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LABORATORY EXPERIMENT

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Readily Made Solvated Electrons

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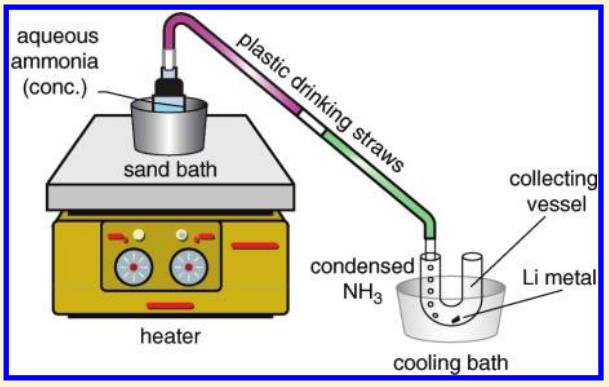
ABSTRACT: The existence of solvated electrons has been known for a long time. Key methods for their production (i.e., photoionization of reducing ions, water radiolysis, and the reaction between H· and OH^-) are unsuitable for most school laboratories. We describe a simple experiment to produce liquid ammonia and solvated electrons using materials commonly available, without the dangers associated with the use of solid Na or K metal.

KEYWORDS: First-Year Undergraduate/General, Upper-Division Undergraduate, Physical Chemistry, Laboratory Instruction, Hands-On Learning / Manipulatives, Amines/Ammonium Compounds, Laboratory Equipment/Apparatus, Lewis Acids/Bases, Oxidation/Reduction



The existence of solvated electrons was speculated long ago.[1] The earliest known example of an established electron excess in a liquid is alkali metals that produce stable blue solutions owing to solvated electrons in liquid NH_3 (i.e., ammoniated electrons).[2,3] These ammoniated electrons display a broad s → p absorption band in the near-infrared[3] and a singlet is observed in the EPR spectrum (e.g., in ethylamine).[2] The shapes of their absorption bands change from one solvent to another.[4]

The ammoniated electron can be viewed as an electron in a solvent cavity in which the ground state of its s-type wave function fills the interstitial void among six to nine NH_3 molecules.[3] Alkali metal cations are not included in the cavity[3] and there is no "central" set of nuclei around which the electrons occupy specific orbitals.[2] Alternatively, it can be viewed as a solvent-stabilized radical anion where most of the excess electron density resides in the N atoms of the NH_3 molecules;[3] this results from the repulsion of negatively charged solvent molecules.[3] In fact, the volume change on electron solvation is estimated to be nearly three times that of a solvent molecule;[3] the effective number of solvent molecules that serve to localize a solvated electron (for example in methylamine) is 0.83.[5]

Key methods for the production of solvated electrons (i.e., photoionization of reducing ions, water radiolysis, and the reaction between H· and OH^-), as well as key properties (i.e., color, spin, and charge), key reactions, and thermodynamic properties, have been reviewed.[1] In hydroxylated liquid solvents (e.g., H_2O), the lifetime of the solvated electrons is short.[3] They are unstable at low pH owing to reaction with readily available H_3O^+ to yield H·;[1] thus, basic solvents such as ammonia, amines, and amides solvate the electrons in a different fashion than H_2O and alcohols and produce more stable arrangements.[3] Solvated electrons behave as reactive ions.[1]

The applications of solvated electrons are numerous, for example, the reduction of some aromatics, known as Birch reduction, for synthetic and environmental remediation purposes.[6−9] These, together with their theoretical interest[10] and use in modeling[11] justify their inclusion in undergraduate education.

In view of the difficulties associated with the preparation methods described above,[1] we present a simple experiment to produce solvated electrons using materials commonly available in undergraduate laboratories without the dangers associated with the use of solid Na or K metals (i.e., vigorous reactions or explosions, see examples in refs 12−14) in a reasonably safe manner. The production of liquid ammonia and the use of a simple and inexpensive source for a metal alkali are also interesting from an educational standpoint.

