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The Mobility of Li^+ Ions in Helium and Argon

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Abstract

A drift tube–mass spectrometer system employing Bradbury–Nielsen shutters has been used to measure the mobility of Li^+ ions in He at 294 and 80 K and Li^+ ions in Ar at 294 K. The E/N range used was 3 to 80 Td (1 Td $\equiv 10^{-21}$ V cm^2). The zero field reduced mobility for Li^+ in He was found to be $22{\cdot}81\pm0{\cdot}11$ cm^2 V^{-1} s^{-1} at 294 K and $19{\cdot}64\pm0{\cdot}29$ cm^2 V^{-1} s^{-1} at 80 K. The value for Li^+ in Ar at 294 K is $4{\cdot}66\pm0{\cdot}22$ cm^2 V^{-1} s^{-1}. The reduced zero field mobility for the cluster ion Li^+. He in He at 80 K and low values of E/N was found to be $14{\cdot}84\pm0{\cdot}22$ cm^2 V^{-1} s^{-1}. The equilibrium constant for the formation and dissociation of Li^+. Ar cluster ions at 294 K was obtained by fitting to the variation of the measured mobility with gas number density at low E/N values. The value obtained, corresponding to thermal equilibrium at 294 K, was $(4\pm0{\cdot}5)\times10^{-19}$ cm^3.

1. Introduction

A long standing aim of ion swarm studies has been to derive accurate ion–atom interaction potentials by the analysis of mobility data (McDaniel and Mason 1973) and there have been a number of potentials derived for alkali ions in inert gases in recent years (see e.g. Viehland 1984). However, the range of internuclear separations over which the potential can be determined is limited by the experimental conditions used for the mobility measurements. To obtain the interaction potential at large internuclear separations, it is necessary to have mobility data at sufficiently low values of E/N and T (where E is the electric field strength, N the gas number density and T the gas temperature) so that the reduced mobility κ, defined as

$$\kappa = \frac{v_{dr}}{E/N}\,\frac{1}{N_s},$$

where v_{dr} is the drift velocity and N_s the standard gas number density, $2{\cdot}687\times10^{25}$ m^{-3}, is determined predominantly by polarization forces and in the limit by the dipole polarization force alone. This is discussed in Section 4 where it is shown that the condition can be met approximately for the case of Li^+ ions in argon at room temperature. However, for Li^+ ions in helium, a gas of much lower polarizability, it is necessary to use low gas temperatures (in this work 80 K) to attain sufficiently low ion energies.

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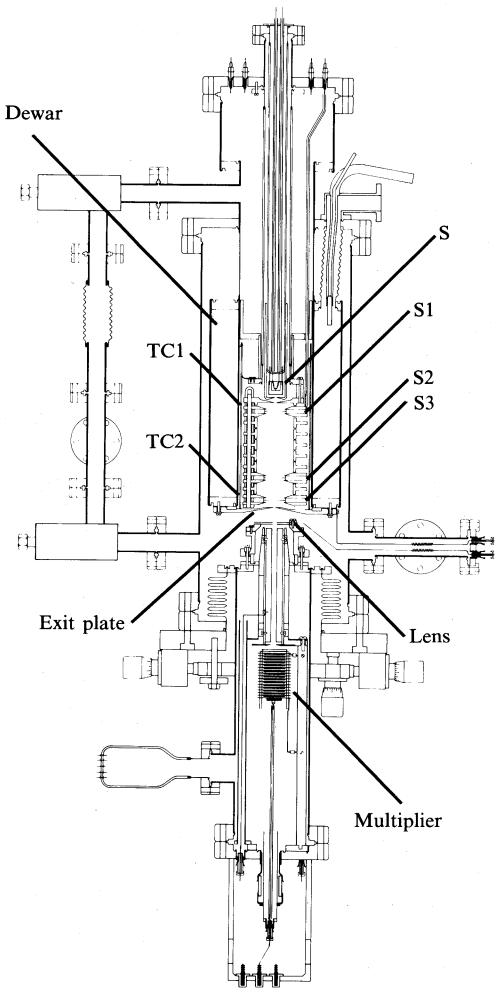

Fig. 1. Drift tube–mass spectrometer: S1, S2, S3 are Bradbury–Nielsen shutter grids; S is a thermionic ion source; and TC1 and TC2 are the positions of thermocouples.

The accuracy of derived interaction potentials depends on the accuracy of the experimental mobility data. Particular care was taken therefore to keep both the statistical scatter and the absolute error small. The experimental apparatus and procedures used are described in Section 2. The upper limit to the values of E/N which could be used for Li^+ ions in helium was set by the failure of the Bradbury–Nielsen grids to operate correctly. The cause of this effect and the avoidance of errors due to the grids are also discussed in Section 2.

