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Arrhenius model to inspect the composition dependence viscosities of binary systems involving ionic liquids

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Abstract: Many viscosity datasets for binary systems analyzed with the Arrhenius model to inspect the composition dependence of the Arrhenius fit parameters activation energy, E_a, and y-intercept, lnA. The majority of the binary systems show linear dependence of E_a and lnA with mole fraction, either over the entire range of composition or over a wide range of compositions, typically between $0.2 < xIL < 1.0$. These findings are useful for estimating unknown viscosities for binary systems involving ILs.

Keywords: ionic liquids, viscosity, activation energy, binary system

1. INTRODUCTION

Consequently, there has been a need for physical property data of binary and multi-component systems involving ILs. Since it is practically impossible to measure physical properties of every conceivable combination of IL and molecular solvent, any predictive models and schemes for these are highly desirable [1,2]. As we will show, we observe some deviation from a linear mole fraction dependence for the activation energy. A linearity of the activation energy with respect to mole fraction was also observed for the binary systems 1-butyl-3-methylimidazolium hexafluorophosphate – N,N-dimethylformamide8 and ethylammonium nitrate with dimethyl carbonate as well as formamide,9 while Gong et al. were using a second order polynomial for the mole fraction dependence of the activation energy [3-6]. This raises the question in how far a linear dependence for the viscosity activation energy can be found in other binary IL – molecular solvent systems. However, except for these cited works, this aspect has generally not been inspected even though there are numerous temperature and composition dependent viscosity studies of binary IL – molecular solvent systems. We thus embarked in a very thorough literature search for binary IL – molecular solvent viscosity datasets and meta-analyzed these to discern which types of binary IL – molecular solvent systems would display a linear relationship between activation energy and the [7-11] composition expressed in mole fraction and which not. A total of 215 binary IL – molecular solvent systems are included in this study covering publication dates up to and including the year 2014. Yu et al. also completed a thorough search on IL viscosity data up to 2009.11 Although they included binary (and ternary) datasets, their presented [12-16] observations and quantitative structure-property analysis was focused only on neat ILs.

2. EXPERIMENTAL SECTION

New viscosities are reported for the $[C_6mim][NTf_2]$ – $CHCl_3$ binary system. The $CHCl_3$ (CAS no. 67-66-3, Acros) was of 99.8% purity and contained < 0.8% by volume ethanol as stabilizer that was not removed. The $[C_6mim][NTf_2]$ (CAS no. 382150-50-7, Iolitec, batch no.: J0019.1.2.Inc, 99% purity) was of clear and colorless appearance and contained a mass fraction of less than 1.5×10^{-4} of water as determined by Karl Fischer titration. Solution preparation was done by mass using an analytical balance in an inert atmosphere glove box where the chemicals were stored. Before filling the capillary tubes and the density meter, each of the prepared sample vials was briefly heated slightly in a microwave to at least partially remove dissolved gas that can compromise viscosity (and density) measurements at elevated temperatures. After measurements the sample was recovered for inspection by ^{1}H-NMR spectroscopy to check by means of spectral integration that handling of the prepared sample for the viscosity and density measurements did not alter their composition. Overall, the precision of the solution compositions is estimated to be within 0.002 mole fraction units. The viscosities were measured with an AMVn Automated Microviscometer rolling ball viscometer from Anton Paar. The densities were measured in parallel with a DMA 4100 vibrating tube density meter with internal sample [20] viscosity compensation, also from Anton Paar, and have already been reported as part of another study. Both instruments are temperature controlled to within 0.02°C by Peltier systems. Viscosities were measured in at least six repetitions and resulted in standard deviations within 2% of the