



*J. Serb. Chem. Soc.* 79 (3) 313–324 (2014)  
JSCS-4586

# Journal of the Serbian Chemical Society

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UDC 661.34+546.34:541.18.045:543.51

Original scientific paper

## Study of the vaporization of LiI, LiI/C<sub>70</sub>, LiI/LiF/C<sub>70</sub> from a Knudsen cell located in the ionization chamber of a mass spectrometer

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(Received 27 June 2012, revised 25 July 2013)

**Abstract:** The vaporization of LiI, LiI/C<sub>70</sub> and LiI/LiF/C<sub>70</sub> was studied using a Knudsen cell located in the ionization chamber of a magnetic sector mass spectrometer in the temperature range from 350 °C to 850 °C. The ion species, Li<sub>n</sub>I<sup>+</sup> ( $n = 2, 3, 4$  or  $6$ ) were identified from the mixture LiI/C<sub>70</sub>, while the clusters Li<sub>n</sub>I<sup>+</sup> and Li<sub>n</sub>F<sup>+</sup> ( $n = 2, 3, 4, 5$  or  $6$ ) were detected from a mixture LiI/LiF/C<sub>70</sub>. The intensities of Li<sub>n</sub>I<sup>+</sup> were higher than the emission of Li<sub>n</sub>F<sup>+</sup> cluster when the ratio of LiI to LiF was 2:1. By contrast, the emission of Li<sub>n</sub>F<sup>+</sup> is favored when the ratio of LiI to LiF was 1:2. These results show that the vaporization of a mixture LiI/LiF/C<sub>70</sub> from a Knudsen cell located in the ionization chamber of a mass spectrometer represents an efficient and simple way to obtain and investigate clusters of the type Li<sub>n</sub>X, X = F or I. In this work, it was also shown that the trends of the *In* (Intensity, arb. units) *versus* temperature for all Li<sub>n</sub>I<sup>+</sup> clusters below and above the melting point of LiI were not same. This suggested that the manner of formation of these clusters could be different due to changes in temperature.

**Keywords:** “superalkali” species; Li<sub>n</sub>I clusters; Li<sub>n</sub>F clusters.

### INTRODUCTION

A Knudsen cell with mass spectrometry (KCMS) has proven to be one of the most useful experimental techniques for investigation the equilibrium between condensed phases and complex vapor. The Knudsen effusion method involves placing a condensed sample in a Knudsen cell, with an orifice of well-defined geometry. The Knudsen cell is uniformly heated and held until equilibrium between the condensed and vapor phases is attained. The orifice dimensions must be kept less than one tenth of the mean free path of the vapor species. The vapor is continuously sampled by effusion through a small orifice in the cell. A mole-

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doi: 10.2298/JSC130627083D

cular beam is formed in the KCMS and directed into a mass spectrometer for identification.<sup>1</sup>

The vaporization of alkali halides such as LiI and LiF by the KCMS method were investigated and discussed in terms of their vapor compositions in equilibrium with the condensed phases.<sup>2–6</sup> As a result,  $\text{Li}^+$ ,  $\text{LiX}^+$ ,  $\text{Li}_2\text{X}^+$  and  $\text{Li}_3\text{X}_2^+$  ( $\text{X} = \text{F}$  or  $\text{I}$ ) ions were detected. The precursor of both  $\text{Li}^+$  and  $\text{LiX}^+$  was the monomer ( $\text{LiX}$ ), whilst  $\text{Li}_2\text{X}^+$  and  $\text{Li}_3\text{X}_2^+$  were obtained from the dimer ( $\text{Li}_2\text{X}_2$ ) and the trimer ( $\text{Li}_3\text{X}_3$ ), respectively.

