

Rheological Study of Polyelectrolytic Protic Ionic Liquids

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Abstract—This paper reports on the synthesis and rheological characterization of a collection of polyelectrolytic protic ionic liquids (2-hydroxy diethylammonium oxalate (2-HDEAOx), 2-hydroxy diethylammonium maleate (2-HDEAMa), 2-hydroxy diethylammonium succinate (2-HDEASu), 2-hydroxy ethylammonium adipate (2-HEAAd), 2-hydroxy diethylammonium adipate (2-HDEAAd) and 2-hydroxy ethylammonium citrate (2-HEACi)), in terms of shear- and temperature-dependency at the range 323.15-343.15 K. $^1\text{H-NMR}$ and FT-IR spectra establish the ionic salt structure of these compounds. The parameters ΔH^* (enthalpy of activation), ΔG^* (free energy of activation), ΔS^* (entropy of activation), and ΔC_p^* (change in heat capacity of activation) for their viscous flow were computed. The temperature dependence of viscosities was fitted using Litovitz, Vogel-Fulcher-Tamman and Ghaatee's equations. The experimental results showed that their viscosity strongly decreases with increasing temperature, and a simple linear relation between shear stress and viscosity with shear rate show a Newtonian trend over the studied range.

Keywords—Viscosity, Protic Ionic Liquids, Temperature, Theoretical Model

I. INTRODUCTION

Ionic liquids (ILs) are a class of new solvents which have attracted much attention as promising compounds for a wide variety of applications due to an amazing number of desirable properties [1-4]. They are good solvents for both organic and inorganic chemicals over a wide range of temperature, highly negligible vapor pressure, thermally stable, non-flammable, polar, weakly coordinating solvents and less toxic than usual organic compounds. Their low volatility makes ILs a serious alternative for traditional volatile organic compounds (VOCs) and then, contributes towards greener chemical processes. Due to these facts, perhaps no other engineering field has been the subject of analogous intensive research and industrial interest nor received such strong attention as ionic liquids are suffering. These ionic compounds can be divided into two broad categories: aprotic ionic liquids (AILs) and protic ionic liquids (PILs). Only recently, the former have received greater attention, due to their potential as strong environmental friendly solvents and new promising applications [5-6]. Besides their biodegradable character, lower cost of production and simple chemical reaction, they show high tolerance into water and polar compounds (alcohols, acids etc) which greatly increases their potential importance in industrial applications terms and reinforce future integrated greener processes. Rheological and

volumetric properties of ionic liquids are of main interest due to the growing number of industrial applications of such new materials. These properties provide key information on molecular basis of these fluids for theoretical studies and modeling development, as well as, necessary values into property balances for engineering design. In general terms, the importance of accurate thermophysical magnitudes for optimal design, avoiding under or over dimensioned processes is well known [7]. In spite of their relevance, and the exponential number of scientific articles related to ionic liquids in the last few years, PILs are relatively new compounds then, there is a scarcity of information on thermodynamic properties and phase equilibria.

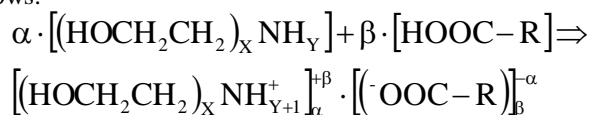
As a continuation of our research work [8-15], in this work, we present new data of temperature (T) and shear rate (SR) dependent viscosities or shear viscosities (η) of six new protic ionic liquids namely 2-hydroxy diethylammonium oxalate (2-HDEAOx), 2-hydroxy diethylammonium maleate (2-HDEAMa), 2-hydroxy diethylammonium succinate (2-HDEASu), 2-hydroxy ethylammonium adipate (2-HEAAd), 2-hydroxy diethylammonium adipate (2-HDEAAd) and 2-hydroxy ethylammonium citrate (2-HEACi).

The measured data were used to estimate the activation thermodynamic parameters, i.e. ΔH^* (enthalpy of activation), ΔG^* (free energy of activation), ΔS^* (entropy of activation), and ΔC_p^* (change in heat capacity of activation) for the viscous flow of the studied PILs as a function of temperature. In order to test the applicability of different viscosity models to this kind of ionic compounds, a collection of models were fitted to the experimental data (Power Law equation [14, 15], Litovitz equation [16, 17], Vogel-Fulcher-Tamman (VFT) equation [18] and Ghaatee equation [17]). As observed in this work, the viscosity is strongly dependent of the ion-ion interactions, as well as, van der Waals interactions among aliphatic ends and hydrogen bonding. The bulk structures gathered by these compounds, where branched aliphatic chains are enclosed, produce considerable steric hydrance, resulting in higher viscosity values than expected. As earlier observed in our laboratory [19], the anion structure (linear chain, open structure) of the studied protic ionic liquids has a far stronger effect on the rheological properties than analogous structures of the cation (short linear substitutions on the nitrogen atom). As observed, the viscosity strongly decreases with increasing temperature, showing these compounds a Newtonian trend over the studied range of shear rate.