The formation of ion–atom clusters in the drift region was observed to occur for Li^+ ions in Ar at 294 K and low E/N values and gave rise to a dependence of the measured mobility on gas pressure. The analysis of this dependence to obtain a value for the equilibrium constant for the reactions

$$Li^+ + Ar + Ar \rightleftharpoons Li^+.Ar + Ar$$

and the correction of the measured mobilities to remove the effect of these reactions is discussed in Section 3.

2. Apparatus

Although the drift tube–mass spectrometer used in this work has been described previously (Milloy and Elford 1975; see also McDaniel and Mason 1973), various minor modifications have been made subsequently and therefore the apparatus will be described in some detail. The present system shown in Fig. 1 consists of two sections, the drift and analyser sections. The drift region contains three Bradbury–Nielsen shutter grids S1, S2 and S3 spaced approximately 9 cm (S1–S2) and 3 cm (S2–S3) apart. The separations were known to four significant figures. Each shutter consists of a grid of parallel and coplanar nichrome wires (0·008 cm in diameter) separated by 0·04 cm. The electric field in the drift region was established and held uniform by 'thick guard ring' electrodes (Crompton *et al.* 1965) at potentials appropriate to their position in the electrode system. The shutter wires and all surfaces exposed to the drift field region were gold coated to reduce errors caused by contact potential differences. Electrode potentials were supplied by a Fluke Model 412B power supply and precision voltage divider. All potentials were within 0·1% of their nominal values. The entire drift region is surrounded by a Dewar container which was either filled with water for temperature stability at room temperature or with liquid nitrogen for measurements at 80 K.

The lithium ions were produced by thermionic emission from a bead of lithium alumino-silicate heated by a tungsten coil (S in Fig. 1). Because the emission of Li^+ ions from such sources requires higher temperatures than for the emission of other alkali ions from their respective alkali alumino-silicates, the Li^+ emitting filaments burnt out in a much shorter time. To avoid frequent exposure of the drift tube to the atmosphere an array of four filaments was used (usually three Li^+ sources and one K^+ source), the ions being deflected into the drift space by appropriate fields.

The vacuum system was constructed to UHV specifications. The analyser region was pumped by 6 and 4 in. (15·1 and 10·1 cm) diffusion pumps, each trapped by a Granville–Phillips Cryosorb liquid nitrogen trap, and base pressures of 2×10^{-7} Pa were achieved routinely in the analyser region without baking. All gases used were Matheson Research Grade.

The temperature of the gas in the drift region was measured by two calibrated copper–constantan thermocouples, one TC1 (see Fig. 1) attached to the electrode immediately before the first shutter S1 and the other TC2 to the electrode after the third shutter S3. The thermocouple EMF values were measured using a Leeds and Northrup 7553-5 Type K-3 potentiometer. No results were taken when the thermocouples indicated a temperature difference greater than 0·5 K. The gas temperature used in the calculation of the number density was taken to be that at the midpoint between the operating shutters and was obtained by linear interpolation. The maximum error in the temperature measurement is estimated to be less than 0·1% in all measurements at room temperature and 1·0% at 80 K.

Measurements were made over the pressure range 0·067–0·41 kPa, the pressure in the drift region being measured by a capacitance manometer (MKS Baratron head type 94 AH, indicator type 170 M) and measured and controlled by a second capacitance manometer (MKS Baratron head type 90H-3E, indicator type 90 M) supplying a control signal to an automatic pressure controller and servo-controlled variable leak valve. The pressure was maintained constant to within $2\cdot5\times10^{-2}$ Pa. Both manometers were calibrated using a double dead-weight tester (Gascoigne 1972)

and the error in the pressure measurement is estimated to be less than 0·1% at all pressures used.

In the Bradbury–Nielsen method the transmitted ion current is measured as a function of the frequency of the sinusoidal potential applied to the shutters, the drift velocity being determined from the frequencies at which current maxima occur. The method has been discussed extensively by Elford (1972) and Huxley and Crompton (1974) and the techniques necessary to obtain high precision given in detail. These procedures were adopted in the present work.

The ion current transmitted by the shutters could be measured either at the exit plate of the drift region or at the output of the quadrupole mass spectrometer. A small fraction of the ions incident on the exit plate passes through a centrally located knife-edged sampling aperture (0·2 mm in diameter) and is focussed into the quadrupole mass spectrometer. The ions transmitted by the mass spectrometer were detected by a particle multiplier (EMI 9643/4B). The multiplier output was fed via a preamplifier to a pulse shaping amplifier, single channel analyser and counter. When high precision data were required and there was no uncertainty concerning the identity of the ions measured, the exit plate was used as the collector. In all cases there was no significant difference between the mobilities measured by using the exit plate as collector or the anode of the multiplier.

