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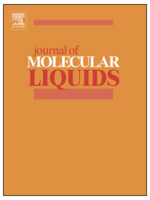

UV–visible spectroscopic study of laser irradiated lithium colloids and ionic liquids

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ABSTRACT

The UV–visible spectroscopy of laser irradiated lithium colloids and ionic liquids has been investigated. TEM00 mode 1064 nm DPSS laser (LSR1064NL) of intensity 148 W/cm^2 and 950 mW power was passed through Li containing Acetonitrile, Methanol, Hexane, 1,4-Dioxane and Chloroform for 30 min. The Li metal and laser irradiation markedly affected the lower wavelength cut-off i.e., pattern of absorption spectrum of solvents and colloids. The sharp band at 190 nm and two new broad bands at 256 nm and 292 nm are presumably due to the formation of monolithium derivatives of Acetonitrile (i.e., $\mathrm{Li{-}CH_2CN}$, $\mathrm{Li{-}CH{=}C{=}NH}$, $\mathrm{Li{-}C{=}CNH_2}$, $\mathrm{CH{=}CN{-}Li{-}H}$ and $\mathrm{CH_{2}{}_{-}{=}N{-}Li}$) on irradiation. However comprehensive research on same is required to be performed. The present study is certainly helpful in understanding the long-term performance and the mechanism by which the properties of colloids change.

1. Introduction

Energy storage devices have been in use for a long time now. Two main approaches currently used are using rechargeable batteries or using super-capacitors. Most common batteries include lithium-ion batteries and more recent flexible lithium-ion batteries [1,2] and lithium-air batteries [3–5]. From the beginning, lithium-air batteries have been a front runner in the research of high density energy store materials [3,5–7] due to high theoretical specific energy [8]. However the progress in this field is still slow due to degradation of various components during the electrochemical cycle [5]. As liquid electrolyte governs the nature and kind of discharge products, a thorough study with various electrolytes is a need of the hour. In this regard some previous work has already been carried out [8–12]. Further to this chemical/electrochemical behaviour of lithium in solution and colloids are important in understanding the underlying chemistry behind working of electrochemical energy storage devices [14,15]. To further look into these aspects of Li based batteries in the present work, we report UV–visible spectroscopy of lithium colloids and ionic liquids in the presence of laser beam irradiation. Our study gives an insight into the electrochemistry of lithium in solutions and colloids in the presence of 1064 nm laser beam.

Ultraviolet–visible (UV–visible) spectrometry is one of the most frequently used characterisation techniques used by chemists. This technique studies the changes in electronic energy levels within the molecule arising due to transfer of electrons from bonding pi (π) or non-bonding (n) electrons. When a molecule absorbs energy, an electron is promoted from an occupied molecular orbital to an unoccupied molecular orbital of higher potential energy. The absorption of incident radiation by bonding/non-bonding electrons (require 100 kcal mol^{-1}) represents a high energy transition. This corresponds to a high frequency or low wavelength and the absorption band appear in the UV–visible range (200 nm–800 nm). The UV–visible spectra are usually measured in dilute solutions and the most important criterion is the choice of the solvent transparent within the wavelength range being examined. The UV–visible spectroscopic data can be of value in determining the kinetics of a process where the disappearance of absorption band represents the starting material. The presence of absorption band at a particular wavelength is often a good indicator of the presence of chromophore or auxochrome i.e., group containing a π-bond [16]. The position and intensity of absorbance maximum are known to depend on the molecular environment of the chromophore or auxochrome and solvent in which solute is dissolved. Other parameters like pH and temperature (T) may also cause change in the intensity and wavelength of the absorbance maximum (λ_{max}). Further addition of metals to the solvents shifts the position and intensity of various absorption bands.