II. EXPERIMENTAL

A. Preparation of the protic ionic liquid

The amine compounds (monoethanolamine or diethanolamine, Merck Synthesis, better than 99%) were placed in a threenecked flask all-made-in-glass equipped with a reflux condenser, a PT-100 temperature sensor for controlling temperature and a dropping funnel. The flask was mounted in a thermal bath. A slight heating is necessary for increasing miscibility between reactants and then allow reaction. The organic acid (adipic, citric, maleic, oxalic and succinic acids, Merck synthesis quality, better than 99%) was added drop wise to the flask under stirring with a magnetic bar. Stirring was continued for 24 h at laboratory temperature, in order to obtain a final viscous liquid. Lower viscosity was observed in the final product by decreasing molar mass of reactants. No solid crystals or precipitation was noted when the liquid sample was purified. The reaction is a simple acid–base neutralization creating an adipate, citrate, maleate, oxalate or succinate salt of mono or diethanolamine, that in a general form should be expressed as follows:



where X is the number of ethanol substitutions into the amine compound, Y number of protons linked to the nitrogen atom ($X+Y=3$) and R the aliphatic chain of the organic acid. The variables α and β are the number of cations and anions into the polyelectrolyte protic ionic liquid.

Owing to the fact that these chemical reactions are highly exothermic, an adequate control of temperature is essential throughout the process, otherwise heat evolution may produce the dehydration of the salt to give the corresponding amide as in the case for nylon salts (salts of diamines with dicarboxy acids). As observed in our laboratory during ionic liquid synthesis, dehydration begins around 420 K, for the lightest ionic liquids. The colour varies in each case from transparent to dark yellow when reaction process and purification (strong agitation and slight heating for vaporization of residual non-reacted acid at low pressure least for 24 h) was completed.

During purification is very important to keep that temperature does not overcome the dehydration temperature because at that point the ionic liquid degradation begins and amides also should be generated by decomposition. At each case, after synthesis, spectrometry and thermodynamic measurements were made in order to ensure purity of the product before experiments. Different synthesis of these compounds didn't show appreciable differences in terms of thermodynamic values (volumetric, optic, acoustic or rheological properties) or spectroscopy results.

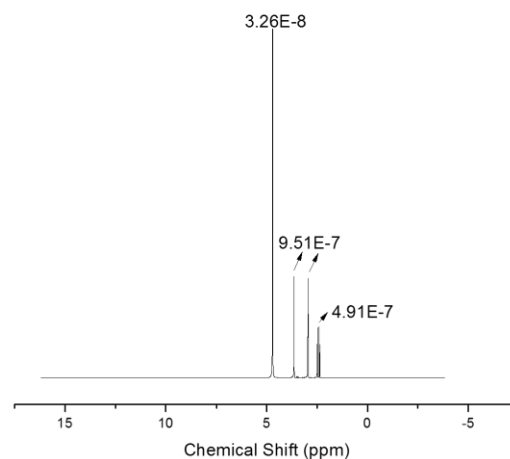
B. Spectroscopic test

^1H NMR and FT-IR spectra were performed in order to characterize the synthesis product and to confirm its ionic structure. The ^1H NMR spectrum was measured on a Bruker Ascend UltrashieldTM Plus-EDS 600 MHz spectrometer, using DMSO- d_6 as solvent with TMS as internal standard).

For example, Fig. 1a describes the corresponding NMR results for 2-HEACi.

The FT-IR spectrum was taken by a Bruker Vertex 70 RAM II spectrometer, direct measurement, platinum ATR, reflectance mode, 4 cm^{-1} resolution. The broad band in the (3500 to 2400) cm^{-1} range exhibits characteristic ammonium structure. The OH stretching vibration is embedded in this band. The broad band centered at 1500 cm^{-1} is a combined band of the carbonyl stretching and N–H plane bending vibrations. Fig. 1b describes the corresponding FT-IR results for 2-HEACi protic ionic liquid.