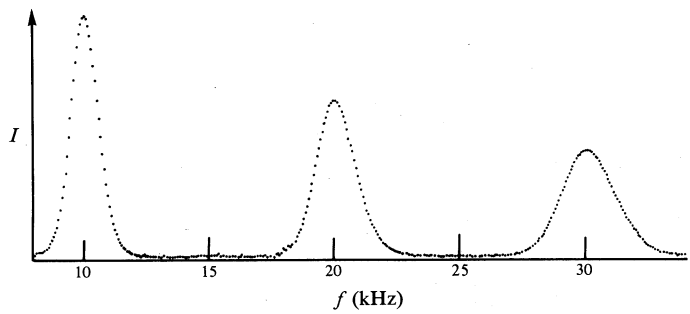

Fig. 2. Typical variation of the ion current I transmitted by the shutter grids as a function of the frequency f of the applied sinusoidal signal (i.e. an arrival time spectrum). The experimental conditions were 11 Td, 0·1343 kPa, 80 K and drift distance 2·958 cm.

The measurement of the ion drift velocity could be made either by manual control or by the use of a computer control system based on an IMSAI 8080 microcomputer. A typical 'arrival time' spectrum is shown in Fig. 2.

The lower E/N limit to the present measurements was set by insufficient ion current and the upper limit by the failure of the electrical shutters to perform satisfactorily.

The Bradbury–Nielsen grids are the source of two types of error, due to the following:

(a) Insulating Layers

When the electric field strength in the drift region is small, i.e. at low pressures and small E/N values, it is sometimes found that the measured reduced mobility does not approach a constant value corresponding to thermal equilibrium as E/N

decreases, but passes through a minimum and then rises. The measured reduced mobility also becomes pressure dependent. This effect, termed 'upcurving', was found by Elford and Milloy (1974*a*) to be caused by the presence of an insulating layer on the shutter wires. The performance of a shutter grid can be monitored and the presence of such layers usually detected by measuring the current transmitted as a function of the potential difference between adjacent wires. A typical plot, known as a cutoff curve, is shown in Fig. 3. Curve A is for a shutter grid in good condition, i.e. after being freshly gilded. When a thick insulating layer is present the cutoff curve becomes broadened (curve B) and the shutter is no longer capable of chopping the incident ion flux satisfactorily. When this condition occurs, the arrival time spectrum is found to have a large background current and the current maxima are found to be anomalously broadened and skewed.

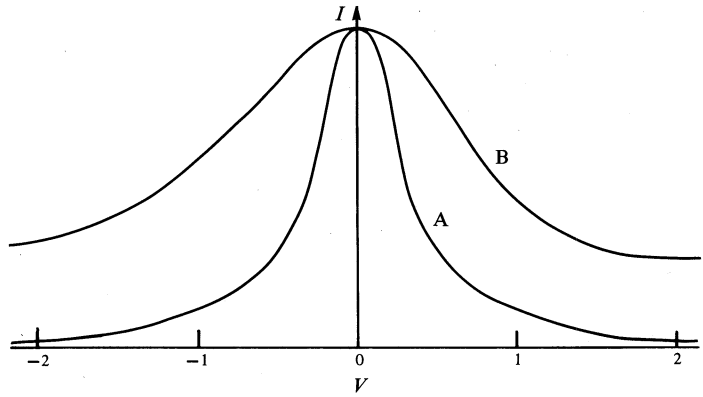

Fig. 3. Typical variations of the current I transmitted by a single shutter as a function of the potential V between adjacent grid wires (i.e. cutoff curves): A, shutters in good condition; B, degraded shutters.

When only a thin insulating layer is present on the wires, upcurving may be found in the K–E/N curves without any detectable broadening of the cutoff curves, although as the layer becomes thicker the cutoff curves eventually exhibit broadening. The amount of cutoff-curve broadening depends on the integrated ion current incident on the shutter grid wires since the last regild. As the shutter closest to the ion source collects about 98% of the total ion current the charged layer effect was always greater for this shutter than for the others.

In order to monitor the state of the shutters, cutoff curves were measured after each assembly and bake of the drift tube and also periodically throughout the measurements. Particular attention was also paid to the measurements at low E/N values to check for the presence of upcurving.

(b) Behaviour of the Shutters at Low Pressures

At low pressures and high E/N values for Li^+ ions in helium the cutoff curves have the form shown in Fig. 4*a* and consist of two contributions, a narrow peak 'a' and a constant background 'b'. Such cutoff curves cause effects in the arrival time spectrum which are very similar to those observed when a charged layer is present. When the current maxima are only slightly skewed it is possible to make a correction by

