



Research paper

Mobilities of Li⁺-attached butanol isomers in helium gas at 85.5 KK. Takahashi^{a,*}, K.M. Moriya^a, S. Matoba^a, T. Koizumi^a, H. Tanuma^b^a Department of Physics, Rikkyo University, Toshima-ku, Tokyo 171-8501, Japan^b Department of Physics, Tokyo Metropolitan University, Minami-Ohsawa, Hachioji, Tokyo 192-0397, Japan

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ABSTRACT

Mobilities of Li⁺-attached butanol isomers, (*n*-BuOH) Li⁺, (*s*-BuOH) Li⁺, (*i*-BuOH) Li⁺, and (*t*-BuOH) Li⁺, in helium gas cooled by liquid nitrogen were measured in reduced electric fields $E/N = 8\text{--}65$ Td. Together with previous measurements at room temperature, the results cover a range of collision energies ($\varepsilon = 10\text{--}130$ meV). Differences in the mobilities of the isomers became pronounced at low collision energies; for example, (*n*-BuOH) Li⁺ showed a mobility about 5% greater than (*t*-BuOH) Li⁺ at 10 meV.

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1. Introduction

Ion mobility in neutral gas is an important physical quantity influencing ion transport [1]. It depends strongly on the interaction potential between the ions and the neutral gas molecules and is also associated with physical quantities, including the momentum transfer cross-section and collision integral. Ion mobilities are generally measured using a drift tube in a low-energy collision system (about 40–100 meV at room temperature and about 10–80 meV at liquid nitrogen temperature). The ion mobilities of atomic and simple molecular ions have been measured in helium gas and in other atomic and molecular gases [2–13], and have also been investigated with respect to electronic states [14–16], thus allowing differences in the cross-sections between different electronic states to be explored.

Ion mobilities are widely applied to ion mobility spectrometry (IMS). IMS is an analytical technique that separates atomic/molecular ions by the difference in their collision cross-sections. The technique is also applicable to isomer separation. Previous studies suggested that mass-selected carbon cluster ions such as C₇⁺ exist in a few different isomeric forms [17–19]. From the viewpoint of physical chemistry and molecular physics, interest in IMS is mainly due to its ability to separate various isomers, and the purpose of this study is to investigate the behavior of mobilities of isomers to reveal differences in their interaction potentials.

Our previous paper [20] investigated the mobilities of Li⁺ attached butanol (C₄H₉OH) isomers in helium gas at room temperature; the measurements were sufficiently accurate to detect the small differences between them. The Li⁺ attachment ion source is

a one of the soft ionization source, which is to keep and not to fragment the difference between isomers [21]. We reported that an attractive long-range dipole-induced dipole interaction becomes important at low collision energies, (about 50 meV) and that the mobilities were determined mainly by the geometric size of the ions but were also affected by rotational isomerism. This paper investigates the behavior of the mobilities of isomer ions at lower collision energies using liquid-nitrogen cooling (to 85.5 K). Mobilities of butanol isomers at lower collision energies (about 10 meV) are reported here.

2. Experimental setup

The experimental apparatus has been described previously [20]. Briefly, it consisted of a Li⁺ attachment ion source, a quadrupole mass selector for primary ions, a drift tube, and a quadrupole mass analyzer for product ions. The overall length of the apparatus was about 2 m.

Vapor of each butanol isomer (1-butanol (*n*-BuOH), 2-butanol (*s*-BuOH), 2-methyl-1-propanol (*i*-BuOH), or 2-methyl-2-propanol (*t*-BuOH)) was independently introduced into the Li⁺ attachment ion source, which generated the Li⁺-attached butanol isomer ions. When *s*-BuOH vapor was introduced into the ion source, primary ions consisted of Li⁺, (*s*-BuOH) Li⁺, and (*s*-BuOH)_{*n*}Li⁺ ($n = 2, 3, \dots$); therefore, primary ions below 1000 amu were selected using the quadrupole mass selector, before being guided to the drift tube region.