(a)



(b)

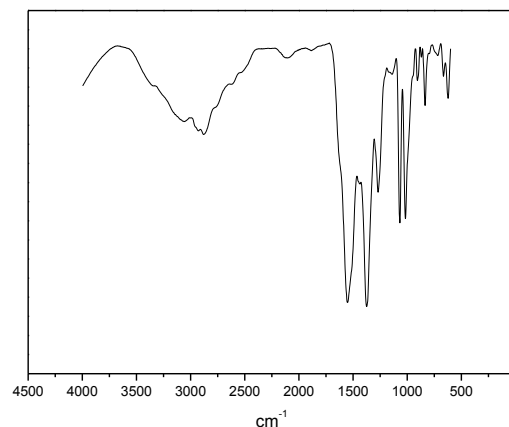


Figure 1 (a) ^1H NMR spectra and (b) FTIR spectra for 2-hydroxy ethylammonium citrate (2-HEACi)

C. Materials and measurement device

The purities of the reagents were verified by measuring the densities and viscosities at different temperatures. The experimental measurements at standard condition for the protic ionic liquids and the literature data are shown in Table 1. As far as we know, there are not previously published data on rheology behavior of these collection of protic ionic liquids. In the present study, the rheological properties of these PILs were measured using a Brookfield Viscosimeter LVDV-III. The viscosimeter drives the spindle immersed into the sample holder containing the test fluid sample. The

viscosity is measured by analysis of the viscous drag of the fluid against the spindle, when it rotates. The spindle type and speed combinations will produce satisfactory results when the applied torque is between 10% and 90%. The spindle SC4-27 was used in these measurements. The sample holder can contain a small sample volume and the temperature of the test sample is monitored by a temperature sensor embedded into the sample holder. The experimental uncertainty for viscosity, shear stress, and shear rate was lower than 10^{-2} mPa s, 10^{-2} mPa and 10^{-2} s⁻¹, respectively. Accurate temperature control is necessary requirement for the rheological measurements. In the current research, the water jacket was connected to a refrigerated/heating circulator (Brookfield, TC-502) to control the water temperature with a accuracy of ± 0.01 K.

TABLE I: Experimental and literature data of density and viscosity at 323.15 K for the studied protic ionic liquids and other relevant information

PILs	Molar Mass (gmol ⁻¹)	Exp. Density (gcm ⁻³)	Lit. Density (gcm ⁻³)	Exp. Viscosity (mPas)	Lit. Viscosity (mPas)
2-HDEAOx	212.204	1.250516	na	68.62332	na
2-HDEAMa	238.241	1.270497	na	680.32358	na
2-HDEASu	240.257	1.218094	na	160.12208	na
2-HEAAAd	268.311	1.184891	na	288.66957	na
2-HDEAAAd	356.417	1.213250	na	553.78808	na
2-HEACi	375.377	1.311640	na	782.36465	na

The Anton Paar DSA-5000 densitometer was used for measuring the density of the pure protic ionic liquids, with a resolution of less than 10^{-5} gcm⁻³. Accuracy in the temperature of measurement was better than $\pm 10^{-2}$ K by means of a temperature control device that applies the Peltier principle to maintain isothermal conditions during the measurements. Earlier works describe the experimental procedure usually applied in our laboratory [8-15].

III. RESULTS AND DISCUSSION

A. Analysis of the rheological data

Fluids showing Newtonian and non-Newtonian trend have completely different rheological behaviors. For a non-Newtonian fluid, the viscosity depends on the shear rate. The equation governing Newtonian behavior of a fluid is given by:

$$\tau = \eta \gamma^0 \quad (1)$$

In this equation, τ is the shear stress, η is the shear viscosity, and γ^0 is the shear rate. As an example, Fig. 2 shows the measured shear stress as a function of shear rate for 2-HDEAOx protic ionic liquid at different temperatures (333.15-348.15 K). This figure shows that the shear stress depends linearly on the shear rate. The intercept represents the shear stress when the shear rate is zero. To give a better presentation of the shear-dependence of the studied PILs, the variation of the viscosity versus shear rate has been shown in the Fig. 3 at different temperatures (333.15-348.15 K). As this figure shows, the studied PILs are Newtonian fluids in this

specific range of studied shear rate (the viscosity remains constant, no matter the amount of shear applied for a constant temperature).

