Discovery of Room Temperature Ionic Liquid*

P C Rây versus P Walden

Rajarshi Ghosh

$[EtNH_3]^+(NO_3^-)$ is generally considered as the first reported room temperature ionic liquid which was synthesized and characterized by Paul Walden in 1914. But the present investigation finds that $[EtNH_3]^+(NO_2^-)$, a similar kind of ionic salt which is liquid at room temperature, was synthesized by Sir P C Rây three years earlier (in 1911) to Walden. Unfortunately, the latter work had not been paid any attention for more than a century because of unknown reasons. As per literature review, henceforth, Sir P C Rây and his coauthor (J N Rakshit) of that very particular synthesis of the ionic compound which was liquid at room temperature should be regarded as the discoverer of room temperature ionic liquid.

Rajarshi Ghosh is associated with post graduation teaching and research in the Department of Chemistry, The University of Burdwan. His research interest covers synthetic coordination chemistry, bio inspired catalysis, biological inorganic chemistry, etc. Besides these, he is also interested in science popularization.

Keywords
Ionic liquid, P C Rây, P Walden.

1. Introduction

Ionic liquids, particularly room temperature ionic liquids, are excellent green solvents in modern synthetic chemistry [1, 2]. These are composed of organic cations like alkylammonium, alkylphosphonium, N-alkylpyridinium, N, N′-dialkylimidazolium, etc., and inorganic anions like chloride, nitrate, nitrite, etc. Being ionic, it has a higher boiling point than common organic solvents. This prevents its easy vaporization during chemical reactions and makes it safe and green to human health. Moreover, ionic liquid has its diverse applications in the field of fluorescence spectroscopy [3], solar cell designing [4], long term storage of biomolecules (enzymes, proteins, etc.), etc [5].

Synthesis and characterization of ethylammonium nitrate [6]

*Vol.26, No.2, DOI: https://doi.org/10.1007/s12045-021-1122-3

Synthesis and characterization of ethylammonium nitrate by Paul Walden in 1914 is generally cited as the first report of the room temperature ionic liquid. But a critical scrutiny of literature reveals that same type of compound with the same kind of characters was synthesized by the celebrated Indian chemist and social reformer Sir P C Rây three years before Walden.

$[EtNH_3]^+(NO_3^-)$ by Paul Walden in 1914 is generally cited [7, 8] as the first report of the room temperature ionic liquid. But a critical scrutiny of literature [9] clearly reveals that same type of compound with the same kind of characters was synthesized by the celebrated Indian chemist and social reformer Sir P C Rây three years before Walden.

P Walden and P C Rây

Paul Walden (1863–1957), the Russian-German chemist, was contemporary of Sir Rây (1861–1944). The former started his career [10] as a lecturer of physical chemistry at Riga Polytechnic Institute in Latvia (a European country, previously in Russia) in 1892. Later on, he moved to the University of Rostock, Germany. Two of his most important contributions [10] in chemical sciences were the discoveries of inversion of the configuration of chiral centre in an organic second-order nucleophilic substitution reaction (SN^2), and a relationship between the equivalent electrical conductivity at infinite dilution and viscosity. Both of these contributions are named after him later (Walden inversion and Walden rule, respectively). Walden, like Sir P C Rây, was also interested in the history of the chemical sciences [10] and authored the book *Ocherk istorii khimiii v Rossii* (*Study in the History of Chemistry in Russia*). On the other hand, Sir Rây[1] had made notable contributions to nitrite chemistry and many other fields [11]. Mercurous nitrite was his first report [12] of the synthesis and characterization of nitrite salts. He was internationally recognized [13] for this very particular discovery. As a part of his contribution in the field of nitrite chemistry, he along with his then-student J N Rakshit (Jitendra Nath Rakshit) synthesized and characterized [9] ethylammonium nitrite $[EtNH_3]^+(NO_2^-)$ in 1911. This is liquid at room temperature but dissociates in between 23°C–30°C [9]. The dissociation was obvious because nitrite is not a very stable anion. On dissociation in acidic medium, it gives up gaseous nitrogen, nitrate and water. As a result, the whole molecule $[EtNH_3]^+(NO_2^-)$ breaks down.

[1] Asim K. Das, Thermodynamic and Kinetic Aspects of the Stability of Sir P C Ray's Mercurous Nitrite Compound, *Resonance*, Vol.25, No.6, pp.787–799, 2020 and R Ghosh, Mercurous nitrite, *Resonance*, Vol.19, No.10, pp. 958–960, 2014.

Conclusion

By the way, whatever be its dissociation temperature, the ionic salt, which was liquid at room temperature, was reported by Rây, *et al*., three years earlier to Walden. Unfortunately, this fact remained shaded for a long period of time. To the best of author's knowledge, only a single publication [14] on 'ionic liquid' has been found where one of P C Rây's work [15] on nitrite chemistry is cited, though the ionic compound reported by Rây, *et al*., in that work was not liquid at room temperature. Now, hopefully, from this very point of time, Sir P C Rây and J N Rakshit will be honoured as the discoverers of ionic liquid, and their work [9] will be cited as the first report of room temperature ionic liquid by the future authors without any hesitation.