In the present work we have studied the absorption spectroscopy of Li containing Acetonitrile, Hexane, Methanol, 1,4-Dioxane and Chloroform. The laser TEM00 mode 1064 nm DPSS laser (LSR1064NL) of intensity 148 W/cm^2 and 950 mW power passed through Li solutions for 30 min. The UV–visible spectra were recorded at the wavelength ranging from 200 nm–800 nm. Choice of the laser is governed by the fact that the absorption maxima of all these solvents fall in UV regions and thus the laser irradiation will not affect the integrity of the solvents. This makes it possible to evaluate the effect of irradiation on the

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Li-solvent solutions with a stable solvent. To further ascertain this fact we have separately carried out control experiments for all the solvents by irradiating them with laser irradiation and recording the UV–visible spectra before and after the laser treatment with the passage of time. We have found no degradation of solvents due to presence of radiation with the power levels of laser we are using for the experiment. In addition we have performed FT-IR spectroscopy on the solutions with same experimental conditions used in the UV–visible spectroscopy.

2. Experimental detail

All the reagents and solvents of high pure grade (>99%) were purchased from Sigma-Aldrich, Merck, Alfa-Aesar and used without further purifications. 1 mM Li solutions using Acetonitrile, Hexane, Methanol, 1,4-Dioxane, Toluene and Chloroform were prepared. Lithium solid (from Sigma-Aldrich), as stored in Paraffin oil was cut into small pieces and dried using butter paper under low humid conditions to avoid oxidation. Required weight was then taken to form the solutions. The laser used for the experimentation was TEM00 mode 1064 nm DPSS laser (LSR1064NL, LASEVER, China) of 1 W power. Although the beam spot shape was quoted as 1:1:1, the ellipticity was removed by anamorphic prism pair to 1.5 mm $1/e^2$ diameter. After the beam shaping, the laser light falls on a convex lens of 50 cm focal length and was passed through quartz cuvette containing Li solution with intensity 148 W/cm^2 for 950 mW power. The laser wavelength at 1064 nm was employed and was monitored with the wavelength meter (Angstrom WS-6) for any temperature drifts in the pumping diode laser. Part of the beam was coupled to a fibre and then sent to the wavelength meter for this purpose. The schematic experimental setup of irradiation of Li solutions is as shown in Fig. 1.

The absorption spectra of irradiated Li solutions taken in the quartz cuvette of length 5 mm were measured of wavelength from 200 to 800 nm using the PerkinElmer UV–visible spectrophotometer.

Caution: Although no problems were encountered during the preparation of Li solutions, greater attention must be paid for all along the preparations. Safety equipments and other necessary precautions are highly recommended during the preparation of solution.

3. Results & discussion

At the outset 1 mM Li solutions in Acetonitrile, Hexane, Methanol, 1,4-Dioxane, Toluene and Chloroform were prepared. The laser TEM00 mode 1064 nm DPSS laser of intensity 148 W/cm^2 passed through Li solutions for 30 min. The experiment was repeated at different laser powers by changing the power supply current and the optimum wavelength was observed at 950 mW power. Then the absorption spectra were recorded from 200 to 800 nm. When laser radiation is passed through a sample of any substance, the intensity is reduced by same factor with the distance travelled. The intensity thus decays exponentially due to absorption of the sample.

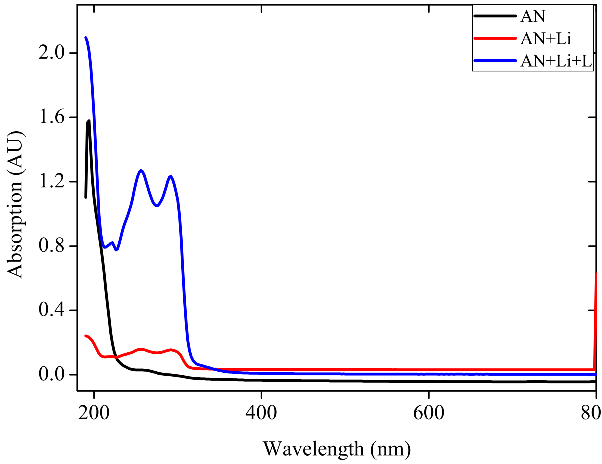

Fig. 1. UV–visible spectra of a) Acetonitrile, b) Acetonitrile-lithium solution and c) irradiated Acetonitrile-lithium solution.