Since the salts of alkali metal are the strongest ion emitters, the KCMS method was also applied for investigations of their homogenous and heterogeneous clusters. Studies on metallic clusters are of considerable interest in research due to their potential application in catalytic processes, materials science, biology, and medicine.<sup>6–10</sup> Especially, lithium homogenous clusters have received great attention from physicists and chemists as prototypes for the investigation of the properties of metallic clusters. The existence of stable  $\text{Li}_2$ ,  $\text{Li}_3$ ,  $\text{Li}_4$  and  $\text{Li}_5$  clusters was proved experimentally and their thermodynamic properties were determined by KCMS.<sup>11–13</sup> The first “hypervalent”  $\text{Li}_3\text{O}$  cluster was also found by KCMS in the equilibrium vapor over  $\text{Li}_2\text{O}$  salt.<sup>14</sup> This method was employed to obtain other small size “hypervalent” lithium clusters, such as  $\text{Li}_6\text{C}$ ,  $\text{Li}_4\text{O}$ ,  $\text{Li}_3\text{S}$ ,  $\text{Li}_4\text{S}$ ,  $\text{Li}_4\text{P}$ ,  $\text{Li}_2\text{CN}$ ,  $\text{Li}_n\text{H}$  ( $n = 1, 2, 3$  or  $4$ ) in the equilibrium vapor over the appropriate salts.<sup>15–20</sup> Generally, “hypervalent” species possess nine or more valence electrons and these clusters are of particular importance because they violate stoichiometry based on the octet rule.<sup>21</sup> Due to their unusual stoichiometries, “hypervalent” clusters have large values of the first hyperpolarizabilities; therefore, they could be considered a new kind of non-linear optical species.<sup>22</sup> In addition, earlier investigation revealed that these clusters are important intermediates in metal cluster and metal surface reactions, which could affect the catalytic and electronic properties of a metal.<sup>23</sup> The most remarkable property of “hypervalent” clusters is their enormously low ionization energy (*IE*). Their ionization energies are lower than the *IEs* of the alkali metals and for this reason, they are called “superalkali”.<sup>24–29</sup> Recently, it was theoretically also shown that “superalkali” clusters are of great significance in chemistry because they can mimic the characteristics of alkali metals and maintain their structural and electronic integrities when assembled with other species. By combining “superalkali” with another element or clusters, a new small “superatom” clusters can be formed. The “superatom” clusters represent potential building blocks for new cluster-assembled materials with unique structural, electronic, optical, magnetic and thermodynamic properties.<sup>30–35</sup> However, experimental results on “superalkali” clusters are scarce.

The present investigation is an extension of previous systematic studies of the way for obtaining “superalkali” clusters by the evaporation of lithium haloge-

nated salts using a thermal ionization source and a Knudsen cell in combination with a mass spectrometer.<sup>36–43</sup> In the earlier papers, it was shown that the experimental setup in which the Knudsen cell was located in the ionization chamber provides better conditions than the standard experimental setup of the KCMS for obtaining both the neutral and positively charged “superalkali” clusters of the type Li<sub>n</sub>X, X = F or I ( $n = 2, 3, 4, 5$  or 6).<sup>40–43</sup> However, the effects of the chemical composition of the samples which are placed in the Knudsen cell on the production of neutrals and positive ions of these clusters have not been investigated. The focus of this work was an investigation of the conditions for obtaining non-stoichiometric Li<sub>n</sub>I and Li<sub>n</sub>I<sub>n-1</sub> clusters, from samples such as lithium iodide salt, a mixture lithium iodide/fullerene (C<sub>70</sub>), a mixture of lithium iodide/lithium fluoride salt and a mixture lithium iodide/lithium fluoride/fullerene (C<sub>70</sub>).

The relation between the intensity of the ions from the condensed phase and the temperature of the cell was also investigated.

#### EXPERIMENTAL

The standard experimental setup of the KCMS implies that the cell is placed outside the ionization chamber. In this work, the Knudsen cell was placed in the ionization chamber of a magnetic sector mass spectrometer (a 12-inch radius and 90° magnetic sector). The scheme for the ion source is presented in Fig. 1.

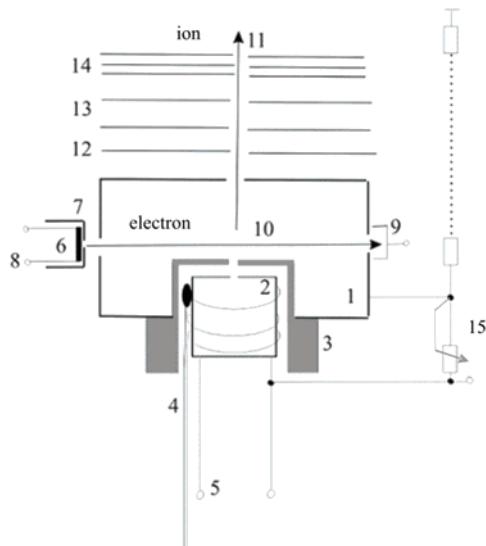


Fig. 1. Schematic diagram of the ion source: 1. ionization chamber; 2. Knudsen cell; 3. ceramic shields; 4. thermocouple; 5. heater for chamber; 6. incandescent rhenium cathode; 7. Vhnelt cylinder; 8. heater for cathode; 9. electron trap; 10. electron beam; 11. ion beam; 12. focusing electrode; 13. accelerating electrode; 14. deflectors electrode; 15. potential repeller.

The nickel Knudsen cell was heated with direct current through a tungsten wire. The height of the cell was 7 mm, the outside diameter was 6 mm and the orifice diameter was 0.1 mm. The heater was surrounded by a shield made of ceramic material. The temperature was

measured by a Pt–Pt/Rh thermo-couple attached to the cell. A cell temperature stability of  $\pm 10$  K was achieved.