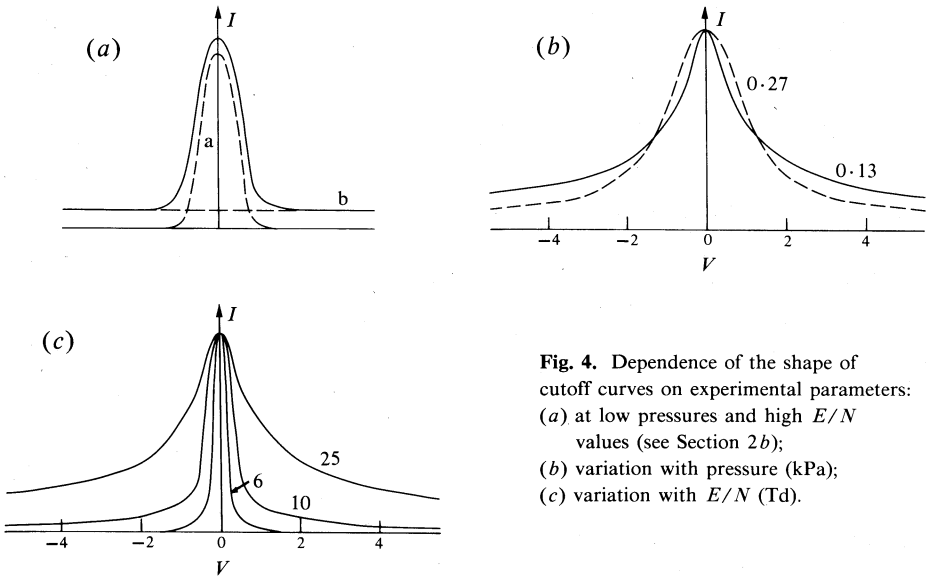

Fig. 4. Dependence of the shape of cutoff curves on experimental parameters:
(*a*) at low pressures and high *E/N* values (see Section 2*b*);
(*b*) variation with pressure (kPa);
(*c*) variation with *E/N* (Td).

extrapolating estimates of the mid-frequency made at various ion current values to the current at the maximum. However, when the skewness is large this procedure becomes inaccurate.

It is believed that the shape of the cutoff curves of Fig. 4*a* is caused by the Li^+ ions making so few collisions in the region of the shutter wires that they partially lose their swarm characteristics and behave like an ion beam. This effect became more severe as the pressure decreased at a given *E/N* value (see Fig. 4*b*) or as the *E/N* value increased at a given pressure (see Fig. 4*c*). As a consequence the measurements of the mobility of Li^+ ions in He were restricted to *E/N* values less than 70 Td. The effect was also found to be a function of the ion to atom mass ratio *m/M*. For small *m/M* values, such as in the case of Li^+ ions in Ar, the effect was not significant at any pressure used and the upper *E/N* limit in this case was determined by the onset of electrical discharge.

A number of tests were made to check the validity of the data. In all measurements of the ion drift velocity the values were found to be independent of the amplitude of the signal applied to the shutters and the value of *E/N* in the region immediately before the first shutter. A number of check points were chosen to test if the measured values were a function of the drift distance. No significant difference was found between the values measured at the two drift distances of 3 and 9 cm. The results could be repeated to within the experimental scatter, which was in general less than $\pm 0{\cdot}1\%$ and in all cases less than $\pm 0{\cdot}3\%$.

3. Results and Comparisons with Previous Data

The reduced mobilities of Li^+ ions have been measured in helium at 294 and 80 K and in argon at 294 K; the data are given in Sections 3*a* and 3*c*. When comparisons with previous mobility data are presented graphically, the present best estimate values are represented by solid curves. No data points are shown as they all fall within the thickness of the curves. All reduced mobility values are in units of $cm^2\,V^{-1}\,s^{-1}$.

The random errors quoted in this work for the mobilities were obtained by adding the individual random errors in quadrature. The systematic errors in the mobilities were obtained by adding the individual systematic errors arithmetically.

(a) Results for Li^+–He

The reduced mobility values for Li^+ ions in helium are shown in Table 1 and Fig. 5. Measurements were made at 294 K at *E/N* values from 3 to 70 Td and at pressures from 0·1343 to 0·4133 kPa. At 80 K, data were taken over the *E/N* range 2–18 Td and at pressures from 0·0725 to 0·3307 kPa. The best estimate values listed in Table 1*b* are not simple averages of the data at each *E/N* value but were obtained from the curves of best fit at each pressure and making corrections for end effects of the type discussed in Section 2.

The study of the mobility of Li^+ in helium at low temperatures was accompanied by the determination of the reaction rate coefficients for the clustering of He to Li^+ in the gas phase. This work is reported separately (Cassidy and Elford 1985; present issue p. 577). No evidence of lithium ion–helium clusters at room temperature was found by using either the mass spectrometer or by examination of the arrival time spectra. The 294 K results show no dependence on pressure to within the experimental scatter of ±0·2%.

The major error in the determination of the reduced mobility at 80 K is the temperature measurement, estimated to be uncertain by 1·0%. This error is reduced to 0·1% at 294 K. Other sources of error arise from the determination of the potential difference between the shutters (random 0·02%, systematic 0·06%), the pressure measurement (random 0·02%, increasing to 0·04% at 0·544 Torr [≡0·0725 kPa], systematic 0·1%), the determination of the drift distance (systematic 0·1% and the determination of the effective transit time of the ions between the shutters. For the 294 K measurements this is estimated to be 0·1% at low *E/N* and 0·2% at high *E/N*. The error in the measurement of the transit time is 0·2% at all *E/N* values at 80 K. The values given are estimated maximum errors. The total errors for the reduced mobility of Li^+ in He at 294 K are estimated to be 0·5% at low values of *E/N* and 0·6% at high *E/N*. The total error increases to 1·5% at 80 K.

