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Comparison between transport parameters for K^+ and Li^+ in 1, 2-dimethoxy ethane (DXE) gas

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Abstract – In this paper, a theoretical study of 1, 2-dimethoxy ethane (DXE) and K^+/Li^+ binary mixture in low-temperature plasmas is reported. The most probable reactions of alkali metal ions K^+ and Li^+ with dimethoxy ethane molecule and its fragment ions are selected in order to obtain appropriate gas phase enthalpies of formation for the products. The scattering cross-sections set as a function of kinetic energy and transport parameters as a function of E/N (E is the electric field, N the gas density) were obtained by using the Monte Carlo technique.

Introduction. – Transport properties of species in gas plasmas are of great importance in understanding the nature of molecular and ionic interactions in gas mixtures [1–3]. These properties include the mean energy, drift velocity, diffusion coefficients, ionization and chemical reaction coefficients, chemical reaction coefficients for ions and (rarely) excitation coefficients, and they are very useful in chemical industries for the design of many types of transport and process equipment.

The ether-based molecule 1,2-dimethoxy ethane (DXE) is a clear colorless volatile liquid at room temperature and atmospheric pressure [4]. As being the smallest oligomer, *i.e.*, the building block of the polyethylene oxide (PEO) polymer, it has a widespread application in the medical and pharmaceutical field [5–7]. Nevertheless, DXE is also used as a precursor in the production of ceramics [8] or as a sole compound to and other chemicals such as those used in lithium batteries production [9–12], superconductor production [13], nanoparticles synthesis [14–16], in etherification [17] etc.

Being a suitable medium for a number of chemical reactions, it forms chelate complexes with metal cations. Having all that in mind, it would be of great importance to observe a binary gas mixture of DXE and K^+ or Li^+. To the best of our knowledge, the transport properties of such mixtures in gas plasmas have received no attention.

At atmospheric-pressure three-body reactions of ions are of increasing importance for the reaction kinetics. In many modeling cases information about the three-body processes is missing. The Denpoh-Nanbu theory (DNT) [18] can be exploited to calculate cross-section sets as a function of the kinetic energy for cases where no or limited information is available about scattering data [19]. Nikitović *et al.* [20] showed how radiative association for three-body reactions can be included in cross-section sets obtained by the DNT. The approach presented in [20] was compared with the existing experimental data for association cross-section as a function of pressure [21] and showed good agreement at energies below a few eV. Such information is of great importance in atmospheric-pressure plasmas containing complex molecules such as DXE and can be highly valuable in modeling clustering in various plasmas.

In all of the reactions studied experimentally to date [22,23], the only produced ions were the association complexes Li^+(DXE) and K^+(DXE). Therefore, in this work we will apply the approach in [20] to the case of alkali ions in DXE.

In this paper we selected the most probable reactions of alkali metal ions K^+ and Li^+ with dimethoxy ethane (DXE) molecule (and its most probable products) for thermodynamic threshold energies below about 15 eV. Appropriate gas phase enthalpies of formation [24] for the products were used to calculate thermodynamic thresholds.

Although DXE consists of many atoms its dipole moment is negligible, so the simplest capture theories can be applied. The scattering cross-sections as a function

Table 1: Heats of formation $\Delta_f H^0$ at 298 K(kJ/mol).

Species	$\Delta_f H^0$	Species	$\Delta_f H^0$
Li	159.4	Li^+	679.6
K	89	K^+	507.8
DXE	−340	DXE^+	557
$C_3H_8O_2$	−364	$C_3H_8O_2^+$	562
C_2H_6O	793.1	$C_2H_6O^+$	775.4
C_2H_4O	821.1	$C_2H_4O^+$	−165.8
CH_4O	−201.6	CH_4O^+	845.3
CH_2O	−108.7	CH_2O^+	940.5
CH_4	−74.5	CH_4^+	1132.0
CO	−110.53	CO^+	1241.59
H_2	0.0	H_2^+	1488.3

of kinetic center of mass energy is calculated with the DNT [18,25].