The experimental setup presented in Fig. 1 allows the detection of both the ionic and neutral components. Neutral species were detected in the conventional way in the electron impact ionization (EI) mode. Electrons were obtained from a rhenium cathode inside a Vehnelt cylinder and extracted by a plate at a positive potential of 15 V with respect to the cathode that was positioned at a distance 2 mm from the cathode. The clusters, electron and ion beams were mutually perpendicular. In this case, the Knudsen cell was held at the same voltage as the ionization chamber. The Knudsen cell was placed in the ionization chamber; the distance from the cell orifice to the electron beam of the ion source was about 2 mm.

In the case when the Knudsen cell was held at voltage of 30 V with respect to the ionization chamber, the experimental setup permitted the direct identification of positively charged ionic components generated in the cell, thermal ionization (TI) mode.

In this work, the Knudsen cell was used as a chemical reactor for the production of the iodine-doped lithium clusters. In all experiments, the samples weighing 0.089 g were placed into the Knudsen cell at atmospheric pressure. The samples were lithium iodide salt, a mixture lithium iodide/fullerene ( $C_{70}$ ), a mixture lithium iodide/lithium fluoride salt and a mixture of lithium iodide/lithium fluoride/fullerene ( $C_{70}$ ). In order to remove the adsorbed moisture, the cell with the substance was dehydrated directly in the mass spectrometer at 150 °C for several hours.

In earlier work, it has been shown that in the vapor over a salt of lithium fluoride the ions  $Li_2F^+$  ( $m/z$  33) and  $Li_3F_2^+$  ( $m/z$  59) clusters were obtained.<sup>2</sup> Also, the ions as  $Li_2I^+$  ( $m/z$  141) and  $Li_3I_2^+$  ( $m/z$  276) were identified to be generated from the vapor of LiI.<sup>6</sup> As can be observed, the peaks corresponding to the clusters of lithium fluoride were detected at lower mass than the mass of clusters of lithium iodide, for this reason, a salt LiF was used as an additional source of  $Li^+$ .

## RESULTS AND DISCUSSION

In the present work, as the first step, the vaporization of lithium iodide salt by the Knudsen cell located in the ionization chamber of the magnetic sector mass spectrometer over the temperature range from 350 to 600 °C was investigated. The temperature dependence of the natural logarithm of the ion intensity at an ionizing electron energy of 40 eV for all detectable ions is shown in Fig. 2. Similar curves were obtained for other electron energies, such as 20 and 30 eV.

The following ion species were detected:  $I^+$ ,  $I_2^+$ ,  $Li^+$ ,  $LiI^+$ ,  $Li_2I_2^+$ ,  $Li_2I^+$ ,  $Li_3I_2^+$  and  $Li_4I_3^+$ , which coincides well with previous results obtained using a standard KCMS.<sup>6</sup> The results obtained in the present study are compared in Table I with those obtained by other researchers.

In the present case, the relative intensities of  $I^+$ ,  $I_2^+$ ,  $Li^+$ ,  $LiI^+$ ,  $Li_2I_2^+$ ,  $Li_3I_2^+$  and  $Li_4I_3^+$  to the  $Li_2I^+$  were much larger than the literature values.<sup>6</sup> This indicates that the experimental setup in which the Knudsen cell is placed in the ionization chamber provides an efficient way to detect all of the above-mentioned ions.

In the second step, when a mixture LiI/ $C_{70}$  was evaporated from the Knudsen cell and electron bombardment ionization was performed, the ions  $I^+$ ,  $I_2^+$ ,

$\text{Li}^+$ ,  $\text{LiI}^+$ ,  $\text{Li}_2\text{I}_2^+$ ,  $\text{Li}_2\text{I}^+$ ,  $\text{Li}_3\text{I}_2^+$ ,  $\text{Li}_4\text{I}_3^+$ ,  $\text{Li}_2\text{I}^+$ ,  $\text{Li}_3\text{I}^+$ ,  $\text{Li}_4\text{I}^+$  and  $\text{Li}_6\text{I}^+$  were observed. The natural logarithm of ion intensity as a function of temperature of the Knudsen cell for  $\text{Li}_2\text{I}^+$ ,  $\text{Li}_3\text{I}^+$ ,  $\text{Li}_4\text{I}^+$ , and  $\text{Li}_6\text{I}^+$  are presented in Fig. 3. The ions  $\text{I}^+$ ,  $\text{I}_2^+$ ,  $\text{Li}^+$ ,  $\text{LiI}^+$ ,  $\text{Li}_2\text{I}_2^+$ ,  $\text{Li}_3\text{I}_2^+$ ,  $\text{Li}_4\text{I}_3^+$  were detected at similar temperature ranges as in the case of  $\text{LiI}$ ; for this reason, these ions are not shown in Fig. 3.