The present best estimate results for Li^+–He are compared with those of earlier workers in Fig. 5. The results of Milloy (1973) are not shown as they have been found to be in error due to the phenomenon described in Section 2*a* (Elford and Milloy 1974*a*), which can artificially increase the measured mobility at low pressure and low values of *E/N*. The present results are consistently lower than those of I. R. Gatland (personal communication 1982) by about 1–2%, and those of Takata (1975) by about 2% at low values of *E/N*. The results of Kaneko *et al.* (1978) are not shown because of the large scatter in their data.

Reduced zero field mobilities κ_0 derived by extrapolation to zero *E/N* are shown for Li^+ ions in He in Table 2. With the exception of the value by Kaneko *et al.* the present value for κ_0 agrees with previous determinations to within the combined error limits. The only reduced mobility results available for comparison at temperatures near 80 K are those obtained by Hoselitz (1941) at 78 K. When normalized following the present day convention, his result for κ_0 is 5% above the present value.

(b) Results for Li^+. He–He

At 80 K, 0·2791 kPa and *E/N* values less than 7 Td a significant number of Li^+. He cluster ions were formed during the transit of the Li^+ ions from the source to

Table 1. Reduced mobility of Li^+ ions in He at (*a*) 294 K and (*b*) 80 K

Values in parentheses were taken using the 3 cm drift distance; all other data with the 9 cm drift distance. Values of κ are in $cm^2 V^{-1} s^{-1}$ and p in kPa

E/N (Td)	(*a*) 294 K: κ at p values of 0·1343	0·2791	0·4133	Best estimate
3·0			22·81	22·81
4·0		22·90	22·85 (22·91)	22·88
5·0		22·95	22·93	22·94
6·0		23·10 (23·14)	23·03	23·06
8·0	23·37	23·37	23·32 (23·29)	23·35
10·0	23·79	23·76		23·77
10·36			(23·71)	
12·0	24·28	24·26	24·24 (24·21)	24·26
13·0		24·59	24·52	24·56
14·0		24·94	24·88 (24·87)	24·91
15·0	25·37	25·32	25·28	25·32
16·78	26·09			26·09
17·9	26·65			26·65
18·0	26·70			26·70
20·0	27·55	27·54		27·55
25·0	29·59	29·64 (29·64)		29·62
30·0	31·18			31·18
35·0	32·13			32·13
40·0	32·47			32·47
50·0	32·35			32·35
60·0	31·72			31·72
70·0	31·35			31·35

E/N (Td)	(*b*) 80 K: κ at p values of 0·0725	0·1343	0·2791	0·3307	Best estimate[A]
2·0		19·64		(19·66)	19·63
4·0	19·74	19·69	19·64		19·63
5·0				(19·68)	19·64
6·0		19·72	19·69		19·67
8·0		19·74			19·79
10·0	19·86	19·85			19·92
12·0		(20·02)			20·10
14·0	20·38	20·36			20·36
15·0		20·54			20·54
16·0		20·88			20·88
18·0	21·59	21·56			21·58

[A] See Section 3*a*.

shutter S2 (see Fig. 1). It was therefore possible to observe distinct current maxima for Li^+. He ions when shutters S2 and S3 were used to measure mobilities. A typical arrival time spectrum showing the presence of Li^+. He clusters is shown in Fig. 6*a*. It was not possible to observe cluster ions when shutters S1 and S2 were used because in this case the distance over which the cluster ions form before shutter S1 is only 1 cm. The reduced mobility of Li^+. He ions in He at 80 K was measured at 0·279 kPa and found to be constant at 14·85 for *E/N* values from 4 to 7 Td.

The conditions under which Li^+. He mobility measurements could be made were very restricted. At lower pressures insufficient cluster ions were formed to yield a measurable cluster ion peak, while at higher pressures the arrival time spectra became

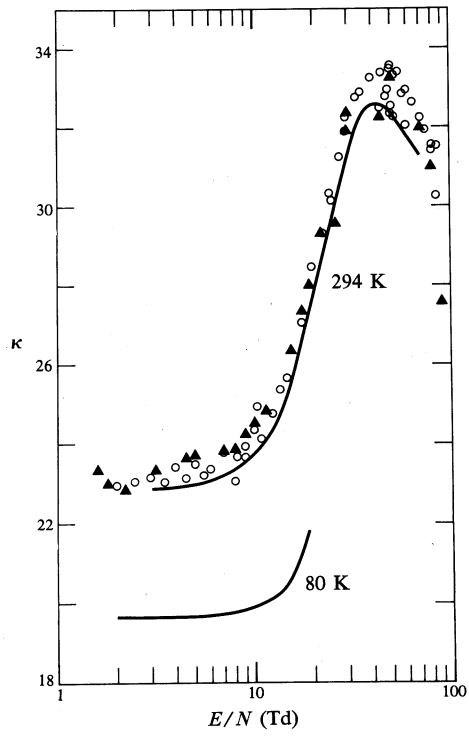

Fig. 5. Reduced mobility of Li^+ ions in helium as a function of E/N at 80 and 294 K: curves, present work; triangles, Takata (1975); circles, Gatland (personal communication 1982).

