapour pressure. [6]. Today in most of the areas applications, they use ILs because of its good characterises and the role it plays to be more environmentally friendly. It was investigated as a green solvents for energy application and industrial processes. Not only because it has the ability in dissolving many compounds but also used to form two-phase system [7]. The figure below give a brief summarise of the beneficiary use of ILs in different fields.



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www.sigmaaldrich.com/technical-documents/articles/chemfiles/ionic-liquids0.html

Figure 1. The common uses of ILs

There are still many more promising uses of Ionic liquid rising up. For example; for new research found that ILs are seen as a promising candidates for use in electric vehicles.

Due to the strong need for environmentally technologies ILs stand out their ability for dissolving cellulose and other natural polymers. This ionic liquid includes imidazolium based with acetate, chloride or alkyphosphate anions. [20]

1.4 Use of Ionic Liquids + mixtures

In the development process of cellulose using ILs attract a lot of attention in the last years. [30-36] they gain popularity as a means to access the attractive properties of individual ILs but in large scale they are less desirable characteristic. One of the main difficulties arises in the development of cellulose in ILs, is the high viscosity of ILs. In most case the viscosity increases especially in ILs which as chloride anion [20] and also in mixture it can also cause viscosity to increase significantly. For this reason ILs are often used in combination with co-solvent in order to reduce viscosity and enhance the transport properties. One of the main co-solvent that causes not precipitation of cellulose is dimethyl sulfoxide (DMSO). [20, 38 –

39]. Several published works has find interesting behaviour of mixture where the density and viscosity of several imidazolium chloride based IL are determine with co- solvent. [20] Additions of DMSO in mixture tend to decrease dramatically the viscosity. In additions the density decreases with temperature and with co-solvent concentration. Also the melting point increases with decrease concentration of co-solvent.

Chapter 2. Experimental

2.1 High pressure DMA 512 HPM Densitometer

Vibrant – tube densitometry is regarded to be a highly precise and relatively rapid technique for measuring densities under pressure. [17, 18] It is based on the measurement of the resonance frequency of a tube filled with fluid and excited electronically. [19] The high pressure densitometer used in this work, Anton Paar, DMA 512 HPM can be used up to 140 Mpa over a wide range of temperatures, from -10 to 200 °C. It is suitable for high accuracy determination of density at the range (0 to 30000) kg. m⁻³, with a resolution of 10⁻²kg.m⁻³[19]. The vibrating tube consist mainly of a thin “U” tube filled with the liquid which the density is determined. The temperature of the tube is controlled by recirculation using a mineral oil bath, Julabo F50, [20]. And inside the cell block having a Pt100 thermometer placed in the curve part of the “U” with an uncertainty of ±0.05 K. The pressure was controlled manually by manual piston and measured using a digital manometer GE Druck DPI 104. The manometer has an uncertainty of ±0.02 bar[20]. The DMA was connected to a mPDS 2000V3 evolution units which then give the vibration period with seven significant digits. [21]

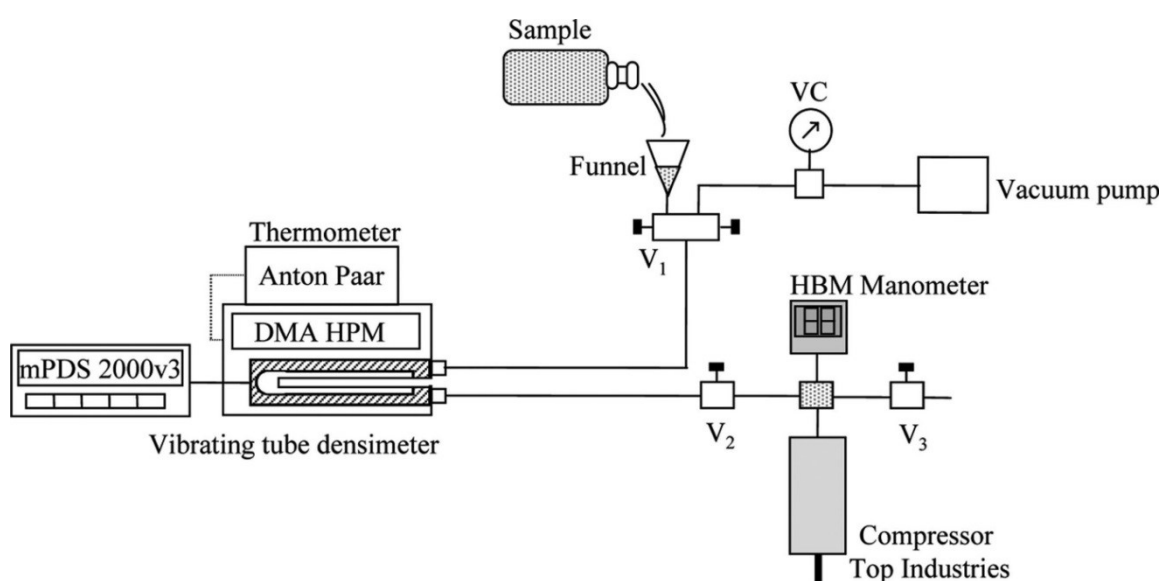


Figure 2. Illustration diagram of densitometer

For the calibration of the densitometer, pure water and vacuum were used because of their well-known density. Water used was distilled before measuring, nitrogen was put into the system to create vacuum approximately it takes a whole day. The vacuum period was then measured with different set of temperatures, as the values were shown in Table 2. With distilled water, the air bubbles inside were removed by boiling. The pure water was then added to the funnel and into the system, the bath then were put to a set temperature. Periods of the different pressure with the set temperature were measured; shown in table 2 below.

Density

Using the oscillation period of the vacuum and water, the density can be calculated with respect to temperature and pressure of interest. Using this values the two characteristic parameter of the apparatus A (T, p) and B (T, p) is defined.

$$\rho = A\tau^2 - B$$

$$\text{Density of water: } \rho_w = A\tau_w^2 - B$$

$$\text{Density of Vacuum: } 0 = A\tau_o^2 - B$$

Where τ_w = Period of water, τ_o = Period of vacuum, A and B = constant values (which is calculated).

Using Lagourette et al, we are able to substitute the equations with the know period of vacuum and water and density of water over all the (T, p) studies range. [26]

Derivatives of constant A and B

$$B = A\tau_o^2$$

$$\rho_w = A\tau_w^2 - A\tau_o^2 = A(\tau_w^2 - \tau_o^2)$$

$$A = \frac{\rho_w}{(\tau_w^2 - \tau_o^2)} = \rho_w / (\tau_w^2 - \tau_o^2)$$

For B

$$\rho_w = [\rho_w \tau_w^2 / (\tau_w^2 - \tau_o^2)] - B$$

$$B = [\rho_w \tau_w^2 / (\tau_w^2 - \tau_o^2)] - \rho_w$$

The density values of water have been taken from the equation of state of Wagner and Pruss [27]

2.2 Stabinger viscometer

Stabinger viscometers base their measurement on coquette measuring principle [22, 23]. The measuring cell consists of a tube that rotates at constant speed filled with the liquid to be measured. Inside this tube freely floats a measuring rotor. This rotor consists of a magnet that also rotates induced by the external movement of the tube. The shear force from the sample tend to drive the rotor while having magnetic effects retard its rotation. The rotating magnetic field can be measured and its speed determined. [22, 24] Changing rotor speed and size allows for the measurement of different ranges of viscosity.

