

Experimental Study of Characteristics Rheological of an ionic liquid

SOUDANI Youcef¹, KARAS Abdelkader², MAZOUZI Ridha², BELARBI El habib¹

¹*LSCT Synthesis and Catalysis Laboratory, Ibn Khaldoun University, Tiaret, Algeria*

²*Laboratory of Industrial Fluids, Measurement and Application (FIMA) University Djilali Bounâama, Khemis-Miliana, Algeria,*

Soudani.youcef94@gmail.com

karasaek@yahoo.fr

r.mazouzi@univ-dbkm.dz

Belarbi.hb@gmail.com

Abstract - Ionic liquids (IL) are a class of new solvents which have been increasingly used in a wide variety of applications in recent years due to an astonishing number of desirable properties. However, the rheological properties of ionic liquids have not been studied in detail, and there is currently confusion as to the choice of mathematical models for this type of fluid. To advance the current state of knowledge, a laboratory study was carried out to investigate constant shear viscosity. The flow characteristics of ionic liquid (1-Ethyl-3-methylimidazolium thiocyanate) were determined over a temperature range (20–60C) using the geometry of the coaxial cylinder using the Anton Paar MRC 302 Rheometer. finds that the Herschel-Bulkley model is more accurate in describing the flow properties of ionic liquid.

Keywords—Ionic liquids, viscosity, Rheology.

I. INTRODUCTION

Ionic liquids (LIs) are salts comprising ions, which exist in the liquid state at room temperature. They have many unique physical and chemical properties such as negligible vapor pressure, thermal and chemical stability, high ionic conductivity, and excellent solubility of many substances [1]. Several studies have been reported on the use of LI without reaction solvents [2], separate extraction solvents [3] and electrolytic materials [4, 5]. They can also be used as covering elements in polymers [6, 7]. From the point of view of processing and application, the mechanical and rheological properties of LI are of vital importance [8].

Rheological analysis of these liquids is of great importance in determining even minimal changes in morphology. Due to the "notorious" differences related to the measurement of the rheology of LI, significant gaps in the knowledge on the study of flow properties remained large.

The rheological properties of LI are of major interest due to the increasing number of industrial applications of these new materials. These properties provide key information on the molecular basis of these fluids, as well as the values needed for engineering design.

Viscosity is one of the most important rheological properties of liquids, as a transport property, has a great effect on the rate of mass transferred, and therefore, the viscosity of the solvent is an important factor in all chemical processes and design [9]. Their biodegradable character, their low production cost and their simple chemical reaction, they tend to be very soluble in water and polar compounds (alcohols, acids, etc.), which considerably increases their potential importance in industrial terms [9].

In rheological studies, parameters such as temperature and composition must be taken into account.

The objectives of this research study are: (i) to study the variation of viscosity as a function of the shear rate, (ii) to obtain a mathematical model to properly describe the rheological behaviors of LI, finally, to study the effect of temperature on the rheological behavior of this liquid.

II. EXPERIMENTAL SECTION

In this study, the ionic liquid used is 1-Ethyl-3-methylimidazolium thiocyanate $\geq 95\%$ HPLC H-NMR, marketed by the company SIGMA-ALDRICH. This ionic liquid has the formula $C_7H_{11}N_3S$, and its molar mass is 129.25 g/mol.

Stable shear experiments were carried out using a dynamic rheometer (Anton Paar MRC 302), which is equipped at the Laboratory of Industrial Fluids, Measurements and Application (FIMA) DjilaliBounâama University of Khemis-Miliana, Algeria. The geometry of the coaxial cylinder was chosen because of its greater sensitivity with low viscosity materials and fluid suspensions [10].The measuring device was equipped with a temperature control unit, which enables efficient temperature control over a long period. A 10 ml sample of LI was loaded into the cylinder and allowed to equilibrate at the set temperature (20 to 60 °C).

For isothermal measurements, the rheometer was set at room temperature (23.15 °C) followed by a programmed shear from 1 to 500 s⁻¹. Parameters such as viscosity, shear rate and shear stress were obtained from the rheometer. As previously indicated, there is currently no consensus on the choice of the mathematical model to interpret the rheological

data for the LIs.

The experimental shear stress and shear rate data of 1-Ethyl-3-methylimidazolium thiocyanate were analyzed using the Herschel Bulkley rheological model.