Table 2. Reduced zero field mobility κ_0 of Li^+ ions in He

Authors	T (K)	κ_0
Tyndall (1938)	291	24·2
Hoselitz (1941)	291	24·2
Akridge *et al.* (1975)	—	23·06±0·45
Takata (1975)	311	23·2 ±0·7
Kaneko *et al.* (1978)		23·5 ±0·5
Present work	294	22·81±0·11
Hoselitz (1941)	78	20·5
Present work	80	19·64±0·29

complex due to contributions from higher order clusters (see Fig. 6*b*). Measurements made using such spectra gave reduced mobilities of 13·2 for the Li^+.2He ions and 11·2 for Li^+.3He ions.

Data for the reduced mobility of Li^+.He ions in helium were also obtained from mass analysed spectra and agreed with the values presented here to within the stated experimental error. In general, it was not possible to obtain satisfactory results for the mobility of cluster ions using such mass analysed spectra because of the small signal-to-noise ratio at low values of E/N. Furthermore, when the mass spectrometer was tuned to select a given cluster ion mass, the measured spectrum showed large

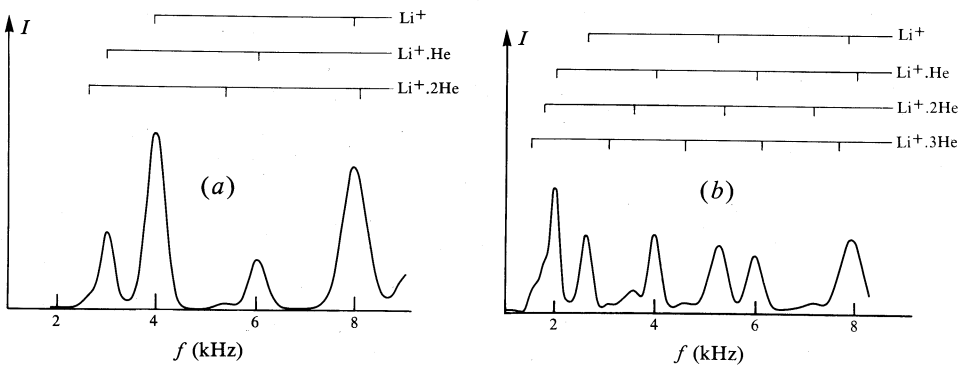

Fig. 6. Arrival time spectra showing the presence of Li^+ and Li^+. *n*He cluster ions for a 3 cm drift distance and temperature of 80 K: (*a*) 4·5 Td and 0·267 kPa; (*b*) 3 Td and 0·413 kPa.

Table 3. Reduced mobility of Li^+ ions in Ar at 294 K

Values in parentheses were taken using the 3 cm drift distance; all other data with the 9 cm drift distance. Values of κ_m are in $cm^2\,V^{-1}\,s^{-1}$ and p in kPa

E/N (Td)	κ_m measured at p values of 0·1033	0·1343	0·2791	Calc. value ($p \rightarrow 0$)
8·0			(4·592)	
10·0			(4·594)	4.66
12·0			4·591 (4·594)	4·66
15·0	4·639	4·620 (4·624)	4·590 (4·595)	4·66
20·0	4·654	4·629 (4·626)	4·606 (4·601)	4·67
25·0	4·668	4·650 (4·646)	4·631 (4·618)	4·68
30·0	4·710	4·703 (4·684)		4·72
35·0	4·806	4·789 (4·795)		4·81
40·0	4·929	4·921		4·93
50·0		5·330		5·33

peaks at frequencies corresponding to the passage of parent ions through the drift region, indicating that significant clustering occurred in the sampling region.

(c) Results for Li^+–Ar

The measured reduced mobility values of Li^+ ions in argon (see Table 3) were obtained at 294 K and pressures from 0·1033 to 0·2791 kPa and E/N values from 8 to 50 Td. The results for the two drift distances (9 and 3 cm) agree to within the experimental scatter of ±0·2%. The results are plotted in Fig. 7. Experimental errors were estimated as for Li^+–He at 294 K, the estimated total error being 0·5%.