Before the measurement start the rotor reaches equilibrium speed. This speed is a measure of fluid's viscosity. Kinematic viscosity can be calculated from it.

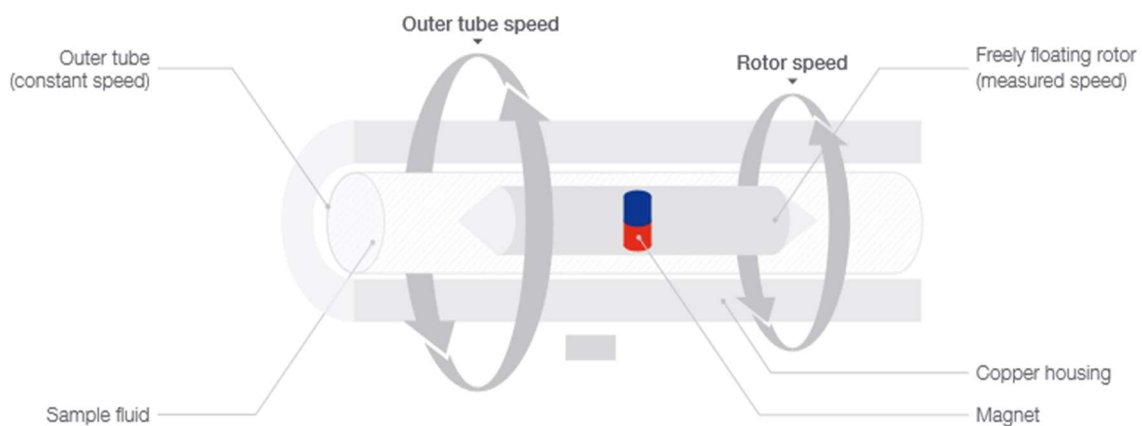


Figure3. Internal structure of Stabinger viscometer.

Density cell has quite similar principle to the vibrating tube densitometer. But it is capable for measure under atmosphere pressure. Base its measurement on the resonance frequency of a tube filled with fluid and the applied shear force. The viscosity of the fluid can affect the density measured by density cell.

The standard uncertainties of the apparatus were $u(T) = 0.02$ K, $u(\rho) = 0.05\%$ and $u(\eta) = 2\%$. Combining the expanded uncertainties with the level of confidence of 0.95 ($k = 2$) for the ILs were estimated from the standard uncertainties and the standard deviation of the density and viscosity measurements. [20, 30].

2.3 Experimental procedure

2.3.1 Densitometer and Measuring procedures

Calibrations of the thermometer

The Pt 100 probe was calibrated against a Standard Temperature probe using a controlled bath to set different temperatures, [20]. Thus the nominal temperature can be related to the real one. Results are shown next:

$$T_{\text{set}} = 0.9974 T + 0.4506$$

Table 1; Calibration values of thermometer Pt100

T (°C)	T _{set} (°C)	T (°C)	T _{set} (°C)
10	10.42	70	70.27
20	20.40	80	80.24
30	30.37	90	90.22
40	40.35	100	100.19
50	50.32	110	110.16
60	60.29	120	120.14

The density ρ as a function of pressure and temperature were measured with high pressure vibrating tube densitometer Anton Parr DMA HPM.

The DMA HPM was connected to mPDS 2000V3 evaluation unit, which the vibration period were then measured having set of certain temperature and pressure range. The system pressure was applied with a piston pressure intensifier. This calibration was done for an elevation of the densitometer to measure the response of the equipment, how much it has been change over a year. The measurement was made under two different conditions, firstly with the tube under vacuum and secondly with a known density fluid, which water was chosen (high purity distilled water). The conditions of pressure and temperature of two calibrations were the same for the final intended measuring conditions.

The measurement was done to understand density in different temperature and pressure conditions. A set of different pressure were taken, 20°C, 40°C, 60°C, 80°C 100°C, with pressure of 350Pa, 300Pa, 250Pa, 200Pa, 150Pa, 100Pa, 80Pa, 60Pa, 40Pa, 30Pa, 20Pa, 10Pa and 5Pa.

The vibration period of the cell was determined at different pressure. After each calibration the temperature of the liquid bath was change to another set temperature.

2.3.2 Viscometer and Measuring procedures

For the calibration of the Stabinger viscometer, toluene, water and air were used. Density and viscosity of toluene and water were measured in order to check the calibration. Both the deionized water and toluene were supplied by Sigma – Aldrich, toluene with a purity of 99.8%. Standard procedures set by the manufacturer were followed.

Preparation of samples

Chemical compound used in the measurement; DMSO has a purity of 99.9% and is also supplied by Sigma – Aldrich with humidity of ≈ 200 ppm. [20]; Choline acetate with NMR = 98% supplied by Iolitec; 1-ethyl-3-lmethyl imidazolium acetate (EMIM Ac) by Iolitec, $>95\%$. In additions, n – hexan with 99.0% purity with distilled water were used for cleaning. The ionic liquids were previously dried and degassed under vacuum at 60 °C during at least 48 h.

For this paper work two different set of mixtures were prepared for measurement. Mixture one with DMSO + choline acetate and mixture two DMSO + 1-ethyl-3-lmethyl imidazolium acetate (EMIM Ac). All components were weighed in a balance of ± 0.05 g precision. Both mixtures were prepared inside the dry box with ≈ 0.8 ppm, purposely to avoid moisture absorption from the air. After the procedure the water content of each mixture were measured using Karl Fisher titrator showing good results of humidity as it is shown in table 3 and table 4.

Measuring procedures

Ionic liquids are handled with extra care to avoid humidification; due to their ability of absorption of water as they are very hygroscopic [20]. Thus of this each samples of the two mixture were covered and kept carefully. Firstly, before measuring the mixtures in the viscometer, all the parts of the viscometer were taken out for cleaning and then fitted back. The viscometer is washed using first purified water, after hexane and then dried with air. The cleaning was done each time a sample is introduced into the device. Secondly, the sample to be measured was inserted into inlet using a syringe, slowly and carefully to prevent air bubbles. The air bubbles entering into the tube avoid stabilisation of the measurement. The

density and viscosity were measured by duplicated by increasing and subsequently decreasing the temperature. ChAc is solid at room temperature so some of the mixtures DMSO + ChAc are solid when concentration of the IL is high and Temperature is low enough. Only the samples that remain liquid after mixing were introduced to the viscometer. Melting point of each sample were measured using bath heated (Hart scientific). The mixture was prepared into a sealed vial and introduced in the bath while continuously stirred, then the temperature was slowly increased until complete melting of the crystals.

Chapter 3. Results and discussion

3.1 Calibration of the densitometer

The fluid selected for this present work was water (water deionized) because of its well-known density at atmospheric pressure and wide range of temperature.

The density, ρ , of a fluid is related to the vibrations period. To understand the relations between, density, temperature and period; the Lagourette hypothesis were taken into account [25]

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

This equation tends to present a good correlation with the properties.

Table 2. Values of the measured periods for water and vacuum.

