Accepted Manuscript

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PII: S0167-7322(18)32535-2

DOI: doi:10.1016/j.molliq.2018.08.006

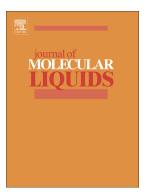
Reference: MOLLIQ 9451

To appear in: Journal of Molecular Liquids

Received date: 16 May 2018
Revised date: 4 July 2018
Accepted date: 1 August 2018

Please cite this article as: Paula Berton, Steven P. Kelley, Hui Wang, Robin D. Rogers, Elucidating the triethylammonium acetate system: Is it molecular or is it ionic? Molliq (2018), doi:10.1016/j.molliq.2018.08.006

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ACCEPTED MANUSCRIPT

Elucidating the Triethylammonium Acetate System: Is it Molecular or Is it Ionic?

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ABSTRACT

The speciation of protic ionic liquids (ILs) has attracted high attention in the recent years, due to its effect in the properties of the resulting liquids. In this work we analyze the behavior of mixtures between triethylamine (N_{222}) and acetic acid (HOAc), a system that generates controversy about its speciation. Using different synthetic strategies, liquids were obtained with molar compositions that were always between 1:2 and 1:4 mol/mol N_{222} :HOAc. However, the experimentally observed normal boiling points indicate that the actual IL has a molar composition of 1:4 N_{222} :[HOAc]/[OAc]^r. Furthermore, when the synthesized liquid is mixed with the aprotic IL 1-ethyl-3-methylimidazolium acetate, more triethylamine is expelled, indicating that the excess N_{222} forms an $[HN_{222}]^+$ - N_{222} complex rather than becoming ionized by the remaining HOAc present in the system. Our experimental data emphasizes the consideration of these systems not as mere "mixtures of ions and non-ionized molecules," but as complex systems of oligomeric ions, with distinctive and characteristic properties.

Keywords: Acetic acid; Oligomeric Ions; Protic Ionic Liquid; Speciation; Triethylamine.

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