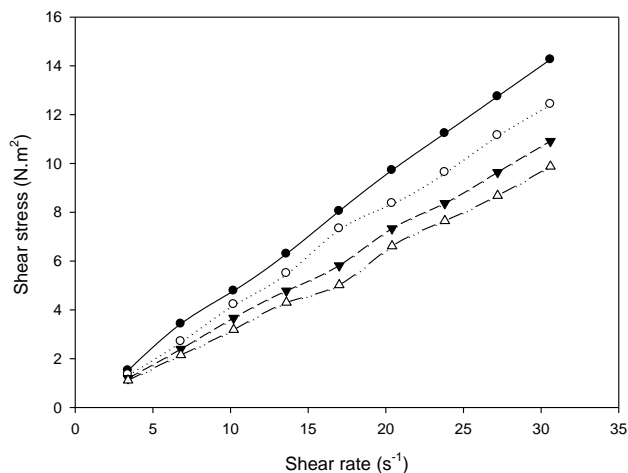


Figure 2 Shear stress versus shear rate for 2-hydroxy diethylammonium oxalate (2-HDEAOx) at different temperatures (●, 333.15 K; ○, 338.15 K; ▼, 343.15 K; △, 348.15 K)

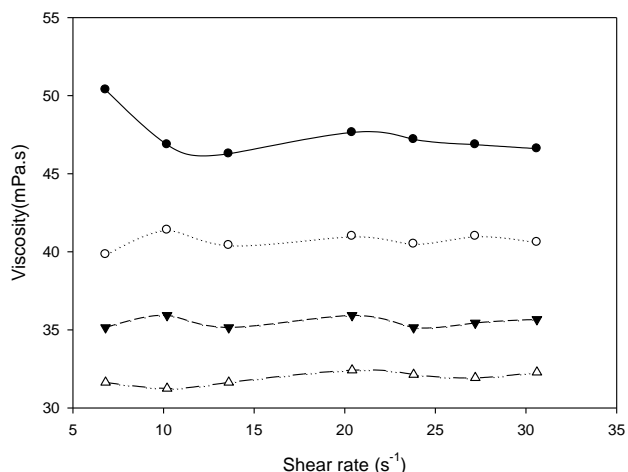


Figure 3 Viscosity versus shear rate for 2-hydroxy diethylammonium oxalate (2-HDEAOx) at different temperatures (●, 333.15 K; ○, 338.15 K; ▼, 343.15 K; △, 348.15 K)

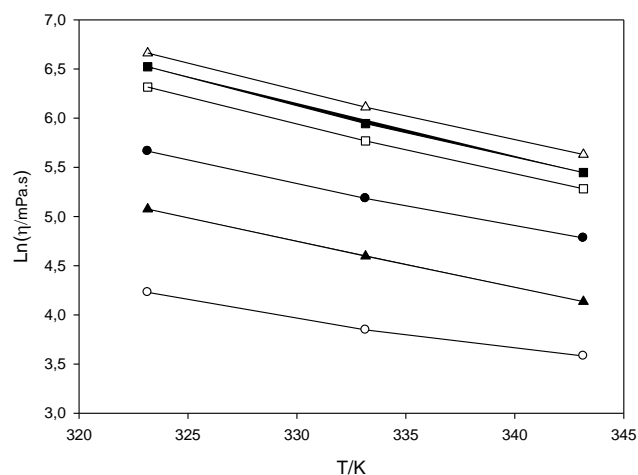


Figure 4 Logarithmic viscosity versus temperature at constant shear rate (SR=10.2) for the studied protic ionic liquids (○, 2-HDEAOx, ■, 2-HDEAMa, ▲, 2-HDEASu, ●, 2-HEAAAd, □, 2-HDEAAAd, △, 2-HEACi).

The Newtonian behavior of these PILs appears to be similar to that of observed previously for other PILs of lower molar mass [19]. The viscosity of the studied protic ionic liquid at different temperatures (323.15-343.15 K) was measured and shown in Fig. 4 (SR=10.2), as an example. As this figure shows, the measured viscosity of PILs decreases significantly with increasing fluid temperature at a fixed shear rate. The viscosity of PILs depends strongly on their ion-pair geometry (molecular size) and their packing and orientation into the bulk fluid [20-21].