P bar	$\tau_{40^\circ\text{C}} / \text{s}$	$\tau_{60^\circ\text{C}} / \text{s}$	$\tau_{80^\circ\text{C}} / \text{s}$	$\tau_{100^\circ\text{C}} / \text{s}$	$\tau_{120^\circ\text{C}} / \text{s}$
vacuum	1.867804	1.875495	1.883323	1.891305	#DIV/0!
5	1.990476	1.997832	2.005045	2.012077	2.019057
10	1.990515	1.997867	2.005077	2.012118	2.019096
20	1.990586	1.997944	2.005163	2.012194	2.019186
30	1.990667	1.998033	2.005247	2.012273	2.019264
40	1.990745	1.998103	2.005324	2.012353	2.019355
60	1.990897	1.998264	2.005474	2.012548	2.019534
80	1.991046	1.998422	2.005640	2.012708	2.019712
100	1.991196	1.998566	2.005797	2.012877	2.019886
150	1.991572	1.998952	2.006182	2.013286	2.020313
200	1.991953	1.999327	2.006573	2.013686	2.020743
250	1.992322	1.999707	2.006977	2.014107	2.021166
300	1.992688	2.000077	2.007355	2.014503	2.021577
350	1.993053	2.000453	2.007736	2.014904	2.021998

3.2 Drift calculations

In this work the drift of the high pressure densitometer is studied. The drift is indicative of how much the calibrations has changed over time. The last calibration was done in April, 2016

To evaluate the drift, density of water was calculated from the periods measured in this work and the calibration parameters determined for the previous calibration. These values are compared to those using the current calibration (the literature values).

$$\% \text{ drift} = \frac{\rho_w^{\text{last}} - \rho_w^{\text{current}}}{\rho_w^{\text{current}}} 100$$

Where ρ_w^{last} is the density of water calculated using the last older calibration and ρ_w^{current} is the density of water calculated using the current calibration that is the same than the literature values.

Table 3. Values for the drift of the calibration between April 2016 and April 2018

P / bar	%drift (40 °C)	%drift (60 °C)	%drift (80 °C)	%drift (100 °C)
5	-0.030	-0.048	0.043	-0.039
10	-0.030	-0.051	0.039	-0.036
20	-0.028	-0.054	0.046	-0.040
30	-0.026	-0.044	0.051	-0.044
40	-0.024	-0.046	0.048	-0.047
60	-0.025	-0.047	0.041	-0.027
80	-0.028	-0.046	0.044	-0.033
100	-0.019	-0.047	0.046	-0.028
150	-0.013	-0.039	0.025	-0.032
200	0.001	-0.045	0.023	-0.054
250	-0.006	-0.039	0.035	-0.036
300	-0.008	-0.043	0.047	-0.042
350	-0.009	-0.045	0.034	-0.039

3.3 Percentage (%) of drift Vs Pressure

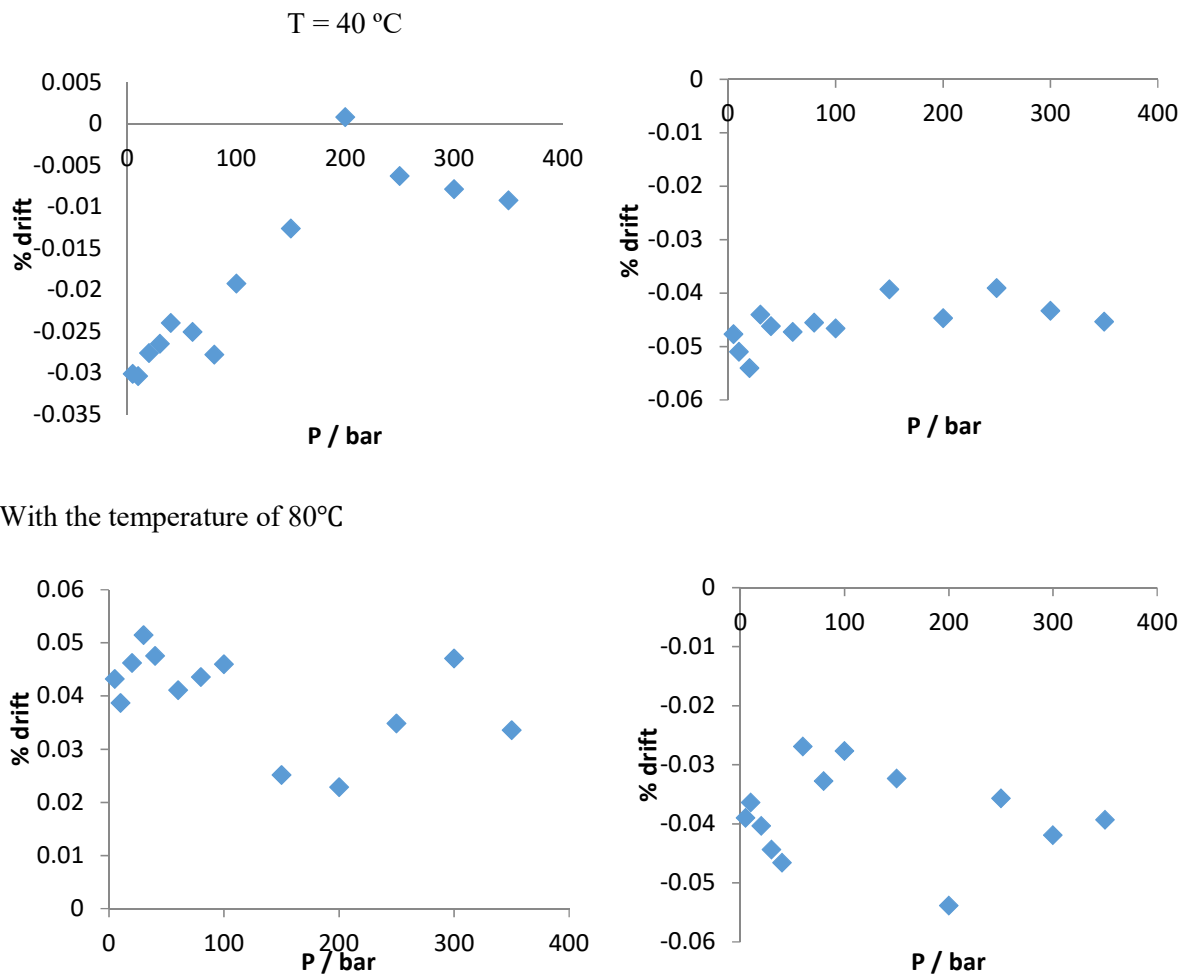


Figure 4: Drift vs pressure of the calibration between April 2016 and April 2018

From the drift calculation, it shows that the calibrations have not change much over the year. All values have presented to be below 0.1% compare with the last calibrations. The drift values gives all negative values except at 80°C where the drift values tend to be positive. The drift is apparently non dependant on the pressure except at 40 °C which appear to be slightly higher at lower pressure.

Chapter 4

System of Choline Acetate + DMSO (Dimethyl sulfoxide)

4.1 Analysis of the samples (Melting point and water content)

Table 4 melting points and water content for the mixtures Choline Acetate + DMSO

X_{DMSO}	MP / °C	Moisture / ppm
1.0	liquid	385.4
0.9	liquid	1215
0.8	35.53	1133
0.7	48.25	1169
0.6	57.68	3600
0.5	67.23	4696

4.2 Density and viscosity

Densities at different DMSO molar fractions as a function of temperature presented in table 1 below. The densities at each molar fractions was also represented on graph, as densities verse temperature and density versus kinematic viscosity.