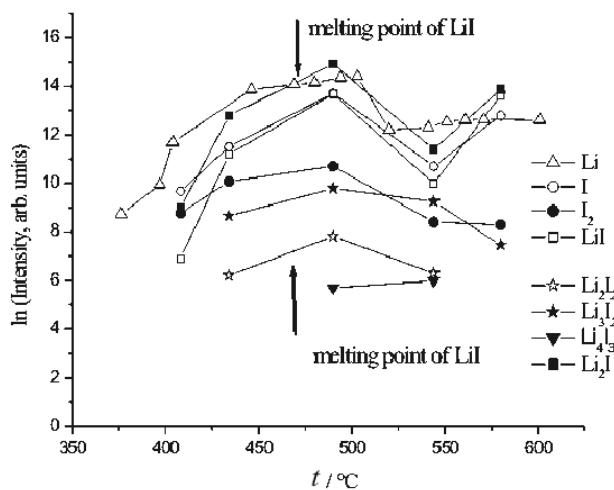


Fig. 2. The natural logarithm of the ion intensity ( $\ln$  (Intensity, arb. units)) versus temperature of the Knudsen cell ( $\ln$  (Intensity, arb. units) versus temperature) for all detectable ions formed from the vapor over pure lithium iodide salt. These results were measured between 350 to 600 °C at 40 eV ionizing electron energy.

TABLE I. Comparison of results obtained in this work with those obtained previously<sup>6</sup>

Ion	$\text{Li}^+$	$\text{I}^+$	$\text{LiI}^+$	$\text{Li}_2\text{I}^+$	$\text{I}_2^+$	$\text{Li}_2\text{I}_2^+$	$\text{Li}_3\text{I}_2^+$	$\text{Li}_4\text{I}_3^+$	$E / \text{eV}$
Literature	16.41	6.99	42.8	100	0.95	0.72	1.67	0.19	30
This work	95.3	91.9	91.94	100	71.81	52.34	65.1	38.25	40

The threshold temperature for the start of the observation of ion signal was found to be about 355 °C for  $\text{Li}_n\text{I}^+$  ( $n = 2, 3$  and 4) clusters (Fig. 3). Initially the ion intensity increased with temperature, then decreased after a maximum at about 395 °C for  $\text{Li}_3\text{I}^+$  and  $\text{Li}_4\text{I}^+$  clusters. Above 455 °C, the emission of  $\text{Li}_3\text{I}^+$  finally decreased to an undetectable level. The ion intensity of  $\text{Li}_4\text{I}^+$  clusters decreased to a minimum at about 455 °C, then slightly increased, and then slightly varied with temperature (from 469 to 657 °C). By contrast, the intensity of  $\text{Li}_2\text{I}^+$  increased to a maximum, had almost constant values in the temperature range from 467 to 593 °C and then decreased. The emission of this ion was not observed above 672 °C.

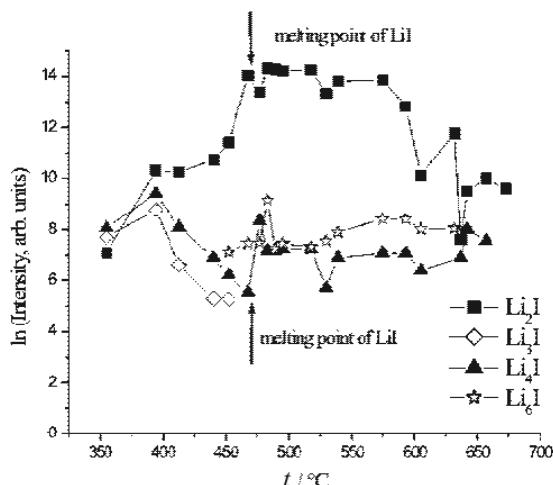


Fig. 3. The natural logarithm of the ion intensity as a function of the temperature of the Knudsen cell ( $\ln$  (Intensity, arb. units) *versus* temperature) for all detectable ions formed from the vapor over a mixture  $\text{LiI}/\text{C}_{70}$ . These results were measured from 350 to 600 °C at 40 eV ionizing electron energy.

The value of threshold temperature for observation of  $\text{Li}_6\text{I}^+$  is lower than the temperature for the appearance of  $\text{Li}_n\text{I}^+$  ( $n = 2, 3$  and  $4$ ). The intensity *vs.* temperature for  $\text{Li}_6\text{I}^+$  increases to a maximum at 485 °C, similar as with  $\text{Li}_2\text{I}^+$ . The intensity of the  $\text{Li}_6\text{I}^+$  cluster after the maximum, somewhat decreases and has almost constant value in the temperature range from 490 to 635 °C. As it can be seen in Fig. 3, the order of the intensities was  $\text{Li}_2\text{I}^+ >> \text{Li}_6\text{I}^+ > \text{Li}_4\text{I}^+$ , while the  $\text{Li}_3\text{I}^+$  cluster was not detected in the temperature range between 450 to 635 °C.