Calculation of the cross-section. – DXE selected in this study is of *trans, trans, trans* conformation [22] and is known not to have permanent dipole moment in its ground state. The average polarizability $9.94 \times 10^{-30}\,\mathrm{m}^3$ [22] is used for the DXE target. Similar to our recent papers [26] the DNT method is used to separate elastic from reactive endothermic collisions by accounting for the thermodynamic threshold energy and branching ratio according to the Rice-Rampsperger-Kassel (RRK) theory [18]. Within the RRK theory the internal energy is being distributed among an empirical number of $\boldsymbol{s}$ equivalent effective modes of the complex selected from the total number of atoms involved in the complex.

Appropriate gas phase enthalpies of formation for the products [23] (table 1) were used to calculate thermodynamic thresholds (table 2). The cross-section for the exothermic reaction (EXO) forming a molecular ion X^+ in DXE is commonly represented by ion capture cross-section:

$$\sigma_{\mathrm{exo}} = \beta\sigma_{\mathrm{L}}, \tag{1}$$

where σ_{L} is the orbiting cross-section [27] and β is the probability of a specific exothermic reaction.

By combining the relation (1) and the thermal rate coefficient we determined the probability of exothermic reaction and the contributions of association cross-section and elastic cross-section. In the low-energy limit [2,23], the cross-sections are similar due to dominant polarization of the target. At higher energies reactive collisions including the non-conservative collisions become efficient for various possible processes.

The elastic momentum transfer cross-section be modified in order to fit approximate mobility peak characteristic for presented systems. This is done using the swarm method [28,29] and the reduced mobilities (experimental [30] or theoretical values [31]) in the peak region for these ions in neutrals of equal or similar reduced mass. From Langevin's cross-section we deduced experimental

Table 2: X^+-DXE reaction paths (X = Li, K) showing reaction products and the corresponding thermodynamic threshold energies Δ.

No.	Products	Li^+	K^+
1	$X^+ + DXE$	0	0
2	$X + C_4H_{10}O_2^+$	3.905	4.9561
3	$X^+ + C_3H_8O_2 + CH_2$	3.793	3.793
4	$X + C_3H_8O_2^+ + CH_2$	7.999	9.050
5	$X + C_3H_8O_2 + CH_2^+$	8.724	9.775
6	$X^+ + C_2H_6O + CH_2 + CO$	4.513	4.513
7	$X + C_2H_6O^+ + CH_2 + CO$	9.147	10.198
8	$X + C_2H_6O + CH_2^+ + CO$	9.444	10.495
9	$X + C_2H_6O + CH_2 + CO^+$	13.135	14.186
10	$X + C_2H_4O^+ + C_2H_6O$	4.7353	5.7862
11	$X + C_2H_4O + C_2H_6O^+$	4.5322	5.5831
12	$X^+ + CH_2O + C_2H_6 + CO$	0.3811	0.3811
13	$X + CH_2O^+ + C_2H_6 + CO$	5.8636	6.9145
14	$X + CH_2O + C_2H_6^+ + CO$	6.5145	7.5654
15	$X + CH_2O + C_2H_6 + CO^+$	9.0031	10.054
16	$X^+ + CH_4O + C_3H_4 + H_2O$	0.8620	0.8620
17	$X + CH_4O^+ + C_3H_4 + H_2O$	6.3207	7.3716
18	$X + CH_4O + C_3H_4^+ + H_2O$	5.8305	6.8814
19	$X + CH_4O + C_3H_4 + H_2O^+$	8.0818	9.1328
20	$X^+ + C_4H_6 + 2H_2 + O_2$	5.0307	5.0307
21	$X + C_4H_6^+ + 2H_2 + O_2$	9.2012	10.2521
22	$X + C_4H_6 + 2H_2 + O_2^+$	15.064	16.115
23	$X + C_4H_6 + H_2^+ + H_2 + O_2$	11.716	12.7674