Table 5a) $\chi_{\text{DMSO}} = 1.0$, $\chi_{\text{ch Ac}} = 0$

T/ °C	$\rho(\text{g/m}^3)$	η (mPa.s)	$\nu(\text{m}^2\text{s}^{-1})$
20	1.1002	2.44335	2.22082349
30	1.09015	2.02555	1.85804706
40	1.08035	1.7023	1.57569306
50	1.0702	1.4643	1.36824893
60	1.0603	1.27825	1.20555503
70	1.05015	1.13485	1.08065514
80	1.04015	1.0135	0.9743787
90	1.0299	0.91097	0.88452277
100	1.0198	0.81224	0.7964699

Table 5b) $\chi_{\text{DMSO}} = 0.9$, $\chi_{\text{ch Ac}} = 0.1$

T/ °C	$\rho(\text{g/m}^3)$	η (mPa.s)	$\nu(\text{m}^2\text{s}^{-1})$
20	1.1027	5.76390	5.22707899
30	1.0939	4.45145	4.06933906
40	1.0851	3.54295	3.26524123
50	1.0763	2.89750	2.69221835
60	1.0674	2.42055	2.26770658
70	1.0586	2.05675	1.94289628
80	1.0498	1.77315	1.68911646
90	1.0409	1.54835	1.48751081
100	1.0323	1.36175	1.31914172

Table 5c) $\chi_{\text{DMSO}} = 0.8$, $\chi_{\text{ch Ac}} = 0.2$

T/ °C	$\rho(\text{g/m}^3)$	η (mPa.s)	$\nu(\text{m}^2\text{s}^{-1})$
35.53	1.08960*		6.93*
40	1.08600	6.786850	6.24940147
50	1.07790	5.333250	4.9478152
60	1.06995	4.306850	4.02528156
70	1.06185	3.559950	3.35259217
80	1.05375	2.986500	2.8341637
90	1.04565	2.540050	2.4291589
100	1.03760	2.194750	2.11521781

* This value was extrapolated to the melting temperature

Table 5d) $\chi_{\text{DMSO}} = 0.7$, $\chi_{\text{ch Ac}} = 0.3$

T/ °C	$\rho(\text{g/m}^3)$	η (mPa.s)	$\nu(\text{m}^2\text{s}^{-1})$
48.25 MP	1.08089*		10.91*
50	1.07965	11.25050	10.4205066
60	1.07230	8.63240	8.05035904
70	1.06500	6.82050	6.40422535
80	1.05765	5.53025	5.22880915
90	1.05045	4.57050	4.35099243
100	1.04330	3.84330	3.68379181

* This value was extrapolated to the melting temperature

Table 5e) $\chi_{\text{DMSO}} = 0.6$, $\chi_{\text{ch Ac}} = 0.4$

T/ °C	$\rho(\text{g/m}^3)$	η (mPa.s)	$\nu(\text{m}^2\text{s}^{-1})$
57.68 MP	1.07515107*		14.83*
60	1.07360	14.92750	13.9041542
70	1.06670	11.33550	10.6266992
80	1.05985	8.87160	8.37061848
90	1.05305	7.12440	6.76549072
100	1.04640	5.84460	5.58543578

* This value was extrapolated to the melting temperature

Table 5f) $\chi_{\text{DMSO}} = 0.5$, $\chi_{\text{ch Ac}} = 0.5$

T/ °C	$\rho(\text{g/m}^3)$	η (mPa.s)	$\nu(\text{m}^2\text{s}^{-1})$
67.23 MP	1.06898394*		19.77*
70	1.0673	19.4925	18.2633749
80	1.06085	14.6755	13.8337182
90	1.0546	11.384	10.7946141
100	1.04835	9.04035	8.62340821

* This value was extrapolated to the melting temperature

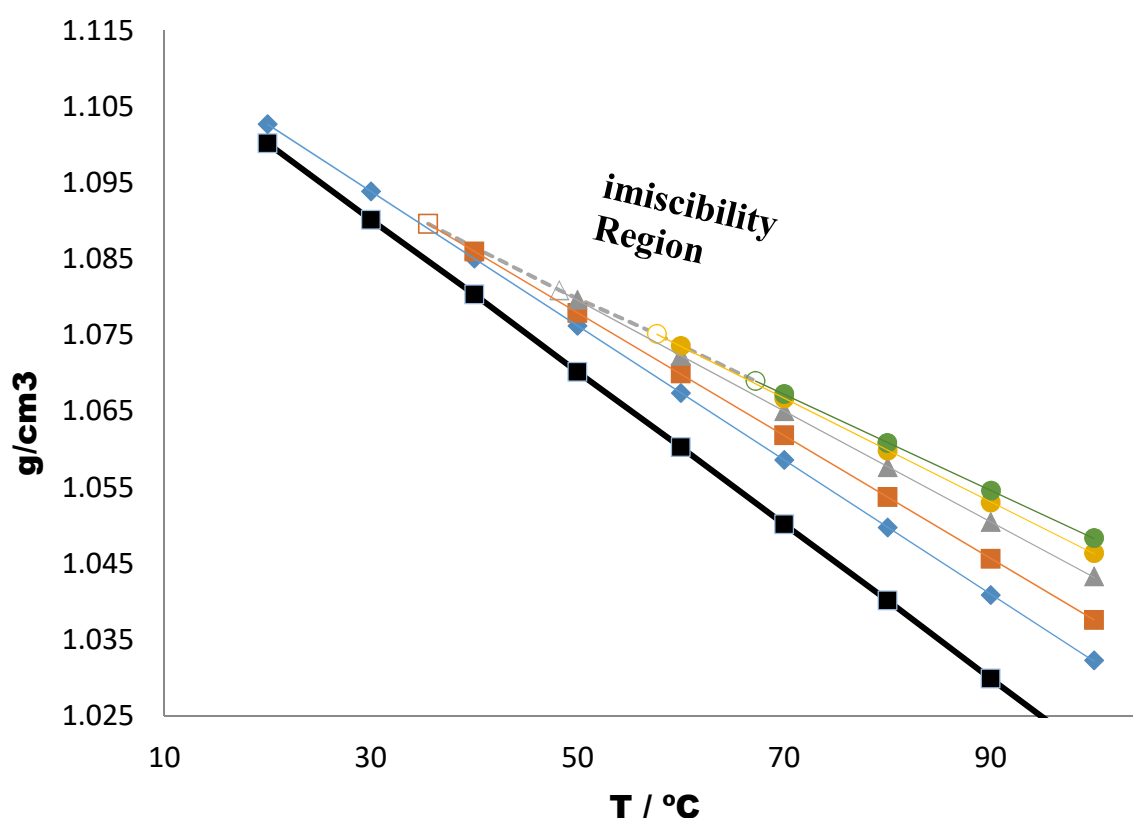


Figure 5: Density values of mixture DMSO + choline acetate

The graph above shows the density with respect to temperature and the behaviour of mixture compositions of DMSO with choline acetate. When having high concentration of DMSO in the mixture the density is less, in comparison to the increase concentrations of choline acetate. Ch Ac increases in the mixture tends to increase the density dramatically. For instance, when the solution with $\chi_{\text{DMSO}} = 0.9$ with $\chi_{\text{ch Ac}} = 0.1$ is less dense; $\chi_{\text{DMSO}} = 0.5$ with $\chi_{\text{ch Ac}} = 0.5$ more dense. In additions the increase concentrations of Ch Ac give an increase in melting point. Above the imiscibility region the mixture were not able to be measured thus of the region becoming two phase system.