Although the raw data show no dependence on drift length, they do display a variation with gas pressure. This pressure dependence was not observed for K^+ ions in argon and hence is unlikely to be due to experimental error. The current maxima in the current–frequency spectra were symmetrical gaussians and mass analysis of the ions leaving the drift region showed a small quantity of Li^+. Ar clusters. The abundance of this ion cluster increased with pressure, no ions being observed at the

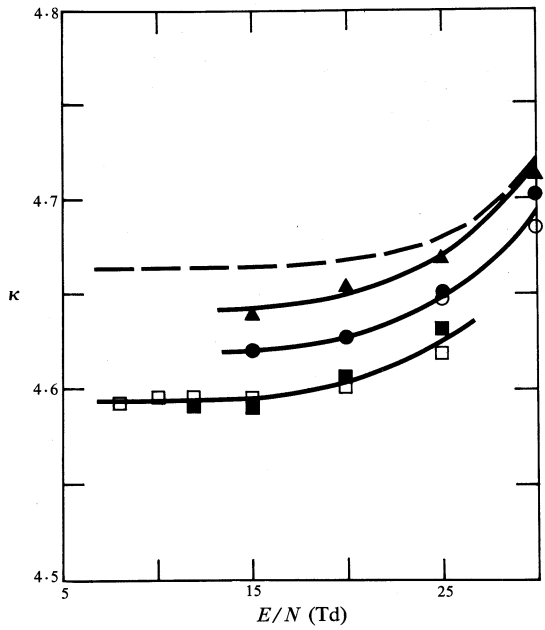

Fig. 7. Reduced mobility of Li^+ ions in argon at 294 K and low values of E/N at pressures of 0·775 kPa (triangles), 1·007 kPa (circles) and 2·093 kPa (squares). The full and open symbol values were measured using drift distances of 9 and 3 cm respectively. The dashed curve was obtained by fitting (see Section 3*c*).

lowest pressure and highest values of E/N. These observations are consistent with the presence of the equilibrium reactions

$$Li^+ + Ar + Ar \rightleftharpoons Li^+ . Ar + Ar . \tag{1}$$

The measured reduced mobilities κ_m were used to determine the reduced mobility of the Li^+ ion, κ_1, using the relation (Elford and Milloy 1974*b*)

$$\kappa_m = (\kappa_1 + \kappa_2 K_E N)/(1 + K_E N), \tag{2}$$

where N is the gas number density, K_E is the equilibrium constant for the reactions (1) and κ_2 is the mobility of the $Li^+ . Ar$ cluster ion. The data for κ_m as a function of pressure at a given value of E/N were fitted to expression (2) using the value $\kappa_2 = 2{\cdot}0$ (Keller *et al.* 1973) in order to obtain κ_1 and K_E. The fits were shown to be largely insensitive to the value of κ_2 assumed over the pressure range used. Due to the presence of trace levels of gas contaminants, the value of K_E determined by fitting the data to expression (2) is an upper limit to the equilibrium constant for the clustering of Ar to Li^+. The fitted values of K_E obtained are shown as a function of E/N in Fig. 8. The value of K_E obtained by extrapolation to $E/N = 0$, i.e. the value corresponding to thermal equilibrium at 294 K, is $(4 \pm 0{\cdot}5) \times 10^{-19}$ cm^3.

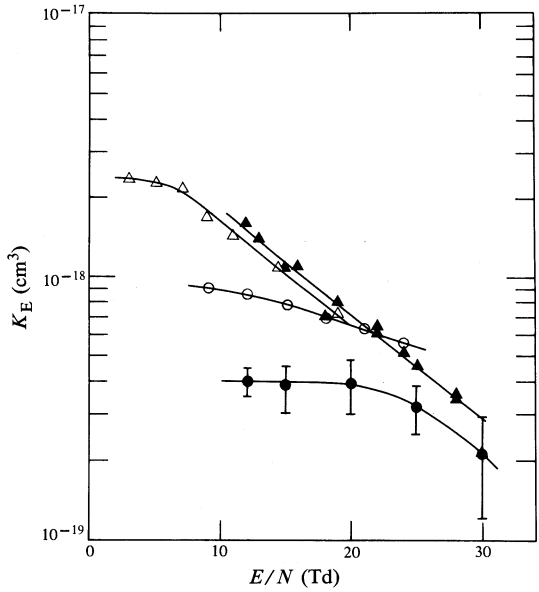

Fig. 8. Equilibrium constant K_E as a function of E/N at room temperature for the reactions $Li^+ + Ar + Ar \rightleftharpoons Li^+.Ar + Ar$: closed circles, present work; open circles, Takata (1977); closed triangles, Takeba *et al.* (1982); and open triangles, Keller *et al.* (1973).

The mobility data obtained for Li^+–Ar by the fitting procedure described above are compared with the results of earlier workers in Fig. 9. The value of the zero field reduced mobility estimated from the present work is $4{\cdot}66 \pm 0{\cdot}02$. The results of Akridge *et al.* (1975) for Li^+ ions in Ar (circles) are higher than the present results at high values of E/N (as in the case of Li^+–He), yet lower than the present results at low values of E/N where the present results indicate the presence of an equilibrium clustering reaction.

The present results agree with those of Takebe *et al.* (1982) (closed triangles) at high values of E/N, but are higher at low values of E/N. The measurements of Takebe *et al.* were made using pressures 0·04–0·267 kPa and they commented that under their conditions of measurement the effects of forward and backward clustering on the mobility could be ignored. However, the present work indicates that their mobility measured at the higher pressures and low values of E/N may have been lowered by the presence of clustering and dissociation reactions in equilibrium. The apparatus used by Takebe *et al.* did not employ ion sampling.