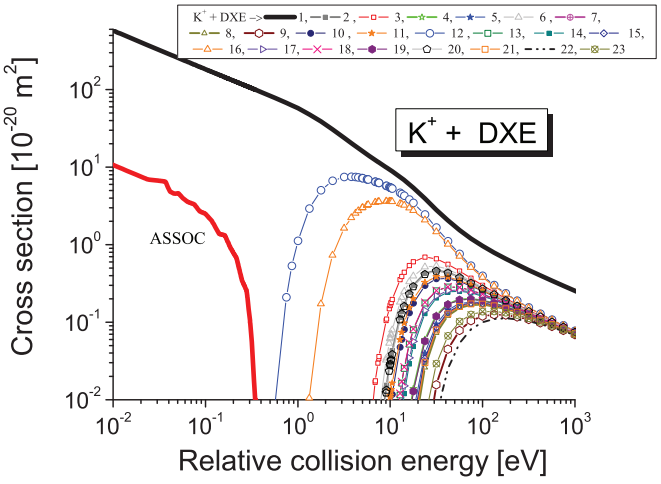

Fig. 1: (Color online) Cross-section set for scattering of K^+ with DXE. "ASSOC" denotes the experimentally obtained association cross-section [22] while theoretical curves are denoted in the legend.

association cross-sections and theoretical endothermic cross-sections in order to obtain elastic momentum transfer cross-section. The elastic momentum transfer cross-sections for elastic collisions of K^+ with DXE is presented in fig. 1. In fig. 2 we present cross-sections for Li^+ in DXE.

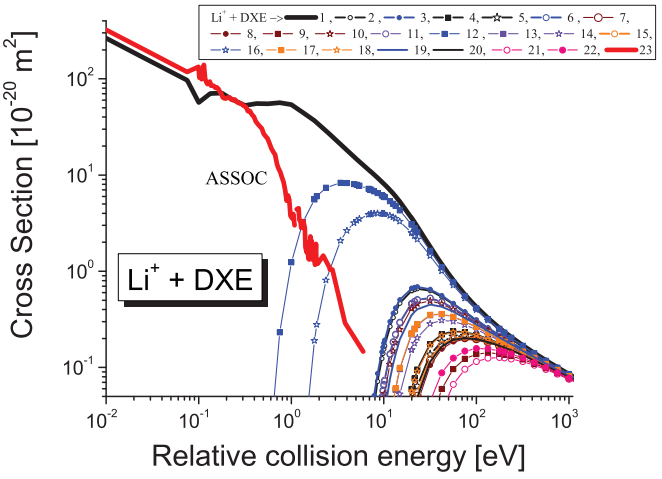

Fig. 2: (Color online) Cross-section set for scattering of Li^+ with DXE. "ASSOC" denotes the experimentally obtained association cross-section [22] while theoretical curves are denoted in the legend.

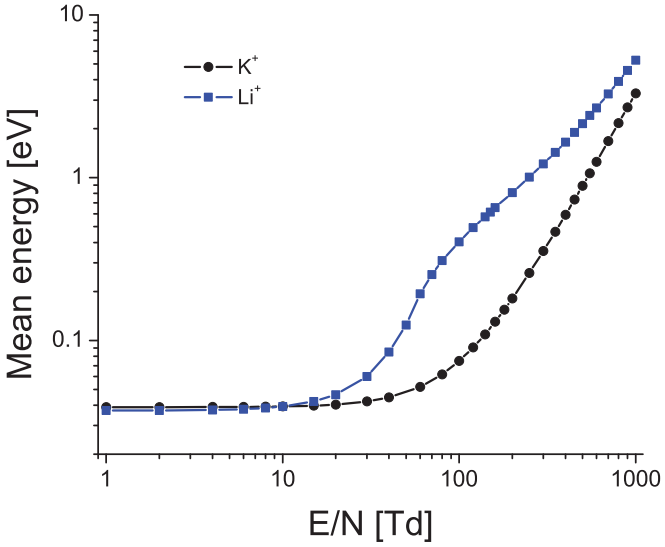

Fig. 3: (Color online) Mean energy as a function of E/N for K^+ and Li^+ in DXE.