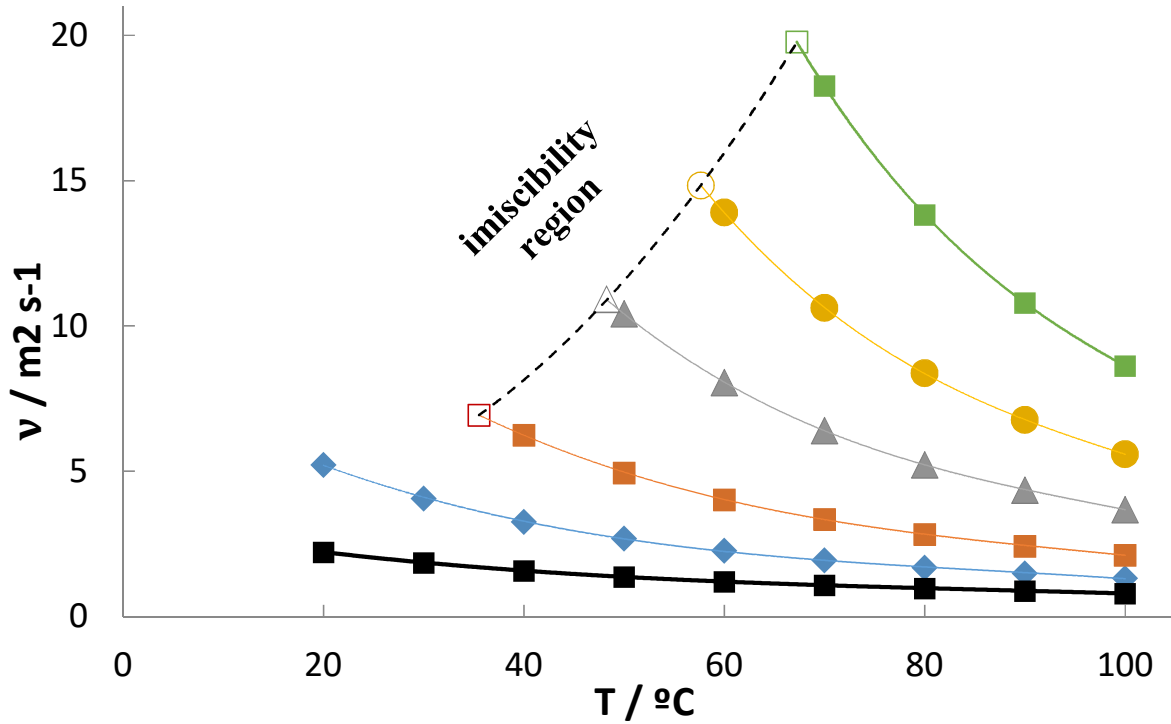


Figure 6: kinematic viscosity values of mixture DMSO + choline acetate

The graph shows the kinematic viscosity behaviour of different concentrations of DMSO in the mixture. Similar to density, when the DMSO decreases with increasing concentration of Ch Ac in the mixture; the kinematic viscosity increase rapidly. At concentration of $\chi_{\text{DMSO}} = 0.9$ this kinematic viscosity is less compare to $\chi_{\text{DMSO}} = 0.5$ which the viscosity increases rapidly.

Chapter 5

System of 1-ethyl-3-methyl imidazolium acetate (EMIM Ac) + DMSO (Dimethyl sulfoxide)

For the mixtures of EMIM Ac + DMSO, the densities represent as a function of temperature with varying kinematic viscosity. Table (3/-a,b,c,d,e,f,g,h,I,j,k) present values of the densities in different compositions range of DMSO.

5.1. Analysis of the samples (water content)

Table 6. Water content in Mixture DMSO + EMIM Ac

X_{DMSO}	Moisture / ppm
0.05	2126.15
0.1	2093.35
0.2	3049.75
0.3	2961.7
0.4	2152.1
0.5	1954.5
0.6	1580.15
0.7	1725.5
0.8	1654.55
0.9	1670.95
1.0	385.4

5.2 Density and viscosity

Table 7a. $\chi_{\text{DMSO}} = 0.05$, $\chi_{\text{EMIM Ac}} = 0.95$

T/ °C	$\rho(\text{g/m}^3)$	η (mPa.s)	$\nu(\text{m}^2\text{s}^{-1})$
20	1.1024	194.235	176.192852
30	1.0963	100.495	91.6674268
40	1.09025	59.52	54.5929833
50	1.0842	38.329	35.3523335
60	1.0781	26.329	24.4216677
70	1.072	18.961	17.6875
80	1.0661	14.233	13.35053
90	1.0601	11.039	10.4131686
100	1.0541	8.7956	8.34417987

Table 7b. $\chi_{\text{DMSO}} = 0.1$, $\chi_{\text{EMIM Ac}} = 0.90$

T/ °C	$\rho(\text{g/m}^3)$	η (mPa.s)	$\nu(\text{m}^2\text{s}^{-1})$
20	1.10295	158.605	143.800716
30	1.0969	86.4405	78.8043577
40	1.09075	52.1865	47.8446023
50	1.0845	34.062	31.4080221
60	1.0783	23.645	21.9280349
70	1.07215	17.223	16.0639836
80	1.0661	13.0365	12.228215
90	1.05995	10.1855	9.60941554
100	1.054	8.17435	7.75555028

Table 7c. $\chi_{\text{DMSO}} = 0.2$, $\chi_{\text{EMIM Ac}} = 0.80$

T/ °C	$\rho(\text{g/m}^3)$	η (mPa.s)	$\nu(\text{m}^2\text{s}^{-1})$
20	1.1038	120.765	109.408407
30	1.0975	68.23	62.1685649
40	1.09115	42.36	38.8214269
50	1.0848	28.2855	26.0743916
60	1.0784	19.966	18.5144659
70	1.0722	14.7455	13.7525648
80	1.0659	11.2805	10.5830753
90	1.05975	8.88095	8.38023119
100	1.0536	7.1573	6.79318527

Table 7d. $\chi_{\text{DMSO}} = 0.3$, $\chi_{\text{EMIM Ac}} = 0.70$

T/ °C	$\rho(\text{g/m}^3)$	η (mPa.s)	$\nu(\text{m}^2\text{s}^{-1})$
20	1.10485	80.385	72.7564828
30	1.09835	47.6835	43.413757
40	1.09175	30.7415	28.1580032
50	1.08515	21.1415	19.48256
60	1.07865	15.3055	14.1894961
70	1.0721	11.535	10.7592575
80	1.0656	8.98395	8.43088401
90	1.0593	7.1951	6.79231568
100	1.05285	5.89315	5.59733105