The association activation parameters, namely, ΔH^* (enthalpy of activation), ΔG^* (free energy of activation), ΔS^* (activation entropy), and ΔC_p^* (change in heat capacity of activation) for their viscous flow were evaluated based on the viscosity results of the studied PILs under the influence of temperature and shear rate. Considering the energy of activation (ΔG^*) equivalent to the enthalpy of activation (ΔH^*), the Arrhenius form of viscosity relation can be written as,

$$\eta = \left(\frac{hN}{V} \right) \cdot e^{\Delta H^*/RT} e^{-\Delta S^*/R} \quad (2)$$

where, ΔS^* , h , N , and V are the activation entropy, Planck's constant, Avogadro's number, and the molar volume of the ionic liquid at the same temperature, respectively. With a little bit of algebra:

$$\ln \eta = \ln \left(\frac{hN}{V} \right) - \frac{\Delta S^*}{R} + \frac{\Delta H^*}{RT} \quad (3)$$

The molar volume was computed as the molar mass divided by its density at the temperature range of our measurements (313.15 to 343.15) K. Considering negligible the other terms, by differentiation on temperature, we obtain the following relation:

$$-\frac{\Delta H^*}{RT^2} = \frac{d \ln \eta}{dT} \quad (4)$$

Fig. 4 shows $\ln \eta$ versus T profiles at $SR = 10.2 \text{ s}^{-1}$ for all the studied protic ionic liquids. It can be observed that this variation can be fitted appropriately by a quadratic polynomial:

$$\ln \eta = a + bT + cT^2 \quad (5)$$

where a , b , and c are the fitting coefficients of the polynomial, then:

$$-\frac{\Delta H^*}{RT^2} = \frac{d \ln \eta}{dT} = b + 2cT \quad (6)c$$

The ΔH^* values were then computed at different temperatures by using Eq. (6) and the experimental measurements. The change in heat capacity of activation, ΔC_p^* , the free energy of activation, ΔG^* , and the entropy of activation, ΔS^* , could be obtained from the following equations:

$$\Delta C_p^* = \frac{d\Delta H^*}{dT} = -2RT(b + 3cT) \quad (7)$$

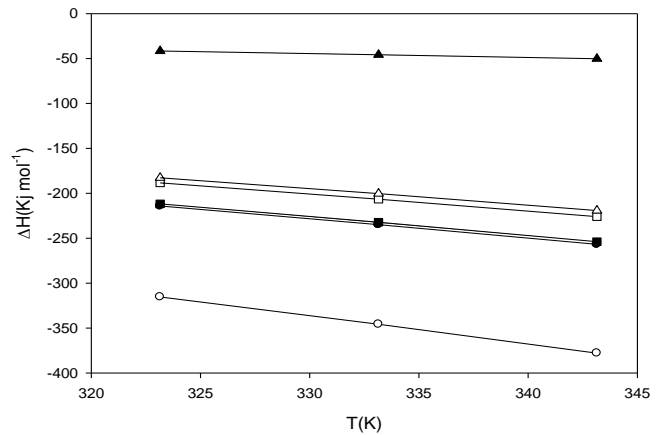


Figure 5. Activation parameter ΔH^* dependence on temperature for the studied protic ionic liquids (○, 2-HDEAOx, ■, 2-HDEAMa, ▲, 2-HDEASu, ●, 2-HEAAAd, □, 2-HDEAAAd, △, 2-HEACi).

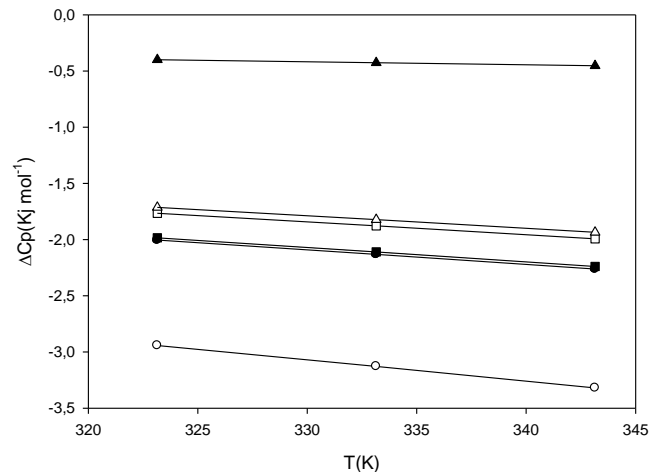


Figure 6. Activation parameter ΔC_p^* dependence on temperature for the studied protic ionic liquids (○, 2-HDEAOx, ■, 2-HDEAMa, ▲, 2-HDEASu, ●, 2-HEAAAd, □, 2-HDEAAAd, △, 2-HEACi).