Suggested Reading

[1] (a) C Wheeler, K N West, C L Liotta and C A Eckert, Ionic liquids as catalytic green solvents for nucleophilic displacement reactions, *Chem Commun*., p.887, 2001; (b) M J Earle and K R Seddon, Ionic liquids: Green solvents for the future, *ACS Symposium Series*, p.10, 2002.

[2] (a) T Welton, Ionic liquids in green chemistry, *Green Chem*., Vol.13, p.225, 2011; (b) A Rehman and X Zeng, Ionic liquids as green solvents and electrolytes for robust chemical sensor development, *Acc Chem Res*., Vol.45, p.1667, 2012.

[3] (a) S Patra and A Samanta, Microheterogeneity of some imidazolium ionic liquids as revealed by fluorescence correlation spectroscopy and lifetime studies, *J Phys Chem B*., Vol.116, p.12275, 2012; (b) A Samanta, Dynamic stokes shift and excitation wavelength dependent fluorescence of dipolar molecules in room temperature ionic liquids, *J Phys Chem B*., Vol.110, p.13704, 2006.

[4] M Watanabe, M L Thomas, S Zhang, K Ueno, T Yasuda and K Dokko, Application of ionic liquids to energy storage and conversion materials and devices, *Chem Rev*., Vol.117, p.7190, 2017.

[5] (a) S N Baker, T M McCleskey, S Pandey, G A Baker, Fluorescence studies of protein thermostability in ionic liquids, *Chem Commun*., p.940, 2004; (b) A Chandran, D Ghoshdastidar and S Senapati, Groove binding mechanism of ionic liquids: A key factor in long-term stability of DNA in hydrated ionic liquids? *J Am Chem Soc*., Vol.134, p.20330, 2012.

[6] V P Walden, Ueber die Molekulargrösse und elektrisehe Leitfähigkeit einiger geschmolzenen salze, *Bull Acad Imper Sci*., (St Petersberg), Vol.8, p.405, 1914 (in Russian).

[7] (a) T Welton, Room temperature ionic liquids, solvents for synthesis and catalysis, *Chem Rev*., Vol.99, p.2071, 1999; (b) Ionic liquids: A brief history, *Bio-*

phys Rev., 2018, https://doi.org/10.1007/s12551-018-0419-2; (c) Paul Walden (1863–1957): The man behind the Walden inversion, the Walden rule, the Ostwald–Walden–Bredig rule and ionic liquids, G Boeck, Chem Texts, 2019, https://doi.org/10.1007/s40828-019-0080-9.

[8] (a) W A Henderson, P Fylstra, H C D Long, P C Trulove and S Parsons, Crystal structure of the ionic liquids $EtNH_3NO_3$ – Insights into the thermal phase behaviour of protic ionic liquids, *Phys Chem Chem Phys*., Vol.14, p.16041, 2012; (b) V N Emel'yanenko, G Boeck, S P Verevkin and R Ludwig, Volatile times for the very first ionic liquid: Understanding the vapor pressure and enthalpies of vaporization of ethyl ammonium nitrate, *Chem Eur J*., Vol.20, p.11640, 2014; (c) J Claus, F O Sommer and U Kragl, Ionic liquids in biotechnology and beyond, *Solid State Ionics*, Vol.314, p.119, 2018.

[9] P C Rây and J N Rakshit, Nitrites of the alkylammonium bases: Ethylammonium nitrite, dimethylammonium nitrite and trimethylammonium nitrite, *J Chem. Soc., Trans*., Vol.99, p.1470, 1911.

[10] A G Morachevskii, Academicial Pavel Evanovich Walden (on 140th anniversary of his birthday), *Russian J Appld Chem*., Vol.76, p.1186, 2003.

[11] A Chakravorty, The chemical researches of Acharya Prafulla Chandra Ray, *Indian J Hist Sci*., Vol.49.4, p.361, 2014.

[12] (a) P C Rây, On mercurous nitrite, *J Asiatic Soc Bengal*, Vol.65, p.1, 1896; (b) P C Rây, Über merkuronitrit, *Z Anorg Chem*., Vol.12, p.365, 1896 (in German).

[13] Noted in *Nature*, 54, 83, 1896.

[14] R Dutta, S Kundu and N Sarkar, Ionic liquid-induced aggregate formation and their applications, *Biophys Rev*., 2018, https://doi.org/10.1007/s12551-018-0408-5

[15] P C Rây and H K Sen, Tetramethylammonium hyponitrite and its decomposition by heat, *J Chem. Soc Trans*., Vol.99, p.1466, 1911.

Address for Correspondence
Rajarshi Ghosh
Department of Chemistry
The University of Burdwan
Burdwan 713 104, India.
Email:
rghosh@chem.buruniv.ac.in