The drift tube (length 94 mm) was filled with He gas of number density *N*. It was under a uniform electric field *E*, and was covered by a reservoir filled with liquid nitrogen. The temperature of the He gas in the drift tube was measured at two different positions using a K-type thermocouple (Chromel/Alumel). The difference of temperature between these positions was within two kelvins.

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The temperature was corrected using a calibration curve determined using liquid nitrogen and liquid oxygen. The He gas was cooled to 85.5 K, which lowered the collision energy to nearly 10 meV. The pressure in the drift tube was measured using a capacitance manometer (MKS Baratron, MA, USA). The effect of thermal transpiration was considered by correcting the pressure using Takaishi and Sensui's equation [23].

The mass-selected incident ions were guided by the electrodes, and injected with a kinetic energy lower than 10 eV into the drift tube through an aperture 0.5 mm in diameter. The drift tube consisted of thirteen ring electrodes and six mesh electrodes, which were produced the uniform electric field in the drift tube. The mesh electrodes functioned as three electrical shutters for the ions. The injected ions immediately thermalized before the first shutter in collisions with He atoms, and then drifted along the uniform electric field E . Their movement in the drift tube was pulsed by a blocking voltage applied to the shutter installed in the drift tube. The pulsed ions traveled toward the end of the drift tube with mean velocity v_d , and were ejected through an outlet aperture 0.5 mm in diameter. Ions leaving the drift tube were mass analyzed with the quadrupole mass analyzer and detected with a secondary electron multiplier.

The arrival times of the pulsed ions from first, second, and third shutter to the detector were measured, respectively. The uniform electric field and the uniform temperature in the drift tube were confirmed by linearity between the arrival times and the positions of the shutters. The drift velocity v_d was calculated from the time gap between different shutters. The reduced ion mobility K_0 was then calculated by

$$K_0 = \frac{v_d}{N_0 E} N, \quad (1)$$

where N_0 is the number density of an ideal gas under standard conditions; i.e., the Loschmidt number ($N_0 = 2.687 \times 10^{19} \text{ cm}^{-3}$).

3. Results and discussion

3.1. Behaviour of mobilities

Fig. 1 shows reduced mobilities K_0 of (*n*-BuOH) Li⁺, (*s*-BuOH) Li⁺, (*i*-BuOH) Li⁺, and (*t*-BuOH) Li⁺ in He gas at 85.5 K. The horizontal axis is the reduced electric field E/N in Td (1 Td = 10^{-17} Vcm^2). Statistical errors of one standard deviation of relative K_0 are a few percent for (*n*-BuOH) Li⁺ and 0.3–1% for the other ions. All the isomers show decreasing K_0 with increasing E/N . Around 60 Td, the K_0 plots of each ion are almost equal to each other, while the differences are clear at 8–40 Td.

To allow comparison with previous results recorded at room temperature [20], the E/N was converted into the mean collision energy $\bar{\epsilon}$ and the effective temperature T_{eff} as follows [22]:

$$\frac{3}{2} k T_{\text{eff}} = \frac{1}{2} M v_d^2 + \frac{3}{2} k T = \bar{\epsilon}, \quad (2)$$

where k is the Boltzmann constant, and M is the mass of helium as the buffer gas. The obtained K_0 of each isomer ion with respect to $\bar{\epsilon}$ and T_{eff} is shown in Fig. 2, along with the previous results obtained at 303.6 K [20]. Although the plots at both temperatures decrease with increasing $\bar{\epsilon}$, there is a discontinuity in the absolute values recorded at the two different temperatures. In the experiment using liquid nitrogen, absolute K_0 values are affected by a temperature measurement and a pressure correction due to the effect of thermal transpiration. Therefore, the obtained K_0 at 85.5 K has a systematic error about several percent. However, the results at the two different temperatures good agreement with each other within systematic error.