Takata (1977) observed a pressure dependence in his data taken at approximately 306 K over the pressure range 0·027–1·07 kPa, but he used a different procedure to obtain the zero field reduced mobility. Takata extrapolated the data obtained for each pressure to $E/N = 0$ and then fitted relation (2) to the extrapolated reduced mobilities to obtain a κ_0 value for Li^+ in Ar of $4{\cdot}76 \pm 0{\cdot}17$.

Previous determinations of κ_0 for Li^+ in Ar are listed in Table 4. With the exception of the values of Takebe *et al.* and Kaneko *et al.* all other values of κ_0 for Li^+ in Ar at room temperature agree to within the combined error limits quoted.

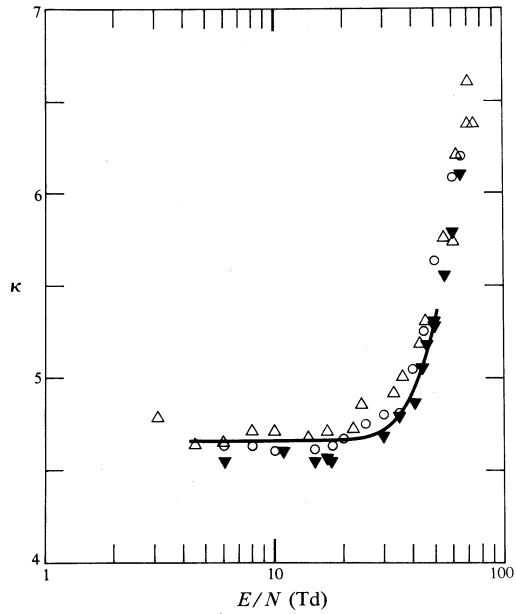

Fig. 9. Reduced mobility of Li^+ ions in argon as a function of E/N at 294 K: curve, present work (fitted values); circles, Akridge *et al.* (1975); open triangles, Takata (1977); and closed triangles, Takebe *et al.* (1982).

Table 4. Reduced zero field mobility κ_0 for Li^+ ions in Ar

Authors	T (K)	κ_0
Tyndall (1938)	291	4·68
Keller *et al.* (1973)	319	4·57±0·12
Akridge *et al.* (1975)	300	4·63±0·09
Takata (1977)	306±3	4·76±0·17
Kaneko *et al.* (1978)		4·5 ±0·09
Takebe *et al.* (1982)	304	4·56±0·05
Present work	294	4·66±0·02

The equilibrium constant K_E determined in this work is compared with that obtained by other workers in Fig. 8. The disagreement is severe, the difference at low E/N values being nearly an order of magnitude.

4. Comparison of Zero Field Mobilities with the Polarization Limit

When the reduced mobility has the value corresponding to the polarization limit, i.e. when the mobility is determined entirely by the dipole polarization component of the interaction potential, the separations r to which the mobility is sensitive are now so large that the potential can be represented by the dipole term only, i.e.

$$V(r) = -\tfrac{1}{2}\alpha e^2/r^4,$$

where α is the dipole polarizability and e is the ionic charge. A comparison of the zero field reduced mobilities (Table 5) indicates that the limit has virtually been

reached for both Li^+–He and Li^+–Ar in the present measurements. There is therefore little advantage in carrying out measurements of Li^+–Ar mobility measurements at gas temperatures much lower than room temperature. Such measurements would in any case be difficult to perform because of the small Li^+ ion abundance due to the relatively fast clustering reaction to form $Li^+.Ar$. Table 5 also demonstrates the necessity for obtaining data at low temperatures in the case of Li^+–He in order to approach the limiting value. Earlier mobility data for Li^+–He were available only at room temperature and hence provided little information on the very long range part of the potential. Beam experiments do not probe this region.

Table 5. Comparison of the reduced zero field mobility κ_0 with the polarization limit

Ion–Gas	T (K)	κ_0 Present	Poln limit	Difference (%)
Li^+–He	294	22·81±0·5%	19·2	19
	80	19·64±1·5%		2
Li^+–Ar	294	4·66±0·5%	4·46	4·5

5. Conclusions

Mobility data taken at 80 K now make it possible to derive the interaction potential for Li^+–He out to separations which are much larger than can be obtained using only data taken at room temperature. In the case of Li^+–Ar the use of more precise data will enable the potential to be determined within closer limits.

The observation of a pressure dependence of the mobility of Li^+ ions in argon has enabled the equilibrium constant to be derived for the clustering and dissociation of $Li^+.Ar$ ions and the mobility data for this case to be corrected to that corresponding to Li^+ ions, which make their transit of the apparatus without being subject to reactive collisions. The removal of the effect of clustering reactions on the mobility is necessary before interaction potentials can be derived.

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