Table 7e. $\chi_{\text{DMSO}} = 0.4$, $\chi_{\text{EMIM Ac}} = 0.60$

T/ °C	$\rho(\text{g/m}^3)$	η (mPa.s)	$\nu(\text{m}^2\text{s}^{-1})$
20	1.10575	54.007	48.8419625
30	1.09895	33.579	30.5555303
40	1.0922	22.479	20.5813953
50	1.0853	15.9285	14.6765871
60	1.07865	11.8125	10.951189
70	1.0718	9.08405	8.47550849
80	1.06515	7.19925	6.7589072
90	1.0584	5.84295	5.52054989
100	1.0518	4.8463	4.60762502

Table 7f. $\chi_{\text{DMSO}} = 0.5$, $\chi_{\text{EMIM Ac}} = 0.5$

T/ °C	$\rho(\text{g/m}^3)$	η (mPa.s)	$\nu(\text{m}^2\text{s}^{-1})$
20	1.10655	37.337	33.7418101
30	1.0995	24.236	22.0427467
40	1.0924	16.789	15.3689125
50	1.0854	12.2445	11.2810945
60	1.0783	9.29925	8.62399147
70	1.0713	7.3014	6.81545785
80	1.06435	5.8922	5.53596092
90	1.05745	4.86505	4.60073762
100	1.0506	4.09305	3.89591662

Table 7g. $\chi_{\text{DMSO}} = 0.6$, $\chi_{\text{EMIM Ac}} = 0.4$

T/ °C	$\rho(\text{g/m}^3)$	η (mPa.s)	$\nu(\text{m}^2\text{s}^{-1})$
20	1.10735	23.702	21.4042534
30	1.0999	16.1505	14.6836076
40	1.09245	11.641	10.6558653
50	1.0851	8.76095	8.07386416
60	1.07775	6.8416	6.3480399
70	1.0704	5.4906	5.1294843
80	1.0631	4.5213	4.25293952
90	1.05575	3.78795	3.58792328
100	1.0485	3.22925	3.07987601

Table 7h. $\chi_{\text{DMSO}} = 0.7$, $\chi_{\text{EMIM Ac}} = 0.3$

T/ °C	$\rho(\text{g/m}^3)$	η (mPa.s)	$\nu(\text{m}^2\text{s}^{-1})$
20	1.1076	15.3655	13.872788
30	1.09985	10.9165	9.92544438
40	1.092	8.13855	7.45288462
50	1.0843	6.3049	5.81471917
60	1.07655	5.041	4.68255074
70	1.06885	4.13395	3.86766151
80	1.06115	3.46415	3.26452434
90	1.05355	2.9545	2.80432822
100	1.046	2.5575	2.44502868

Table 7i. $\chi_{\text{DMSO}} = 0.8$, $\chi_{\text{EMIM Ac}} = 0.2$

T/ °C	$\rho(\text{g/m}^3)$	η (mPa.s)	$\nu(\text{m}^2\text{s}^{-1})$
20	1.10715	8.2368	7.43964232
30	1.09875	6.1993	5.64213879
40	1.09035	4.84915	4.44733343
50	1.082	3.914	3.61737523
60	1.0737	3.2417	3.01918599
70	1.06535	2.74195	2.5737551
80	1.0571	2.35965	2.23219185
90	1.0488	2.059	1.96319603
100	1.0404	1.8172	1.74663591

Table 7j. $\chi_{\text{DMSO}} = 0.9, \chi_{\text{EMIM Ac}} = 0.1$

T/ °C	$\rho(\text{g/m}^3)$	η (mPa.s)	$\nu(\text{m}^2\text{s}^{-1})$
20	1.10535	4.57455	4.1385534
30	1.0963	3.58485	3.26995348
40	1.0873	2.8952	2.66274257
50	1.0783	2.3962	2.22220161
60	1.06925	2.02485	1.89371054
70	1.06025	1.73785	1.63909455
80	1.05125	1.51115	1.43747919
90	1.04225	1.33005	1.27613337
100	1.0332	1.18035	1.1424216

Table 7k. $\chi_{\text{DMSO}} = 1.0 \chi_{\text{EMIM Ac}} = 0$

T/ °C	$\rho(\text{g/m}^3)$	η (mPa.s)	$\nu(\text{m}^2\text{s}^{-1})$
20	1.1002	2.44335	2.22082349
30	1.09015	2.02555	1.85804706
40	1.08035	1.7023	1.57569306
50	1.0702	1.4643	1.36824893
60	1.0603	1.27825	1.20555503
70	1.05015	1.13485	1.08065514
80	1.04015	1.0135	0.9743787
90	1.0299	0.91097	0.88452277
100	1.0198	0.81224	0.7964699

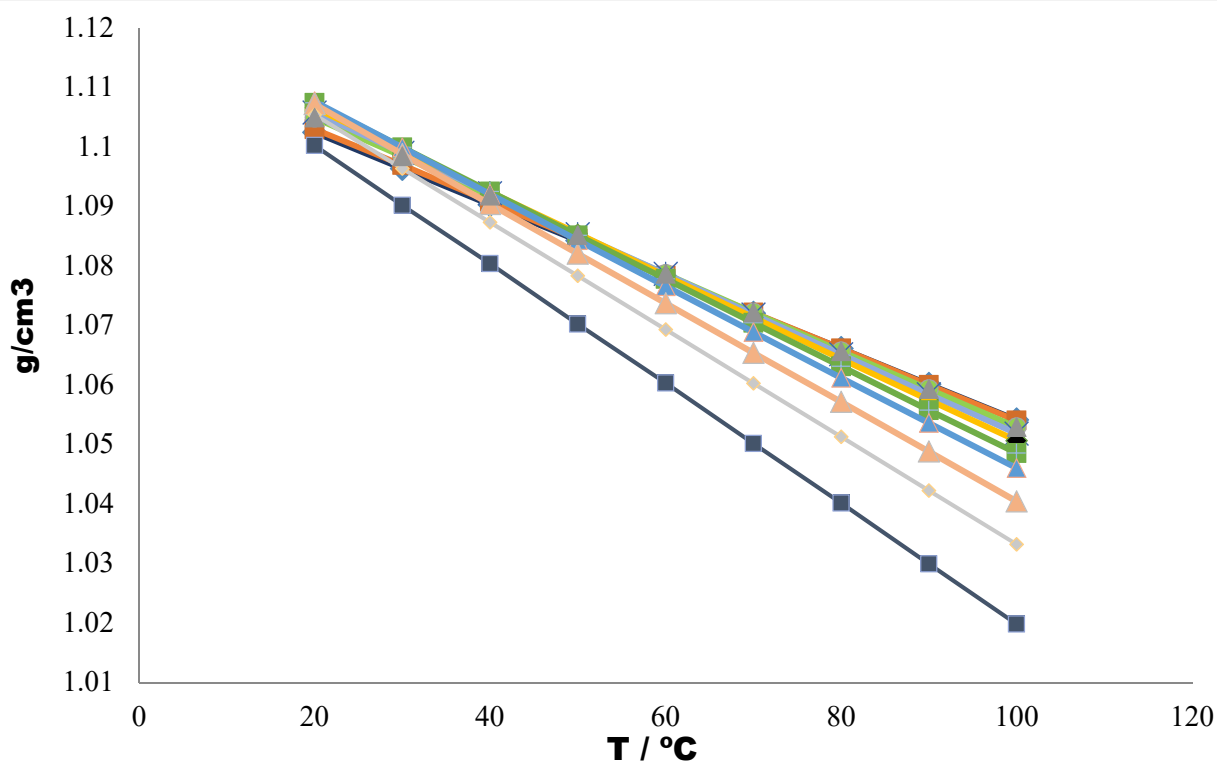


Figure 7: Density values of mixture DMSO + EMIM Ac

The graph present the density values of different composition mixture of DMSO with EMIM Ac. With the pervious results of DMSO and Ch Ac, this result falls in a quite similar way. As the concentration of DMSO increases the densities decrease; but increases rapidly with increasing of EMIM Ac in the mixture. In additions the mixtures of DMSO with EMIM Ac keep its liquid state in room temperature.