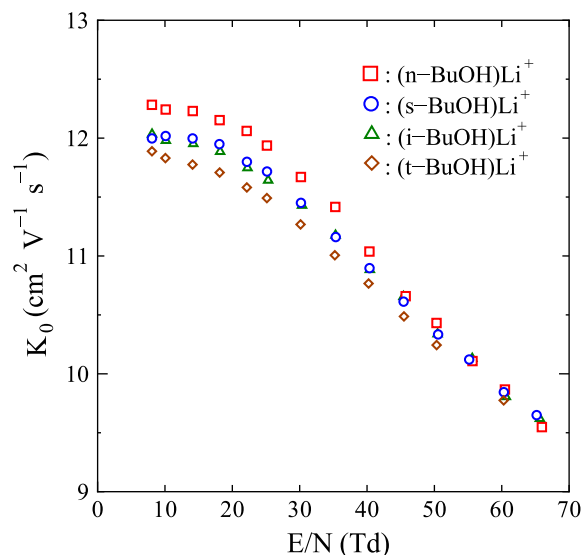


Fig. 1. Reduced mobilities K_0 of (*n*-BuOH) Li⁺ (open squares), (*s*-BuOH) Li⁺ (open circles), (*i*-BuOH) Li⁺ (open triangles), and (*t*-BuOH) Li⁺ (open diamonds) in He gas at 85.5 K as a function of E/N .

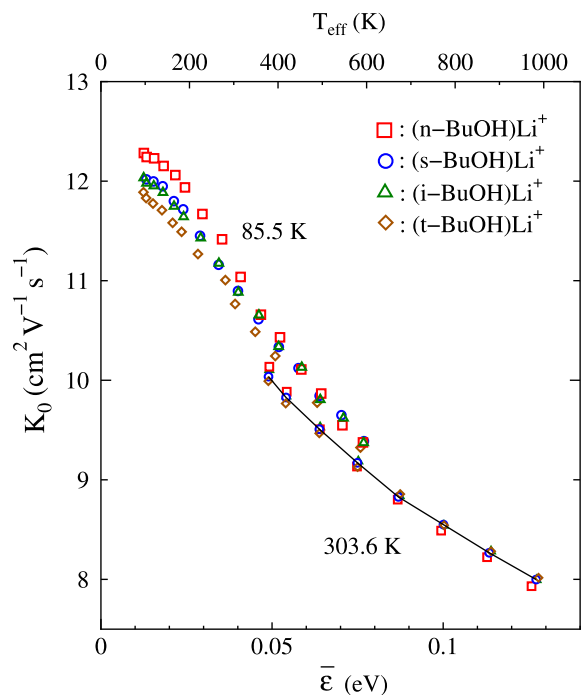


Fig. 2. Reduced mobilities K_0 of (*n*-BuOH) Li⁺ (open squares), (*s*-BuOH) Li⁺ (open circles), (*i*-BuOH) Li⁺ (open triangles), and (*t*-BuOH) Li⁺ (open diamonds) at 85.5 and 303.6 K [20] plotted with respect to collision energy $\bar{\epsilon}$ (bottom horizontal axis) and effective temperature T_{eff} (top horizontal axis). The solid line connecting the measurement points of (*s*-BuOH) Li⁺ at 303.6 K is also shown in the figure.

In order to understand the data for several limiting cases, the collision integral Ω has been calculated following relationship:

$$K_0 = \frac{3qe}{16N_0} \left(\frac{2\pi}{\mu k T_{\text{eff}}} \right)^{1/2} \frac{1}{\Omega(T_{\text{eff}})}, \quad (3)$$

where qe is the ionic charge, and μ is the reduced mass of the collision system. The obtained collision integrals Ω are shown in Fig. 3 as a function of T_{eff} . Assuming rigid-sphere collisions i.e. the limiting case for sufficiently high temperatures, the Ω has a fixed value. In Fig. 3, the Ω seems to approach a fixed value which is generally

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