The earlier experimental study showed that  $\text{Li}_2\text{I}_2$ ,  $\text{Li}_3\text{I}_3$  and  $\text{Li}_4\text{I}_4$  could be precursors of  $\text{Li}_2\text{I}^+$ ,  $\text{Li}_3\text{I}_2^+$  and  $\text{Li}_4\text{I}_3^+$ , respectively.<sup>6</sup> In the present work, it is difficult to assume exclusively precursors of  $\text{Li}_n\text{I}^+$  ( $n = 2, 3, 4$  and  $6$ ) clusters, based on the results presented in Fig. 3.

However, the presented results clearly show that the plot of the  $\ln$  (intensity, arb. units) *versus* temperature trends before and after the melting point of LiI (469 °C) do not correspond. At temperatures below the melting point of LiI, in a preliminary experiment, it was shown that the values of the ionization energies for  $\text{Li}_n\text{I}^+$  ( $n = 2, 3$  or  $4$ ) were much higher than their theoretical values. This fact implies that dimer, trimer, tetramer,  $\text{Li}_3\text{I}_2^+$ , and  $\text{Li}_4\text{I}_3^+$  could be precursors of  $\text{Li}_2\text{I}^+$ ,  $\text{Li}_3\text{I}^+$  and  $\text{Li}_4\text{I}^+$ , respectively. Therefore, the appearance energies of  $\text{Li}_n\text{I}^+$  could be measured at temperatures below 469 °C. On the other hand, in a previous work, it was shown that the ionization energies of  $\text{Li}_n\text{I}^+$  ( $n = 2, 4$  and  $6$ ) could be determined at temperatures higher than 550 °C.<sup>41</sup> These ionization

energies are in agreement with the *IEs* obtained by theoretical calculations, meaning that the precursors of Li<sub>n</sub>I<sup>+</sup> clusters were not the same as mentioned above.

This observation suggests that the shape of the *In* (intensity, arb. units) *versus* temperature curves are different possibly due to the dissimilarity in formation mechanisms of these clusters in the Knudsen cell, such as the thermal decomposition of the evaporation species at low temperatures and the reaction of Li<sup>+</sup> with undecomposed LiI at high temperatures.

It should be mentioned that in previous studies, it was revealed that the clusters Li<sub>n</sub>F<sup>+</sup> ( $n = 2, 3, 4, 5$  and 6) and Li<sub>n</sub>I<sup>+</sup> ( $n = 2, 4$  and 6) were obtained in the vapor over a mixture of lithium fluoride and lithium iodide using the experimental setup presented in Fig. 1.<sup>40,42</sup> For this reason, in step III, the evaporation mixtures LiI/LiF/C<sub>70</sub> from the Knudsen cell was studied. Both types of clusters, Li<sub>n</sub>I<sup>+</sup> and Li<sub>n</sub>F<sup>+</sup> ( $n = 2, 3, 4, 5$  and 6), were obtained using a mixture LiI/LiF/C<sub>70</sub>. If the ratio of LiI to LiF was 2:1, the signals of the Li<sub>n</sub>I<sup>+</sup> clusters were higher than those of the Li<sub>n</sub>F<sup>+</sup> clusters. By contrast, if the ratio of LiI to LiF was 1:2, signals of Li<sub>n</sub>F<sup>+</sup> in the mass spectrum were higher than those of Li<sub>n</sub>I<sup>+</sup>. In this work, the Li<sub>n</sub>F<sup>+</sup> were not studied.

At temperatures below the melting point of lithium iodide, I<sup>+</sup>, I<sub>2</sub><sup>+</sup>, Li<sup>+</sup>, LiI<sup>+</sup>, Li<sub>2</sub>I<sub>2</sub><sup>+</sup>, Li<sub>3</sub>I<sub>2</sub><sup>+</sup> and Li<sub>4</sub>I<sub>3</sub><sup>+</sup> were detected by the evaporation of a mixture LiI/LiF/C<sub>70</sub>. In both cases, when a mixture LiI/LiF/C<sub>70</sub> or a mixture LiIC<sub>70</sub> was evaporated, the *In* (Intensity, arb. units) *versus* temperature for Li<sub>n</sub>I<sup>+</sup> ( $n = 2, 3$  and 4) had very similar trends. In addition, the intensities of all detectable ions obtained from a mixture LiI/LiF/C<sub>70</sub> were lower than the intensities of ions formed from a mixture LiI/C<sub>70</sub> before the melting point of LiI. This may be due to the simultaneous creation of Li<sub>n</sub>I<sup>+</sup> and Li<sub>n</sub>F<sup>+</sup> clusters from a mixture LiI/LiF/C<sub>70</sub>, which did not occur during the evaporation of a mixture LiI/C<sub>70</sub>. For this reason, the plots of the *In* (intensity, arb. units) *versus* temperature of the Li<sub>n</sub>I<sup>+</sup> cluster presented in Fig. 4 were obtained at temperatures above 460 °C.