Agreement with experiment is satisfactory for energies below 1 eV. A further step in both cases will be to add more reactions with multiple radicals that will increase the thermodynamic threshold and generally increase the number of reactions. This may potentially improve agreement with experimental data for cross-sections for association reaction.

In all mentioned experimental cases, the cross-sections show a clear pressure dependence, which indicates the occurrence of collisional stabilization of complex by secondary collisions. The effect of secondary collisions can be eliminated completely by linear extrapolation of the cross-section data to zero reactant pressure. The same trend is easily achieved with theoretical data which have to include effects of all possible reactions providing our theoretical cross sections can be exploited and also used in many other cases.

Transport parameters. – Generally speaking, plasma modelling and simulations requires the use of swarm parameters. The non-equilibrium regime in discharges can be well represented under a broad range of conditions by using the Boltzmann kinetic equation or by following individual evolutions of all ions with Monte Carlo technique. In our Monte Carlo code swarm of ions is traced until they reach hydrodynamic regime when transport properties are calculated [25,26,29]. Internal excitation of the DXE is neglected in the cross-section calculation although is included with association cross-section where we exploited experimental data. Agreement of measured association cross-section at very low energies with Langevin's trend indicate that the effect of internal excitation of the molecule is of less importance than reactive collisions in selected conditions.

We have used a Monte Carlo code that properly takes into account thermal collisions [32]. The code has passed all the relevant benchmarks [25] and has been tested in our work on several types of charged particles [25,33].

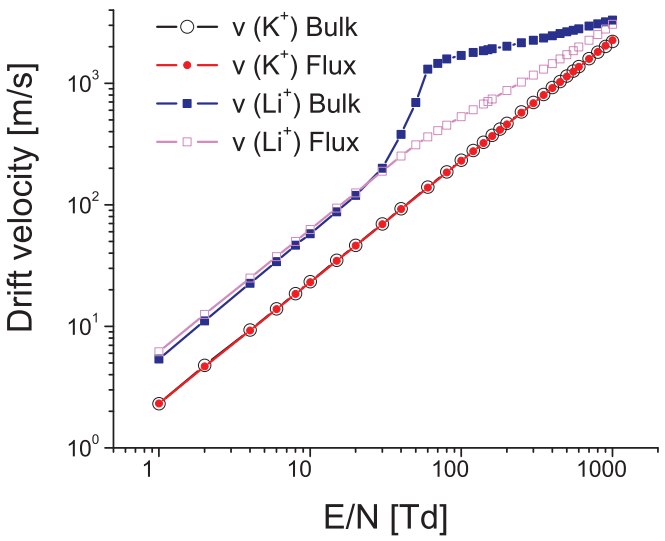

Fig. 4: (Color online) Flux and bulk drift velocity as a function E/N for K^+ and Li^+ in DXE.

In fig. 3 we show the mean energy as a function of collision energy for K^+ and Li^+ in DXE. The mean energy cannot be directly measured in experiments. The difference in the mean energies of Li^+ and K^+ is visible because of the big attachment for Li^+ above 20 Td.

Flux and bulk drift velocities [34–36] for K^+ in DXE as a function of E/N are given in fig. 4. The drift velocities obtained by Monte Carlo simulation calculated in real space (bulk) and in velocity space (flux) values which are obtained as $\langle v \rangle$ and $\mathrm{d}x/\mathrm{d}t$, respectively. The mass of Li^+ is smaller than the mass of K^+, so as a consequence the drift velocity of Li^+ is bigger. In the case of K^+, due to