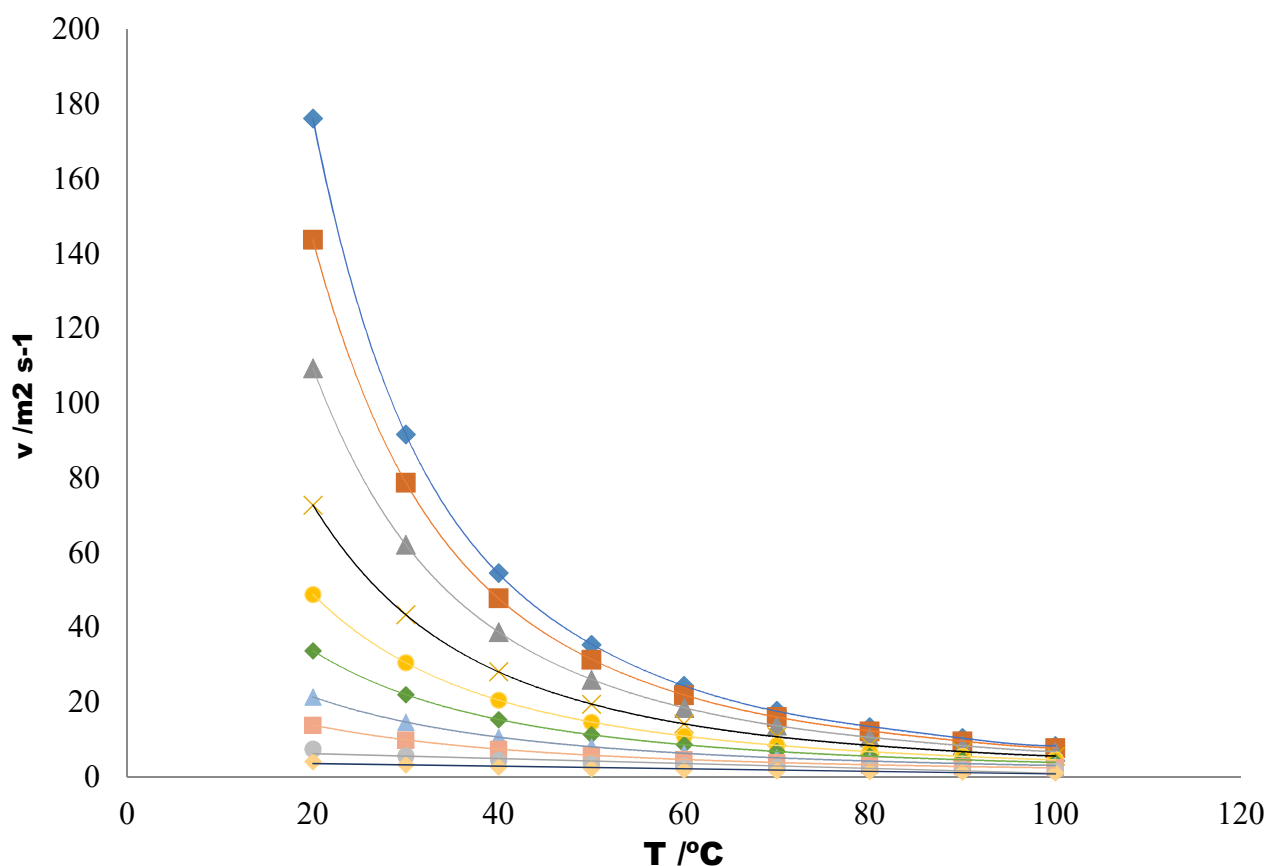


Figure 8: Viscosity values of mixture DMSO + EMIM Ac

The graph shows the viscosity of the mixture DMSO with EMIM Ac as a function respect to temperature. Kinematic viscosity decrease with large concentration of DMSO in the mixture and grow with kinematic viscosity with more concentration of EMIM Ac in the mixture. For instance; with composition $\chi_{\text{DMSO}} = 0.05$ with $\chi_{\text{EMIM Ac}} = 0.95$ the value of kinematic viscosity is greater compare to $\chi_{\text{DMSO}} = 0.9$ with $\chi_{\text{EMIM Ac}} = 0.1$

Chapter 6. Conclusions

In this work density and viscosity of mixtures Dimethyl sulfoxide (DMSO) plus choline acetate (Ch Ac, 2 – Hydroxyethyl – trimethylammonium acetate) and of DMSO plus 1-ethyl-3-methyl imidazolium acetate (EMIM Ac) at range of concentrations with temperatures were determined.

With mixture one DMSO + Ch Ac at a range of concentration; molar fraction $\chi_{\text{DMSO}} = 0.5, 0.6, 0.7, 0.8, 0.9$ and 1.0. The concentration of DMSO in the mixture was not able to less because of Ch Ac extremely increasing of viscosity. Different temperature range were use in different composition, thus of each concentration having different melting point.

For mixture two DMSO + EMIM Ac at the range of concentration; molar fraction $\chi_{\text{DMSO}} = 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$ and 1.0 with temperatures (20°C to 100°C) were used in determining of density and kinematic viscosity. The melting point has not been measured because the mixtures remain liquid phase in room temperature.

The density and kinematic viscosity, both gives a linear trend with temperature, increasing in ionic liquid concentration and decreasing with the temperature.

For the drift elevation the calibrations has shown to have not changed a lot, presenting drift values below 0.1%.