Figure 4, part A, illustrates the variation of the *In* (intensity, arb. units) *versus* temperature for the ion clusters of the type Li<sub>n</sub>I<sup>+</sup> obtained by electron impact ionization. In Fig. 4, part B, the plots of the *In* (intensity, arb. units) *versus* temperature for Li<sub>n</sub>I<sup>+</sup>, obtained by thermal ionization in the Knudsen cell at temperatures above 835 °C, are shown. As can be seen in part B of Fig. 4, the Li<sub>n</sub>I<sup>+</sup> ( $n = 2, 4, 5$ , and 6) clusters could be detected using the TI mode at temperatures higher than the melting point of LiF, while the Li<sub>3</sub>I<sup>+</sup> ion was not detected by the thermal ionization.

From Fig. 4, part A, it can be seen that the intensity of Li<sub>2</sub>I<sup>+</sup> and Li<sub>4</sub>I<sup>+</sup> increased from 468 to 616 °C and have almost constant value in the temperature range 616 to 782 °C. The intensity of Li<sub>2</sub>I<sup>+</sup> decreased above 782 °C, while a decrease in the intensity for Li<sub>4</sub>I<sup>+</sup> was not detected. The intensity *versus* temperature curve for Li<sub>3</sub>I<sup>+</sup> and Li<sub>5</sub>I<sup>+</sup> had almost constant values in the temperature

range presented in Fig. 4. As can be seen, the order of the intensities was  $\text{Li}_2\text{I}^+ > \text{Li}_6\text{I}^+$  or  $\text{Li}_4\text{I}^+ > \text{Li}_5\text{I}^+ > \text{Li}_3\text{I}^+$  at temperatures between 600 and 830 °C. This result showed that the intensities of  $\text{Li}_n\text{I}^+$  increase when a salt LiF was added to a mixture  $\text{LiI}/\text{C}_{70}$ .

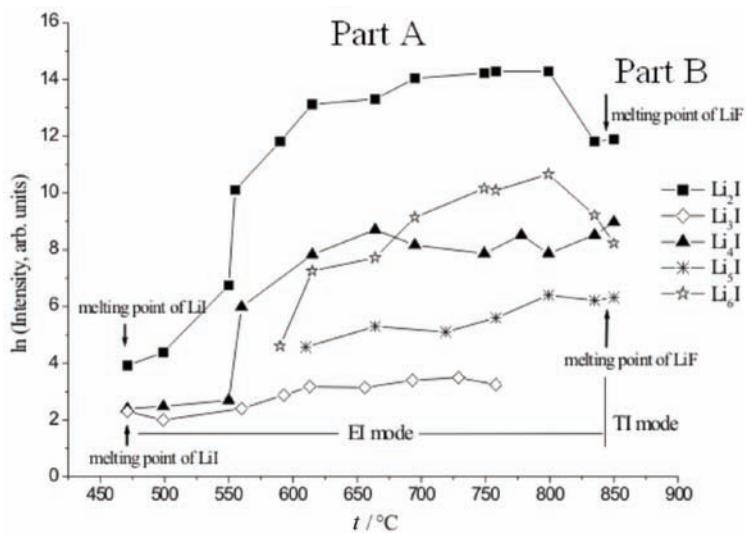


Fig. 4. Plots of  $\ln$  (Intensity, arb. units) *versus* temperature. The ions  $\text{Li}_n\text{I}$  ( $n = 2, 3, 4, 5$  or  $6$ ) clusters were obtained in the electron impact mode (the temperature range of the Knudsen cell was 420 to 830 °C) and the positively charged clusters  $\text{Li}_n\text{I}^+$  ( $n = 2, 4, 5$  and  $6$ ) were generated in the Knudsen cell by thermal ionization (the temperature of the Knudsen cell was higher than 830 °C).

However, it should be noted that the  $\text{Li}_3\text{I}^+$  and  $\text{Li}_5\text{I}^+$  clusters were not detected from a mixture  $\text{LiI}/\text{LiF}$ .<sup>40</sup> In addition, the  $\ln$  (Intensity, arb. units) *versus* temperature trend for the mixture  $\text{LiI}/\text{LiF}$  did not correspond to the trend for the mixture  $\text{LiI}/\text{LiF}/\text{C}_{70}$ .<sup>40</sup> This implies that the presence of both  $\text{C}_{70}$  and LiF provides optimal conditions for obtaining ions  $\text{Li}_n\text{I}^+$   $n = 2, 3, 4, 5$  and  $6$ . Namely, in an earlier experiment, it has been shown that the solid-state reactions of fullerenes with various metal fluorides can be performed in a Knudsen cell. For example, the mass spectra recorded during the KCMS fluorination of  $\text{C}_{70}$  with  $\text{MnF}_3$  contained  $\text{C}_{70}\text{F}_{36}$ ,  $\text{C}_{70}\text{F}_{38}$  and  $\text{C}_{70}\text{F}_{40}$ .<sup>44</sup> Furthermore, the reaction of fluorination of  $\text{C}_{70}$  is more efficient than the reaction of fullerene with lithium.<sup>45</sup> These facts suggest that the enhanced stability of  $\text{Li}_n^+$  may be related to the presence of an additional Li source that remains in the Knudsen cell because the fluorine atom prefers a strong ionic bound with  $\text{C}_{70}$ . From another viewpoint, the fullerene  $\text{C}_{70}$  could form a graphite monolayer on the inner surface of the Knudsen cell at higher temperatures. Generally, the existence of a graphite monolayer decreases the thermal dissociation of the clusters.<sup>46</sup>