III. RESULT AND DISCUSSION

A. The flow curve

Newtonian and non-Newtonian fluids have completely different rheological behaviors. When the stress varies linearly with the strain rate at constant temperature, the proportion constant being viscosity, fluids are Newtonian. The equation governing the Newtonian behavior of a fluid is given by:

$$\tau = \eta \dot{\gamma} \quad (1)$$

Where τ is the shear stress, η is the shear viscosity and is the shear rate.

When fluids do not follow this simple behavior, they are classified as non-Newtonian. There is no consensus on the appropriate mathematical models for the flow behavior of ionic liquids, as no detailed studies have been reported in the construction literature for this type of fluid.

To describe the rheological behavior of 1-Ethyl-3-methylimidazolium thiocyanate, tests were carried out for shear rates of 1 to 500 s⁻¹ according to the procedures described above. All tests were carried out at room temperature (23.15 °C). The data points were fitted with the Herschel Bulkley model, which is expressed as follows:

$$\tau = \tau_0 + K \dot{\gamma}^n \quad (2)$$

In equation (2), With:: Threshold stress (Pa), K: Consistency index (Pa.sn), n: Flow index. If n = 1, the system is Newtonian fluid, the apparent viscosity varies little with the shear speed; if n > 1, the system is dilating fluid, the viscosity increases with the apparent increase in the shear rate; if n < 1, the system is pseudoplastic fluid, the apparent viscosity decreases with increasing shear rate.

To give a better presentation of the shear dependence of the liquid studied, the variation of the viscosity as a function of

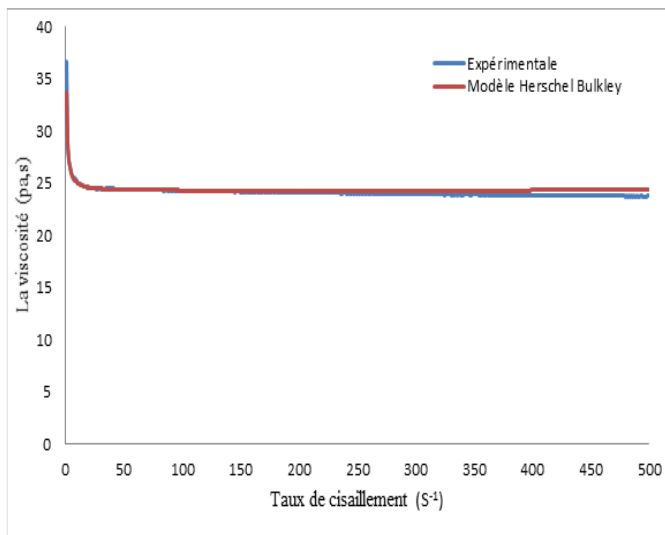


Fig. 1. Viscosity variation of 1-Ethyl-3-methylimidazolium thiocyanate as a function of shear rate, experimental and by Herschel Bulkley model.

the shear rate has been shown in figure 1. 1-Ethyl-3-methylimidazolium thiocyanate shows two different regimes:

The first regime, at low shear rate ($\dot{\gamma} < 30 \text{ S}^{-1}$): the liquid studied is non-Newtonian fluid in this specific range of shear rate (this occurs when the viscosity depends on the shear rate). The non-Newtonian behavior is shown by the non-linearity between the shear stress and the applied shear rate (The shear stress was not linearly dependent on the shear rate values). The viscosity of the LI decreased with increasing shear rate dictating the shear thinning behavior (it is a pseudoplastic fluid). The decrease in viscosity could be due to the breakdown of structural units in the LI due to the hydrodynamic forces generated at the start of shear. The non-Newtonian behavior of 1-Ethyl-3-methylimidazolium thiocyanate seems similar to that observed for other ILs in some previous works [9-11-12]

The second regime, at high shear rate ($\dot{\gamma} > 30 \text{ S}^{-1}$): We see that the shear stress changes linearly with the shear rate (Figure 2) and the apparent viscosity is almost independent of