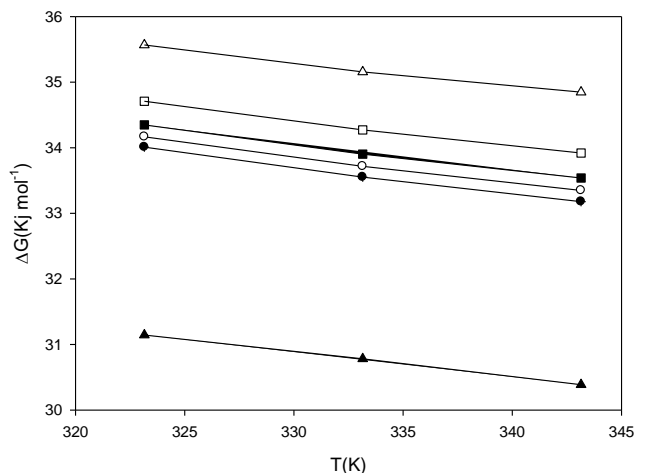


Figure 7. Activation parameter ΔG^* dependence on temperature for the studied protic ionic liquids (○, 2-HDEAOx, ■, 2-HDEAMa, ▲, 2-HDEASu, ●, 2-HEAAAd, □, 2-HDEAAAd, △, 2-HEACi).

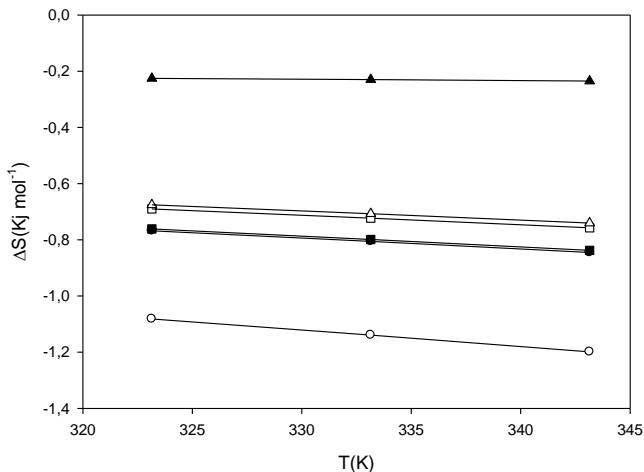


Figure 8. Activation parameter ΔS^* dependence on temperature for the studied protic ionic liquids (\circ , 2-HDEAOx, \blacksquare , 2-HDEAMa, \blacktriangle , 2-HDEASu, \bullet , 2-HEAAAd, \square , 2-HDEAAAd, Δ , 2-HEACi).

$$\Delta G^* = RT \left\{ \ln \left(\frac{\eta V}{h N} \right) \right\} \quad (8)$$

Being ΔS^* , evaluated from its basic thermodynamic definition:

$$\Delta S^* = \frac{\Delta H^* - \Delta G^*}{T} \quad (9)$$

Figs. 5-8 show the profiles of the computed activation parameters versus temperature for the viscous flow of the studied protic ionic liquids. The values of ΔH^* , ΔC_p^* and ΔS^* for these studied PILs are negative whereas ΔG^* values shows positive trend, gathering all of them a decreasing slope for rising temperatures. The variations in these parameters were determined by their stress-induced conditions. The positive values of ΔG^* (Fig. 7) show as the viscous flow faced the activation barrier making the process non-spontaneous, as we expected. The results show that the magnitude of the activation barrier decreases in the order 2-HEACi > 2-HDEAAAd > 2-HDEAMa > 2-HDEAOx > 2-HEAAAd > 2-HDEASu, which gather a molar mass decreasing tendency. The process was associated with exothermic trend resulting in negative ΔH^* , which expectedly declined for increasing temperature (Fig. 5). The values of activation entropies (ΔS^*) are negative (Figs. 8) and hence by means Eq. (9), $\Delta G^* > \Delta H^*$. It can be also observed that ΔC_p^* values (obtained from Eq. (7), as previously indicated) are all negative and they decreased for increasing temperature (Fig. 6). Since ΔH^* decreased with temperature, ΔC_p^* values were all negative and also decrease for all studied compounds, and they are almost linear with more or less comparable slopes at a fixed shear rate.