For clarity, the ions obtained by evaporation from pure LiI, a mixture LiI/C<sub>70</sub>, and a mixture LiI/LiF/C<sub>70</sub>, in the temperature range derived from the curves in Figs. 2 and 3, are summarized in Table II.

TABLE II. The ions obtained by the evaporation from pure LiI, from a mixture of LiI/C<sub>70</sub> and from a mixture of LiI/LiF/C<sub>70</sub>, and the temperature range of the Knudsen cell

Sample	Ions	Ions of the type Li <sub>n</sub> I <sup>+</sup>	Temperature range, °C
LiI	I <sup>+</sup> , I <sub>2</sub> <sup>+</sup> , Li <sup>+</sup> , LiI <sup>+</sup> , Li <sub>2</sub> I <sub>2</sub> <sup>+</sup> , Li <sub>3</sub> I <sub>2</sub> <sup>+</sup> , Li <sub>4</sub> I <sub>3</sub> <sup>+</sup>	Li <sub>2</sub> I <sup>+</sup>	408–581
LiI/C <sub>70</sub>		Li <sub>2</sub> I <sup>+</sup> ,	355–673
	I <sup>+</sup> , I <sub>2</sub> <sup>+</sup> , Li <sup>+</sup> , LiI <sup>+</sup> , Li <sub>2</sub> I <sub>2</sub> <sup>+</sup> , Li <sub>3</sub> I <sub>2</sub> <sup>+</sup> , Li <sub>4</sub> I <sub>3</sub> <sup>+</sup>	Li <sub>3</sub> I <sup>+</sup> ,	355–453
		Li <sub>4</sub> I <sup>+</sup> ,	355–658
		Li <sub>6</sub> I <sup>+</sup>	452–632
LiI/LiF/C <sub>70</sub>	I <sup>+</sup> , I <sub>2</sub> <sup>+</sup> , Li <sup>+</sup> , LiI <sup>+</sup> , Li <sub>2</sub> I <sub>2</sub> <sup>+</sup> , Li <sub>3</sub> I <sub>2</sub> <sup>+</sup> , Li <sub>4</sub> I <sub>3</sub> <sup>+</sup>	Li <sub>2</sub> I <sup>+</sup> ,	355–837
		Li <sub>3</sub> I <sup>+</sup> ,	355–758
		Li <sub>4</sub> I <sup>+</sup> ,	355–835
		Li <sub>5</sub> I <sup>+</sup> ,	609–837
		Li <sub>6</sub> I <sup>+</sup>	452–833

Comparing data in the Table II, a few general trends can be noted. First, the fullerene C<sub>70</sub> provide a wider temperature range for the detection of Li<sub>n</sub>I<sup>+</sup> clusters. Second, the addition of the salt LiF to a mixture LiI/C<sub>70</sub> leads to an increase in the temperature range for the observation of these ions. This suggests that the formation of cluster ions is favored when the extra sources of lithium ions were present in the Knudsen cell.

#### CONCLUSIONS

In this work, the evaporation of LiI, LiI/C<sub>70</sub> and LiI/LiF/C<sub>70</sub> from a Knudsen cell located in the ionization chamber of a magnetic sector mass spectrometer was studied. The following ion species were detected: I<sup>+</sup>, I<sub>2</sub><sup>+</sup>, Li<sup>+</sup>, LiI<sup>+</sup>, Li<sub>2</sub>I<sub>2</sub><sup>+</sup>, Li<sub>3</sub>I<sub>2</sub><sup>+</sup>, Li<sub>4</sub>I<sub>3</sub><sup>+</sup> and Li<sub>n</sub>I<sup>+</sup> ( $n > 2$ ). In all of three cases, the intensities of these ions *versus* temperature of the Knudsen cell were measured. The principal results were as follows:

1. The results indicate that the experimental setup where the Knudsen cell was placed in the ionization chamber provided abundances of all the detectable ions higher than did those obtained with a standard KCMS.
2. By evaporation of the mixture LiI/C<sub>70</sub>, ions of Li<sub>n</sub>I ( $n = 2, 3, 4$  and 6) clusters were obtained, while evaporation of the mixture LiI/LiF/C<sub>70</sub> gave positive ions of Li<sub>n</sub>I ( $n = 2, 3, 4, 5$  and 6). The presence of both C<sub>70</sub> and LiF provides optimal conditions for obtaining Li<sub>n</sub>I<sup>+</sup> ( $n = 2, 3, 4, 5$  and 6).
3. In all three cases, the most intensive peaks in the spectra were Li<sub>2</sub>I<sup>+</sup>. The clusters with an even number of lithium atoms (Li<sub>2</sub>I<sup>+</sup>, Li<sub>4</sub>I<sup>+</sup>, Li<sub>6</sub>I<sup>+</sup>) were more stable than the clusters with an odd number of lithium atoms (Li<sub>5</sub>I<sup>+</sup> and Li<sub>3</sub>I<sup>+</sup>).

4. Trends of the plot  $In$  (Intensity, arb. units) *versus* temperature for  $\text{Li}_n\text{I}^+$  cluster before and after the melting point of LiI do not correspond. It suggests that way of formation of these clusters could be different due to changes in the temperature. At temperatures below the melting point of lithium iodide, the dissociative ionization of  $(\text{LiI})_2$ ,  $(\text{LiI})_3$ ,  $(\text{LiI})_4$ ,  $\text{Li}_3\text{I}_2^+$ , and  $\text{Li}_4\text{I}_3^+$  could be responsible for the generation of  $\text{Li}_2\text{I}^+$ ,  $\text{Li}_3\text{I}^+$  and  $\text{Li}_4\text{I}^+$ , respectively. Unfortunately, based on all the detectable ions, the predominant emission mechanism could not be experimentally determined at temperature higher than the melting point of lithium iodide.

5. The clusters  $\text{Li}_n\text{I}$  and  $\text{Li}_n\text{F}$  were obtained by evaporation of the mixture LiI/LiF/C<sub>70</sub>. The intensities of  $\text{Li}_n\text{I}$  clusters were higher than the emission of  $\text{Li}_n\text{F}$  cluster when the ratio of LiI to LiF was 2:1. In contrast, the emission of  $\text{Li}_n\text{F}$  clusters was enhanced, while the emission of  $\text{Li}_n\text{I}$  clusters was suppressed when the ratio of LiI to LiF was 1:2.

It could be concluded that a Knudsen cell located in the ionization chamber of a mass spectrometer provides an appropriate way to obtain and investigate clusters of the type  $\text{Li}_n\text{X}$ , X = F or I.

*Acknowledgement.* The authors acknowledge the Ministry of Education, Science and Technological Development of the Republic of Serbia for financial support (Contract No. 172019).

#### ИЗВОД

#### ИСПИТИВАЊЕ ОТПАРАВАЊА LiI, LiI/C<sub>70</sub> И LiI/LiF/C<sub>70</sub> ИЗ КНУДСЕНОВЕ ЂЕЛИЈЕ СМЕШТЕНЕ У ЈОНИЗАЦИОНУ КОМОРУ МАСЕНОГ СПЕКТРОМЕТРА

ЈАСМИНА ЂУСТЕБЕК, МИОМИР ВЕЉКОВИЋ И СУЗАНА ВЕЛИЧКОВИЋ

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Отпирање LiI, LiI/C<sub>70</sub> и LiI/LiF/C<sub>70</sub> је испитивано помоћу Кнудсенове ђелије, која је смештена у јонизациону комору магнетног масеног спектрометра, у температурском опсегу од 350 до 850 °C.  $\text{Li}_n\text{I}^+$  ( $n = 2, 3, 4$  и  $6$ ) врсте су детектоване из смеше LiI/C<sub>70</sub>, а кластери  $\text{Li}_n\text{I}^+$  и  $\text{Li}_n\text{F}^+$  ( $n = 2$  до  $6$ ) су детектовани испирањем смеше LiI/LiF/C<sub>70</sub>. Интензитет  $\text{Li}_n\text{I}^+$  био је већи од интензитета  $\text{Li}_n\text{F}^+$  кластера када је однос LiI и LiF био 2:1. С друге стране, стварање  $\text{Li}_n\text{F}^+$  кластера је фаворизовано када је однос LiI и LiF био 1:2. Резултати показују да отпирање смеше LiI/LiF/C<sub>70</sub> из Кнудсенове ђелије, која је смештена у јонизациону комору масеног спектрометра, представља ефикасан и једноставан начин за добијање и испитивање кластера типа  $\text{Li}_n\text{X}$ , X = F или I. У овом раду такође је показано да се зависност природног логаритма интензитета  $\text{Li}_n\text{I}^+$  кластера од температуре разликује на температурама пре и после тачке топљења LiI. Ово указује на то да начин формирања наведених кластера може бити различит услед промене температуре.

(Примљено 27. јуна 2012, ревидирано 25 јула 2013)

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