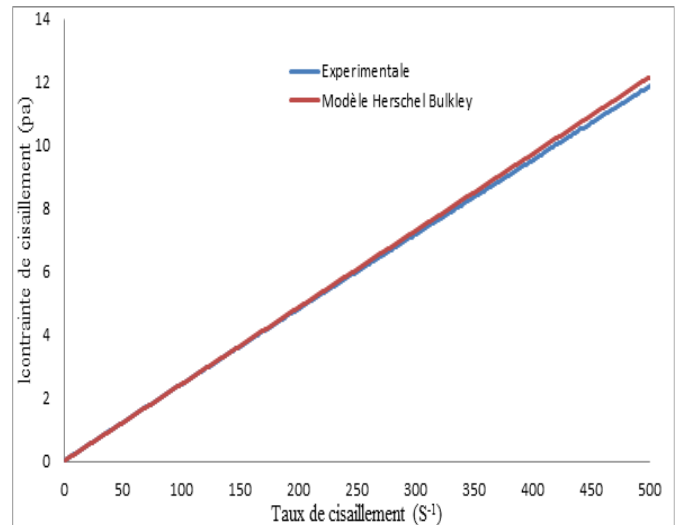


Fig. 2. The flow curve of 1-Ethyl-3-methylimidazolium thiocyanate, experimental and by Herschel Bulkley model.

the shear rate (Figure 1).

The Herschel Bulkley model, which is commonly used to analyze the flow behavior of liquid foods, has shown a good correlation between experimental and predicted data at all diets, and can be expressed as follows:

$$\tau = 0.0096674 + 0.023761 * \dot{\gamma}^{1.0022} \quad (3)$$

B. Temperature effect

This involves testing the viscosity at different temperatures in order to observe how the rheological characteristics change with changes in temperature, as shown in Figure 3.

In Figure 3, we can see that with the increase in temperature, the viscosity of 1-Ethyl-3-methylimidazolium thiocyanate continuously decreases. The reason is that with the increase in temperature, the thermal movement between the thickener and crosslinker molecules accelerates, destroying the chemical bonds between the molecules and the relaxation of the structure, and ultimately resulting in less resistance to flow.

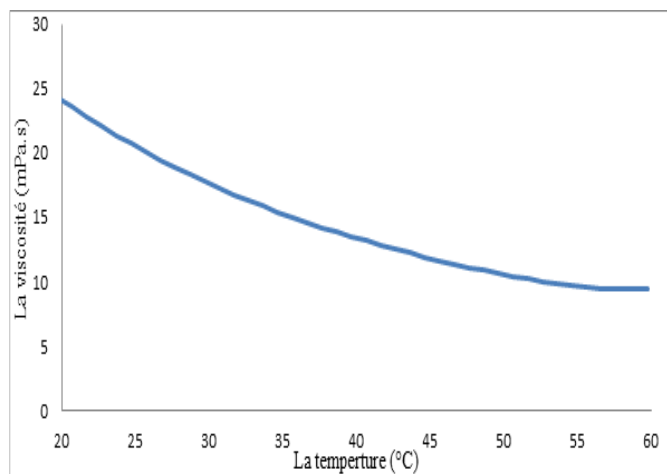


Fig. 3. The influence of temperature on the viscosity of 1-Ethyl-3-methylimidazolium thiocyanate.

The dependence of viscosity on temperature is well described by the Arrhenius type equation [13-14]:

$$\eta = \eta_0 \cdot \exp\left(\frac{E_a}{RT}\right) \quad (4)$$

Where η is the measured viscosity (Pa s), η_0 is constant, E_a

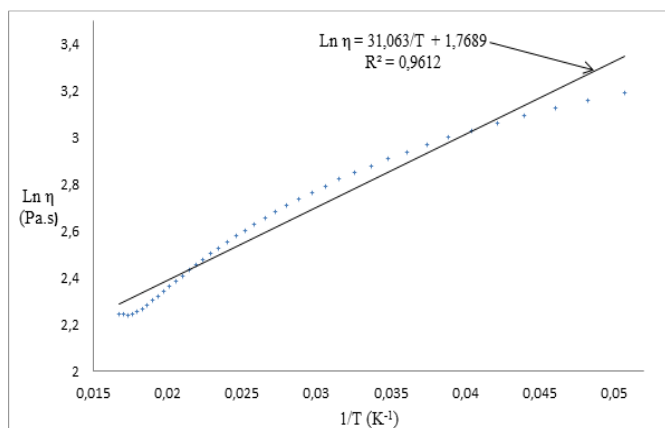


Fig. 4. Graph of $\ln(\eta)$ as a function of T^{-1} for 1-Ethyl-3-methylimidazolium thiocyanate at different temperatures.

is the activation energy (kJ / mol) and R is the universal gas constant (8.314 J / mol / K).