B. Theoretical models analysing the temperature dependence of viscosity of the studied PILs

Viscosity of PILs is a non-linear function of temperature and shows non-Arrhenius temperature dependence even over a short range of temperature [22]. Ionic liquids are highly or moderately fragile (non-Arrhenius) liquids. As the temperature of a fragile liquid decreases, its temperature dependence of viscosity smoothly crosses over to a strong (Arrhenius) liquid. The temperature in which this transition takes place is called fragile-to-strong, FS, crossover temperature, TX. The temperature dependence of viscosity of PILs at $T > TX$, should be reasonably described by any equations, namely, Litovitz equation [16, 17], Vogel-Fulcher-Tammann equation (VFT) [18], and the recent proposed equation by Ghatee et al. [17].

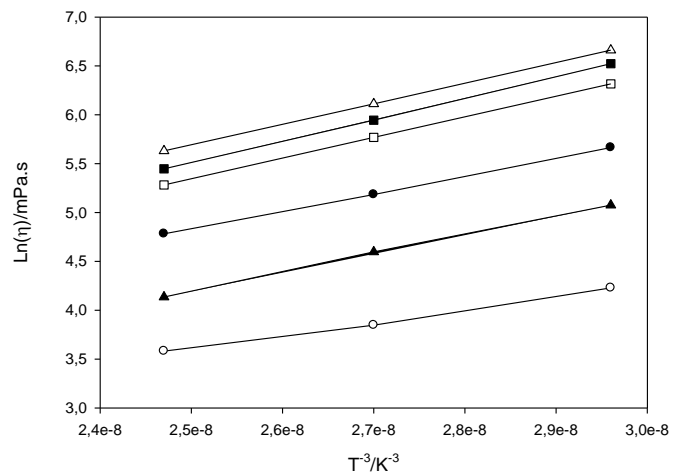


Figure 9. Plot of viscosity versus temperature, fitted with Eqn. (10) (Litovitz equation [16, 17]) for the studied protic ionic (\circ , 2-HDEAOx, \blacksquare , 2-HDEAMa, \blacktriangle , 2-HDEASu, \bullet , 2-HEAAAd, \square , 2-HDEAAAd, Δ , 2-HEACi)

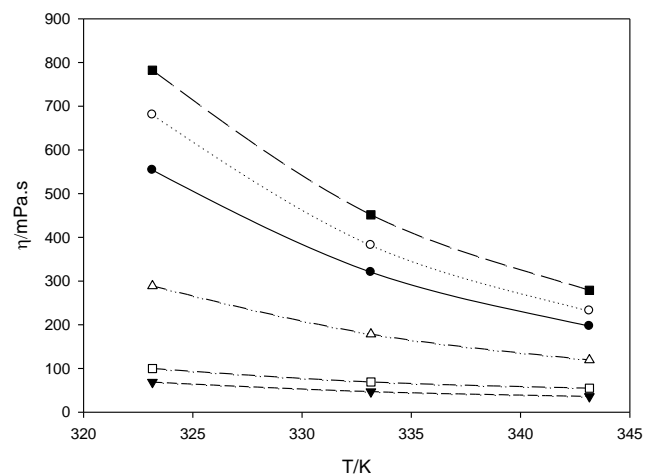


Figure 10. Plot of viscosity versus temperature, fitted with Eqn. (11) (VFT equation [18]) for the studied protic ionic liquids (\blacktriangledown , 2-HDEAOx, \circ , 2-HDEAMa, \square , 2-HDEASu, Δ , 2-HEAAAd, \bullet , 2-HDEAAAd, \blacksquare , 2-HEACi).

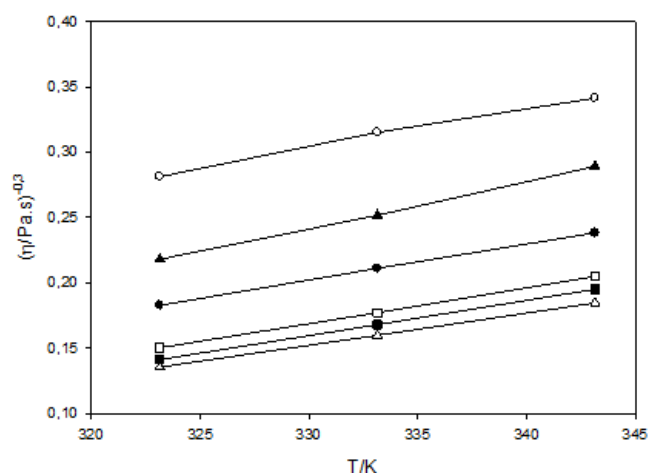


Figure 11. Plot of viscosity versus temperature, fitted with Eqn. (12) (Ghatee et al. equation [17]) for the studied protic ionic liquids (○, 2-HDEAOx, ■, 2-HDEAMa, ▲, 2-HDEASu, ●, 2-HEAAAd, □, 2-HDEAAAd, △, 2-HEACi).