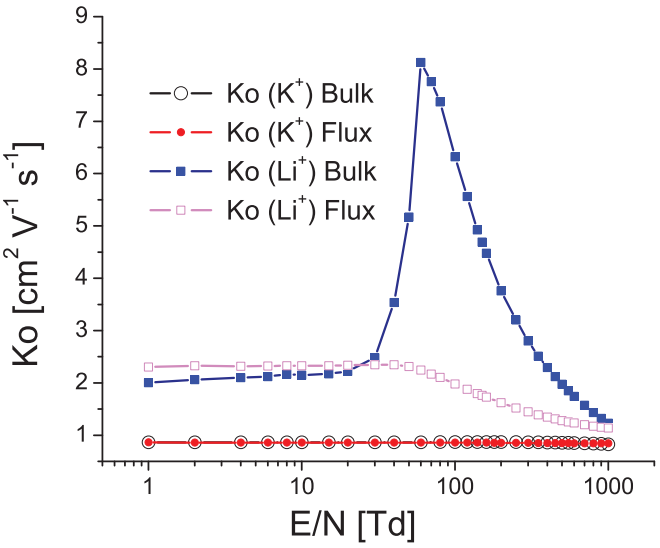

Fig. 5: (Color online) Reduced mobility as a function E/N for K^+ and Li^+ in DXE.

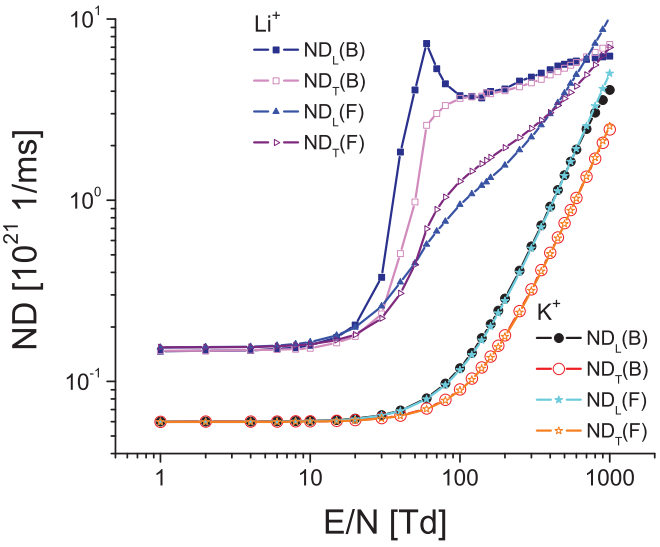

Fig. 6: (Color online) Longitudinal and transversal diffusion coefficients as a function E/N for K^+ and Li^+ in DXE.

weak non-conservation, there is no important difference between the flux and bulk velocity.

The mobility K of an ion is a quantity defined as the velocity attained by an ion moving through a gas under the unit electric field. One often exploits the reduced or standard mobility defined as

$$K_0 = \frac{v_d}{N_0 E} N, \tag{2}$$

where v_d is the drift velocity of the ion, N is the gas density at elevated temperature T, $N_0 = 2.69 \cdot 10^{25}\,\mathrm{m}^{-3}$ and E is the electric field.

In fig. 5 we show the results of Monte Carlo simulation for reduced mobility for K^+ and Li^+ in DXE as a function of E/N. Due to reactive collisions bulk and flux values of reduced mobility are separated. The reduced mobility for K^+ is constant but increasing the resolution shows its structure, while the mobility for Li^+ sharply rises at energies 0.3–2 eV because of resonant association.

Longitudinal and transversal diffusion coefficients for K^+ and Li^+ in DXE as a function of E/N are shown in fig. 6. The peak is visible only in the behavior of longitudinal diffusion coefficients. With the increase of E/N the longitudinal diffusion decreases as a consequence of the big attachment for Li^+.

However, there are no published experimental data for the longitudinal and transverse diffusion coefficients of K^+ and Li^+ in DXE so far.

Conclusion. – The Denpoh-Nanbu theory, supplemented with the swarm method was used to calculate the elastic collisions of K^+ and Li^+ on DXE. Calculated cross-sections are used to obtain transport parameters for K^+ and Li^+ in DXE gas.

DXE is a technologically important gas. Cross-sections and transport data for it have been calculated by a simple theory. Adding a database of measured transport coefficients would open the possibility of refining the calculations.

* * *

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