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References

1. José J. Segovia ^{a,b,*}, Olivia Fandiño ^a, Enriqueta R. López ^a, Luis Lugo^{a,M³}. Carmen Martín ^b, Josefa Fernández ^a Automated densimetric system: Measurements and uncertainties for compressed fluids.
2. www.viscositycontrol.co.uk/viscosity%20applications.html.
3. María J. P. Comuñas,^{*,†,‡} Jean-Patrick Bazile,[†] Antoine Baylaucq,[†] and Christian Boned[†]. Density of Diethyl Adipate using a New Vibrating Tube Densimeter from (293.15 to 403.15) K and up to 140 MPa. Calibration and Measurements.
4. www.researchgate.net/post/Define_Ionic_Liquids
www.electrochem.org/dl/interface/spr/spr07/spr07_p38.pdf.
5. Rasike De Silva . Kylie Vongsanga . Xungai Wang . Nolene Byrne. Cellulose regeneration in ionic liquids: factors controlling the degree of polymerization.
6. Matthew T. Clough,^a Karolin Geyer,^{*b} Patricia A. Hunt,^a Sunghee Son,^b Uwe Vagtb and Tom Welton^{*a}. Ionic liquids: not always innocent solvents for cellulose[†]
7. www.electrochem.org/dl/interface/spr/spr07/spr07_p38.pdf.
8. H. Niedermeyer, J. P. Hallett, I. J. Villar-Garcia, P. A. Hunt and T. Welton, Chem. Soc. Rev., 41, 7780 (2012).
9. G. Chatel, J. F. B. Pereira, V. Debbeti, H. Wang and R. D. Rogers, Green Chem., 16, 2051 (2014).
10. Sharon I. Lall-Ramnarine^{*a}, Eddie D. Fernandez, Chanele Rodriguez, Sujun Weia, Surajdevprakash B. Dhiman^b, and James F. Wishart^{*b}. Transport Properties of Ionic Liquid Mixtures Containing Heterodications
11. A. M. Pinto, H. Rodriguez, Y. J. Colon, A. Arce, A. Arce and A. Soto, Ind. Eng. Chem. Res., 52, 5975 (2013).
12. [E. Thoms](#), [P. Sippel](#), [D. Reuter](#), [M. Weiß](#), [A. Loidl](#), [S. Krohns](#). Dielectric study on mixtures of ionic liquids.
13. www.thoughtco.com/thermodynamics-overview-2699427.
14. Arun S. Wagh, Thermodynamic Basis of CBPC Formation in Chemically Bonded Phosphate Ceramics (Second Edition), 2016.
15. D.W. Oxtoby, N.H. Nachtrieb, W.A. Freeman Chemistry of Change Saunders Publishers, London (1990).
16. Mm
17. W.Wagner, R. Kleinrahm, H.W. Losch, J.T.R. Watson, V. Majer, A.A. Padua, L.A. Woolf, J.C. Holste, A.M.F. Palavra, K. Fujii, J.W. Stansfeld, Measurements of the Thermodynamic Properties of Single Phases, Elsevier, Amsterdam, 2003.
18. A.M.F. Palavra, M.A. Tavares Cardoso, J.A.P. Coelho, M.F.B. Mourato, Chem. Eng. Technol. 30 (2007) 689 – 694.
19. José J. Segovia ^{a,b,*}, Olivia Fandiño ^a, Enriqueta R. López ^a, Luis Lugo^{a,M³}. Carmen Martín ^b, Josefa Fernández ^a . Automated densimetric system: Measurements and uncertainties for compressed fluids.
20. Laura de Pablo Nisa ^{1,2}, José J. Segovia ², Ángel Martín¹, M. Carmen Martín², M. Dolores Bermejo ^{1*} Determination of density and excess molar volume of dimethyl sulfoxide + 1-allyl-3methylimidazolium chloride mixtures at high pressure
21. María J. P. Comuñas,^{*,†,‡} Jean-Patrick Bazile,[†] Antoine Baylaucq,[†] and Christian Boned[†] . Density of Diethyl Adipate using a New Vibrating Tube Densimeter from (293.15 to 403.15) K and up to 140 MPa. Calibration and Measurements.
22. ¹www.sp.se/en/index/services/temperature/powerplantefficiency/measurementprinciple/Sidor/default.aspx / ²wiki.anton-paar.com/en/how-to-measure-viscosity/.

23. www.anton-paar.com/?eID=documentsDownload&document=58424&L=5.
24. H. STABINGER, W. BELITSCH Labor für Messtechnik, Dr. Robert-Graf-Straße 6, A-8010 Graz, AUSTRIA; e-mail: belitsch@lab-stabinger.at THE STABINGER VISCOMETER –
25. B. Lagourette, C. Boned, H. Saint-Guirons, P. Xans, H. Zhou, *Meas. Sci. Technol.* 3 (1992) 699–703.
26. Lagourette, B.; Boned, C.; Saint-Guirons, H.; Xans, P.; Zhou, H. Densimeter Calibration Method Versus Temperature and Pressure *Meas. Sci. Technol.* **1992**, 3, 699.)
27. W. Wagner, A. Pruss, *J. Phys. Chem. Ref. Data* 31 (2002) 387–535.
28. R. Sescousse, K.A. Le, M.E. Ries, T. Budtova, Viscosity of cellulose-imidazolium-based Ionic liquid solutions, *J. Phys. Chem. B.* 114 (2010) 7222–7228. doi:10.1021/jp1024203
29. Yuya Hiraga,[†] Aya Kato,[†] Yoshiyuki Sato,[‡] and Richard L. Smith, Jr.,^{*},[†],[‡]
[†]Graduate School of Environmental Studies, and [‡]Research Center of Supercritical Fluid Technology, Tohoku University, Aramaki.
30. M. Parra Jimenez de la, Cristina; Navarrete, Alexander; Dolores Bermejo, M. Jose Cocero, Patents Review on Lignocellulosic Biomass Processing Using Ionic Liquids, *Recent Pat. Eng.* 6 (2012) 159–182. doi: 10.2174/187221212804583231.
31. J. Vitz, T. Erdmenger, C. Haensch, U.S. Schubert, Extended dissolution studies of cellulose in imidazolium based ionic liquids, *Green Chem.* 11 (2009) 417. doi: 10.1039/b818061j.
32. S. Zhu, Y. Wu, Q. Chen, Z. Yu, C. Wang, S. Jin, Y. Ding, G. Wu, Dissolution of cellulose with ionic liquids and its application: a mini-review, *Green Chem.* 8 (2006) 325. Doi: 10.1039/b601395c.
33. Z. Meng, X. Zheng, K. Tang, J. Liu, S. Qin, Dissolution of natural polymers in ionic liquids: A review, *E-Polymers.* (2012) 1–29. doi:10.1515/epoly.2012.12.1.317.
34. T. Suopajarvi, J.A. Sirviö, H. Liimatainen, Nanofibrillation of deep eutectic solvent treated paper and board cellulose pulps, *Carbohydr. Polym.* 169 (2017) 167–175. doi:10.1016/j.carbpol.2017.04.009.
35. A.A. Elgharbawy, M.Z. Alam, M. Moniruzzaman, M. Goto, Ionic liquid pretreatment as emerging approaches for enhanced enzymatic hydrolysis of lignocellulosic biomass, *Biochem. Eng. J.* 109 (2016) 252–267. doi:10.1016/j.bej.2016.01.021.
36. J.F. Brennecke, E.J. Maginn, Ionic liquids: Innovative fluids for chemical processing, *AIChE J.* 47 (2001) 2384–2389. doi:10.1002/aic.690471102.
37. C. Cuissinat, P. Navard, T. Heinze, Swelling and dissolution of cellulose. Part IV: Free floating cotton and wood fibres in ionic liquids, *Carbohydr. Polym.* 72 (2008) 590–596. doi:10.1016/j.carbpol.2007.09.029.
38. X. Wang, H. Li, Y. Cao, Q. Tang, Cellulose extraction from wood chip in an ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl), *Bioresour. Technol.* 102 (2011) 7959–7965. doi:10.1016/j.biortech.2011.05.064.
39. D. A. Fort, R.C. Remsing, R.P. Swatloski, P. Moyna, G. Moyna, R.D. Rogers, Can ionic liquids dissolve wood? Processing and analysis of lignocellulosic materials with 1-nbutyl-3-methylimidazolium chloride, *Green Chem.* 9 (2007) 63. doi:10.1039/b607614a.