In this work, the experimental data were fitted adequately by these equations.

The Litovitz and VFT equations are given according to the Eqs. (11) and (12):

$$\eta = Ae^{\frac{B}{RT^3}} \quad (10)$$

$$\eta = A'e^{\frac{B'}{(T-T_0)}} \quad (11)$$

where A, B, A' and T₀ are fitting parameters and parameter B' is related to the free activation energy of fluid. Recently, based on the fluidity (e.g. 1/η) concept, which contrary to the viscosity is only a slight function of temperature, Ghatee et al. [17] showed that the viscosity of PILs can be described by the following simple linear equation:

$$\left(\frac{1}{\eta}\right)^\phi = a + bT \quad (12)$$

where a and b are constants characteristics of the PIL and φ is a characteristic exponent (with φ = 0.3 for ILs [21]).

The correlations of Litovitz, VFT and Ghatee equations were plotted as Figs. 9-11.

Table 2 shows the fitted parameters and the root mean square deviation (σ) for Litovitz, VFT and Ghatee equations. As this table gathers, all of these equations describe the temperature-dependent viscosity of the studied PILs with, at least, quality accuracy.

TABLE II: Fitted parameters and σ (Root Mean Square Deviation) for the Litovitz, VFT and Ghatee et al. equations.

PIL	2-HDEAOx	2-HDEAMa	2-HDEASu	2-HEAAAd	2-HDEAAAd	2-HEACi
Litovitz Equation						
ln (A/Pa.s)	5.0797	7.9651	6.3501	6.8458	7.7072	8.0473
(B/R).10 ⁸ /K ³	-2.2999	-3.8406	-3.3664	-3.1503	-3.6946	-3.6837
□	0.0452	0.0486	0.0302	0.0433	0.0433	0.0448
VFT Equation						
A'/Pa.s	2.0945	-1.3745	-2.9755	0.2967	-2.9755	-1.6814
B'/K	98.092 2	1001.3 428	1483.6 138	545.34 49	1483.6 138	1182.7 553
T ₀ /K	277.18 45	196.35 13	163.48 93	221.56 85	163.48 93	181.39 63
□	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Ghatee et al. Equation						
a/(Pa.s) ^{0.3}	-0.6909	-0.7286	-0.9320	-0.7128	-0.7336	-0.6588
b/(Pa.s) ^{-0.3} K ⁻¹ (10 ³)	3.0123	2.6917	3.5570	2.7720	2.7347	2.4578
□	0.0019	0.0001	0.0009	0.0003	0.0002	0.0001

IV. CONCLUSIONS

The shear- and temperature-dependent viscosities of six new ammonium based protic ionic liquids in the temperature range of (323.15 to 343.15) K were measured and analyzed. The protic ionic liquids namely, 2-hydroxy diethylammonium oxalate (2-HDEAOx), 2-hydroxy diethylammonium maleate (2-HDEAMa), 2-hydroxy diethylammonium succinate (2-HDEASu), 2-hydroxy ethylammonium adipate (2-HEAAAd), 2-hydroxy diethylammonium adipate (2-HDEAAAd) and 2-hydroxy ethylammonium citrate (2-HEACi) are Newtonian fluids (in a specific range of shear rate) whose fluidity are influenced only by temperature. The experimental results showed that the viscosity of these fluids decreases with increasing the temperature. The activation parameters (ΔH*, ΔG*, ΔS*, and ΔCp*) for their viscous flow were computed, showing a magnitude of the activation barrier decreasing as follows: 2-HDEASu > 2-HEACi > 2-HDEAAAd > 2-HDEAMa > 2-HEAAAd > 2-HDEAOx.

The temperature dependence of viscosities fit accurately by Vogel-Fulcher-Tammann (VFT), Ghatee equations and Litovitz, in this sequence. As a conclusion, the gathered experimental measurements of these protic ionic liquids make a contribution for a better understanding of the rheological of this kind of new compounds and should help for developing new theoretical models and accurate design of greener processes evolving these ionic compounds.

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