Most absorption by organic compounds results from the presence of π-bonds and often from σ-bonds. Accordingly four types of transitions namely $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions can occur by the absorption of UV–visible radiations. A transition in which a bonding σ-electron is excited to antibonding σ-orbital is referred to as $\sigma \rightarrow \sigma^*$ transition. In the same way $n \rightarrow \sigma^*$ transition represents the transition of one of the lone pairs to antibonding σ-orbital; $\pi \rightarrow \pi^*$ transition represents the transition of one of the lone pairs to antibonding π-orbital and $n \rightarrow \pi^*$ transition represents the transition of one of nonbonding to antibonding π-orbital. The $\sigma \rightarrow \sigma^*$ and $n \rightarrow \sigma^*$ transitions occur in the molecules with saturated centres and require higher energy i.e., in the region 180–240 nm. The $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions occur in the molecules with unsaturated centres that require lower energy (>240 nm). Further the λ_{max} of compounds is changed with the solvent and the concentration of solution. Four types of shifts in the λ_{max} values are possible: (i) shift of λ_{max} to longer wavelength or less energy is due to the substituent or solvent effect is referred as bathochromic or red shift, (ii) shift of λ_{max} to shorter wavelength or higher energy is due to the substituent or solvent effect is referred as hypsochromic or blue shift, (iii) an increase in the absorption intensity called as hyperchromic shift and (iv) a decrease in the absorption intensity called as hypochromic shift. The electronic transitions are usually accompanied by a simultaneous change between the vibrational levels.

Acetonitrile is a volatile colourless versatile solvent used in analytical applications due to its unique properties of polarity and low boiling point and cut-off wavelength 194 nm [17]. It reacts with Li at room temperature to liberate hydrogen gas. After passing laser radiation through the Li solution, the characteristic bands have been found to be changed. The UV–visible spectra of Acetonitrile and its Li containing solutions are shown in Fig. 1. The sharp band at 194 nm moved to the higher wavelength of 190 nm (i.e., red shift) and two new broad bands have appeared at 256 nm and 292 nm. This, as we speculate, is due to the formation of monolithium derivatives of Acetonitrile and released hydrogen gas on irradiation [8,12]. The UV–visible spectrum of the Li solution shows cyanide absorption higher than the parent Acetonitrile indicating a weakening of the cyanide linkage. The nitriles are known to undergo $n \rightarrow \sigma^*$ transition and $n \rightarrow \pi^*$ transition of characteristic cut-off wavelengths of 194 nm and 300 nm. The two distinctive bands observed at 256 nm and 292 nm after irradiation are speculated to be due to the formation of $Li–CH_2CN$, an organometallic compound. The $Li–CH_2CN$ bond is of intermediate character between ionic and covalent bonds. The various bands of solutions both irradiated and non-irradiated apparently of the characteristic bands of lithium containing compounds: $Li–CH_2CN \leftrightarrow Li–CH{=}C{=}NH \leftrightarrow Li–C{=}CNH_2 \leftrightarrow CH{=}CN–Li–H \leftrightarrow CH_2–C{=}N–Li$ [10]. The higher absorption is partially caused by the partial formation of a dilithium compound or by addition to the C≡N bond. The absorption band at 194 nm is assigned to the weakened cyanide in agreement with the literature [13].

Methanol has cut-off wavelength of 218 nm Fig. 2. It is seen that after irradiation of Methanol-Li solution, the cut-off wavelength and the intensity of band have been changed. The sharp band at 218 nm has become two broad bands appeared at 216 nm and 252 nm. It is believed that Li, similar to Na liberated hydrogen gas on irradiation. The O–H bond of the molecules is easily susceptible to be broken on the addition of alkali and alkaline earth metals. Alcohols are known to undergo $n \rightarrow \sigma^*$ transition of characteristic cut-off wavelength of 218 nm. The two distinctive bands at 216 nm and 252 nm after irradiation are probably due to the formation of lithium methoxide (CH_3O-Li) and liberated hydrogen gas on irradiation. The CH_3O-Li bond is of intermediate character between ionic and covalent bonds. The sharp band at