Discovering the discoverer: the case of ionic liquids

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Paul Walden, the Russian–German chemist is generally considered as the discoverer of room temperature ionic liquid as in 1914 he reported the isolation and characterization of [EtNH$_3$](NO$_3$), which despite being ionic in nature remained liquid at room temperature. In 1911, the famous Indian scientist Acharya Prafulla Chandra Rây reported a similar type of ionic compound ([EtNH$_3$](NO$_2$)) which was also liquid at room temperature. So it is both scientifically and historically obvious that Rây should be regarded as the discoverer of room temperature ionic liquid and not Walden.

Ionic liquids are used as important green reaction media in modern synthetic chemistry as they are non-volatile, non-coordinating and immiscible with a number of organic solvents[1]. The common organic solvents, which are mostly volatile in nature, are used in chemical reactions in large amounts in general. The vapours of these solvents easily reach the lungs while breathing and cause severe damage to human health. This is why several chemical reactions are now-a-days done in ionic liquids. The ionic liquids are generally composed of an organic cation and an inorganic anion. The common organic cations used are alkylammonium, alkylphosphonium, *N*-alkylpyridinium and *N*,*N*′-dialkylimidazolium. Chloride, nitrate, nitrite, etc. are the common inorganic anions. To the best of the present author's knowledge, Paul Walden[2] is considered as to be the first person to report room temperature ionic liquid in 1914, when he described the synthesis and characterization of [EtNH$_3$](NO$_3$). Walden was actually searching for molten salts which were liquid at room temperature[3]. A critical scrutiny of the literature reveals that the celebrated Indian scientist Acharya Prafulla Chandra Rây (1861–1944) and Rakshit[4] synthesized a similar kind of molecule, viz. ethylammonium nitrite ([EtNH$_3$](NO$_2$); which was a yellow liquid at room temperature), three years prior to the work of Walden.

Nitrite chemistry by Rây

Rây joined the Presidency College, Kolkata in 1889, and started his teaching and independent research career. The first notable work of Rây[5] was the preparation and isolation of mercurous nitrite, in which both mercurous and nitrite ions are unstable separately. Stability of mercurous nitrite remained questionable for a long period of time. Recently, the molecular structure of mercurous nitrite was derived by single crystal X-ray diffraction, which concluded the long standing controversy regarding its stability [6]. During 1911–13, Rây[7] was engaged in the synthesis and characterization of a number of nitrite salts of organic cations. Ray and Rakshit[4] reported details of [EtNH$_3$](NO$_2$) which appeared as a liquid at room temperature. Rây did not mention it as an 'ionic liquid', but its properties were the same as [EtNH$_3$](NO$_3$), which was reported later by Walden[2]. Further, the nitrite salt synthesized by Rây and coworkers was more difficult to isolate than the nitrate salt of Walden as nitrite is lesser stable than nitrate. In fact, the nitrite salt synthesized by Rây and Rakshit[4] slowly dissociates at room temperature (23°–30°C).

Contributions of Walden

Walden (1863–1957) was appointed as a lecturer of physical chemistry at Riga Polytechnic Institute in Latvia (previously in Russia) in 1892 (ref. 8). Later Walden moved to the University of Rostock, Germany, where he worked from 1919 to 1934. Walden's most important contributions appeared in 1895, when he discovered the inversion of configuration of chiral centre in an organic second-order nucleophilic substitution reaction (SN^2) (ref. 8). This phenomenon was later named after him (Walden inversion). He also discovered a relationship between the equivalent electrical conductivity at infinite dilution and viscosity[8]. This is now known as the Walden rule. Beyond chemistry, like Rây, Walden was also interested in the history of the subject[8] and has authored the book *Ocherk istorii khimiii v Rossii* (*Study on the History of Chemistry in Russia*).

Conclusion

Considering the scientific contributions of both Rây and Walden, there should not be any doubt that Rây synthesized the ionic liquid for the first time before Walden. It is unfortunate that Rây's work was not cited by Walden[2]. Though the concept of ionic liquids was established much later, historically Rây should be regarded as the first scientist to have synthesized liquid ionic salts (which were re-named as ionic liquids later) at room temperature. This important synthesis in 1911 was preceded as well as followed by two more similar types of synthesis by Rây, i.e. those methylammonium nitrite[9] and nitrites of benzylammonium series[10]. All these compounds are solid as expected (as they are ionic). Ethylammonium nitrite, the compound under discussion, is a liquid may be due to imperfect solid-state packing. Considering all these facts, Rây should be credited with the discovery of room-temperature ionic liquids.

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