A graph of the logarithm of the viscosity ($\ln \eta$) versus the inverse of the temperature (T^{-1}) is shown in figure 4. The results show that the relationship between $\ln \eta_0$ and T^{-1} is linear ($R^2 = 0.9612$), which corresponds to the following formula:

$$\ln \eta = \ln \eta_0 + \frac{E_a}{RT} \quad (5)$$

From Fig. 4, it can be seen that the slope in a straight line is 31.063; by calculation, the activation energy of the viscous flow of the LI is 257.717

Finally, the Arrhenius type equation is expressed as follows:

$$\eta = 5.8644 \cdot \exp\left(\frac{31.063}{T}\right) \quad (5)$$

IV. CONCLUSION

In the present study, the geometry of the coaxial cylinders was used for the characterization of the flow of 1-Ethyl-3-methylimidazolium thiocyanate at different temperatures (from 20 to 60 °C). 1-Ethyl-3-methylimidazolium thiocyanate showed shear thinning behavior in a specific range, and was well described by the Herschel Bulkley model.

The effect of temperature on the apparent viscosity of 1-Ethyl-3-methylimidazolium thiocyanate is analyzed. The results show that the apparent viscosity decreases with increasing temperature. By regression analysis, it can be seen that the zero shear viscosity is temperature dependent and agrees with the Arrhenius equation.

REFERENCES

- [1] C. Chen; A functionalised ionic liquid: 1- (3-chloro-2-hydroxypropyl) - 3-methyl imidazolium chloride, *Phys. Chem. Liq.* 48 (3) (2010) 298e306.
- [2] I. Dinar es, CG De Miguel, A. Ib a ~ nez, N. Mesquida, E. Alcalde, Imidazolium ionic liquids: A simple anion exchange protocol, *Green Chem.* 11 (10) (2009) 1507e1510.
- [3] E. Ennis, ST Handy, A facile route to C2-substituted imidazolium ionic liquids, *Molecules* 14 (6) (2009) 2235e2245.
- [4] H.-C. Kan, M.-C. Tseng, Y.-H. Chu, Bicyclic imidazolium-based ionic liquids: synthesis and characterization, *Tetrahedron* 63 (7) (2007) 1644e1653.
- [5] AC Kleinschmidt, Produç ~ ao de grafeno pela abertura de nanotubos de carbonoauxiliadaporlíquidoi ^ onico e usoemnanocompositos de resinaepoxidica, 2014.
- [6] A. Benabdellah, E.-H. Belarbi, H. Ilikti, M. Hatti, B. Fettouhi, Electrical Properties of PANI / Chalcogenide Junctions Doped with Ionic Liquids Anions, *Tenside Surfactants Deterg.* 49 (3) (2012) 241e246.
- [7] B. Fetouhi, A. Benabdellah, EH Belarbi, H. Ilikti, T. Benabdallah, Junction Characteristics System Based on Composite Organic Semiconductors: Polystyrene / Polyaniline Doped by [BMIM] [BF4] Ionic Liquid, *Tenside Surfactants Deterg.* 51 (6) (2014) 541e546.
- [8] RamananKrishnamoorti. And Emmanuel P. Giannelis; Rheology of Silicate Nanocomposites, *Macromolecules*, 4097-4102 (1997).
- [9] Danillo Camargo et al; Investigation of the rheological properties of protic ionic liquids; *journal of physical organic chemistry* (2016).
- [10] KOK, MS; Rheological study of galactomannan depolymerisation at elevated temperatures: Effect of varying pH and addition of antioxidants. *Carbohydr. Polym.* 81, 567–571 (2010).
- [11] JA Smith., GB Webber., GG Warr, and R. Atkin, J; *Phys. Chem. B.* 117, 13930–13935 (2013).
- [12] GL Burrell., NF Dunlop, and F. Separovic; *Soft Matter*, 6, 2080–2086 (2010).
- [13] TONON, RV, ALEXANDRE, D., HUBINGER, MD and CUNHA, RL Steady and dynamic shear rheological properties of açai pulp (*Euterpe oleraceae*Mart.). *J. Food Eng.* 92, 425–431 (2009).
- [14] NINDO, CI, POWERS, JR and TANG, J. Thermal properties of Aloe vera powder and rheology of reconstituted gels. *Trans. ASABE*53, 1193–1200 (2010).