EXPERIMENT

Inside a fume hood, place 30 mL of concentrated aqueous ammonia[15] in a suitable container (e.g., a 50 mL distillation flask). This container may also be any round-bottom flask or another suitable vessel, even baby food glass containers or plastic wash bottles work well. Concentrated aqueous ammonia can be found at drugstores, hardware stores, or local blueprint supply stores. The container is referred to as the *ammonia generator* (Figure 1). A similar generator was used by Ilich and co-workers.[7]

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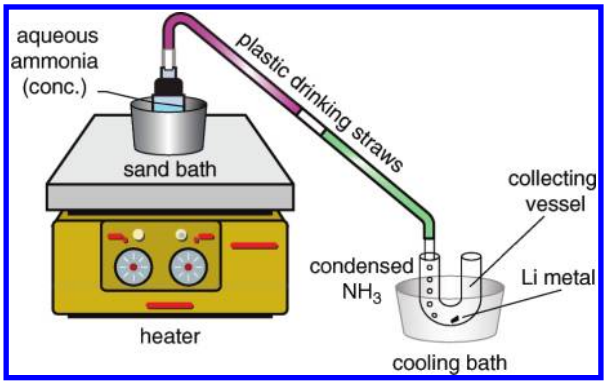

Figure 1. Experimental setup.

Figure 2. Opening a Li battery. Some form of insulation is advisable to prevent the battery from discharging by short circuit with the vise's metal.

Figure 3. Removing Li from the battery components.

Place the generator in a sand bath on a hot plate; cap the container with a one-hole rubber stopper with a 6−7 cm glass tube connected to direct the gaseous NH_3 through a rubber tube into a collecting vessel (plastic drinking straws as shown in Figure 1 can also be used). The collecting vessel can be a 1 cm diameter, 10 cm tall U-tube inside a styrofoam coffee cup filled with a cooling fluid. The cooling fluid can be liquid nitrogen or computer-cleaning fluid. The computer-cleaning fluid can be obtained as a liquid by inverting the spray can and pressing its valve, using a plastic straw attached to the valve for ease in manipulation. Other coolants may be tried as well, for example, dry ice with acetone,[16] 2-propanol,[17] $CaCl_2$,[18] *o*-xylene/*m*-xylene,[19] or 2-butanol.[7]

To produce gaseous NH_3, heat the sand bath to at least 40 °C. To aid the process, a couple of NaOH pellets can be added to the concentrated aqueous ammonia (see discussion section below). An alternative method of $NH_3(g)$ generation consists of the addition of a saturated solution of NH_4Cl to NaOH pellets; the liquid reactant can be introduced into the ammonia generator with a syringe.[20] The cooling fluid surrounding the collecting vessel will radically lower the temperature and force NH_3 gas to condense. The normal boiling point of ammonia is −33.33 °C. Some water vapor may condense as well; if dry NH_3 were desired, place a drying tube loosely packed with dehydrated $CaSO_4$ between the ammonia generator and the collecting vessel. As not all of the NH_3 condenses, one has to be careful not to breathe the excess. A piece of wet pink litmus paper placed at the end of the reaction system is an excellent indicator for NH_3 vapors.[21]

After a small volume, 1−2 mL, of liquid ammonia has collected at the bottom of the collecting vessel, carefully pry open a new disk-type 3 V Li battery (e.g., CR2032) fixed on a mechanics bench vise (Figure 2). With a spatula (Figure 3), scoop out a small quantity of Li (e.g., the size of a lentil)[22,23] and drop the Li piece into the liquid NH_3 inside the collecting vessel. Watch for signs of reaction. Alternatively, the Li can be placed in the U-tube prior to the ammonia gas generation.

HAZARDS

Wear goggles and a lab coat at all times during this experiment. NH_3 gas is harmful, avoid breathing it. Liquid nitrogen or the liquefied computer-cleaning fluid may harm the skin or cause frostbite; handle with care. Avoid inhalation of computer-cleaning fluids as they normally contain chlorofluorocarbons that may prevent oxygen intake by displacement of air. Li and Na are alkali metals and thus very reactive; do not touch with your bare skin nor allow their contact with water or other protonated solvents. According to the manufacturer, Li batteries pose a risk of fire and can explode or leak if disassembled.

RESULTS AND DISCUSSION

The endothermic equilibrium,

$$NH_4^+(aq) + OH^-(aq) \leftrightharpoons NH_3(g) + H_2O(l) \qquad (1)$$

is displaced to the right by heating and by the addition of hydroxide ions. When the Li is added to the liquid NH_3, a blue color develops near the Li surface:

$$Li(s) + (x+y)NH_3(l) \leftrightharpoons [Li(NH_3)_x]^+(solv) + [e(NH_3)_y]^-(solv) \qquad (2)$$

The interactions of unbound electrons with the surrounding solvent molecules give rise to a strong absorption at λ_{max} = 1500 nm.[7] A red coloration would signal a higher concentration of ammoniated electrons. By using Na metal and liquid nitrogen instead of lithium metal and computer-cleaning fluid, the blue coloration is more easily observed but the procedure is more dangerous (see the hazards).

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