Molten Salts and Isotope Separation

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Dedicated to Professor Alfred Klemm on the occasion of his 100th birthday

The work on molten salts and isotope separation performed over the years at Université Pierre et Marie Curie and at Collège de France is critically reviewed. This research, closely related to A. Klemm's pioneering contributions, leads among other things to the discovery of the effect now called the 'Chemla effect', after the late Professor Marius Chemla. These studies of ionic motions in melts, and liquids in general, have greatly benefitted from recent advances in molecular simulations. Some recent results of such simulations – molecular dynamics (MD) and Brownian dynamics (BD) – as well as of related theoretical work are discussed.

Key words: Transport Number; Ionic Mobility; Isotope Effect; Diffusion Coefficient; Molecular Dynamics; Fused Salt.

1. Introduction

The origin of the interest in molten salt in the group at Université Pierre et Marie Curie in Paris lies in the research works performed in Professor Joliot Curie's laboratory at Collège de France to produce separated isotopes. Indeed, since the discovery that chemical elements can consist of several isotopes attempts were carried out to produce separated isotopes.

Apart from the various forms of electromagnetic separation, the main techniques are based on statistical processes such as diffusion, chemical exchange, distillation, thermal diffusion, and ionic migration. The last technique was extensively studied, especially for the elements which have no easily obtainable gaseous compounds. In the 20s of the previous century, several experiments were carried out to enrich isotopes by ionic migration in solutions, enclosed in agar gel to avoid mixing by convection [1]. At that time, no separation was detected by the existing methods. In fact, an isotope effect was present, but it was too small. This was proved later when mass-spectrometric and activation analysis methods became available. According to the kinetic theory, the very low value of the isotope effect in aqueous solution was attributed to the solvation effect, which drastically reduces the relative mass difference of moving particles.

Taking this fact into account, Klemm [2, 3] suggested that it should be easier to obtain isotope separation by carrying out experiments in media where the ions do not move with a solvation atmosphere. So, he started his research by studying migration in a solid salt crystal. For this purpose he chose a crystal of silver iodide, which exhibits a not too small ionic conductivity. He was able to show that the heavy isotope of silver enriched toward the anode.

This successful experiment opened the way to a large number of determinations of mass effect in ionic crystals. However, though ionic crystals give large isotope effects, the separation yields were low due to the generally low conductivity of crystals. Later, Klemm [4] extended his research to molten salts and was able to determine the difference in the mobilities of lithium or potassium isotopes in their fused chlorides.

It is our purpose to describe briefly researches carried out to determine the migration isotope effects in various media, with a survey of the attempts to produce separated isotopes. Then, the contribution of the measurements of isotope effects to the physicochemical properties of ionic liquids will be examined. A fundamental description at the atomic scale by molecular dynamics calculation will be carried out to obtain a valuable insight into the structure and the thermodynamic and kinetic properties of the liquid state.

2. Ionic Migration and Isotope Effect

2.1. Mass Effect

The isotope effect in ionic migration is described by the ratio of the mobilities of two isotopes, u_1 and u_2. Separation takes place when the mobility ratio differs from unity

$$\frac{u_1}{u_2} = 1 + \varepsilon .$$

Since ε is generally much smaller than 1, it may be written

$$\varepsilon = \frac{\Delta u}{\bar{u}} ,$$

where $\Delta u = u_2 - u_1$ and $\bar{u}$ is the mean mobility of the isotope mixture:

$$\bar{u} = \gamma_1 u_1 + \gamma_2 u_2 \ \text{ with } \ \gamma_1 + \gamma_2 = 1 .$$

In order to compare the efficiency of various experiments, Klemm introduced the notion of mass effect:

$$\mu = \frac{\Delta u / \bar{u}}{\Delta m / \bar{m}} ,$$

where Δm is the mass difference, and $\bar{m}$ is the mean mass of the isotopes. According to the simplest kinetic model, the drift velocity of a particle should be proportional to the reciprocal of the square root of the masses, $u_1/u_2 = (m_2/m_1)^{1/2}$, which for $\Delta m/\bar{m} \ll 1$, gives $\mu \approx -0.5$. μ values close to this figure have occasionally been obtained, but generally the measured values are much lower (absolute μ values are considered).

2.2. Migration in Aqueous Solutions and Crystals

Migration in aqueous solutions was the method used in the earliest attempts to separate isotopes. A quite sophisticated device was described [5] to separate the two potassium isotopes ^{39}K – ^{41}K. Latter, a simpler method was proposed by the team of Collège de France [6]. It consisted of a paper strip impregnated with an electrolyte (NaCl solution 0.04%). A spot containing two radioisotopes ^{22}Na and ^{24}Na (periods: ^{22}Na: 2.6 years, ^{24}Na: 14.8 h) was placed in the centre of the strip (Fig. 1). To avoid a too large spreading of the spot by diffusion, the migration time was reduced by using a very high electric field: a voltage of 5000 V was applied between the electrodes at a distance of 40 cm. In order to keep the radioactive spot at the same place during the experiment, the paper ribbon was rolled up on two glass rods and could thus easily be moved. The migration distance was 280 cm for a duration of 1 h 45 min. The radioactive analysis showed that ^{22}Na migrated more rapidly than ^{24}Na; the distance between the centres of gravity of the spots corresponding to the two isotopes was 5.8 mm.

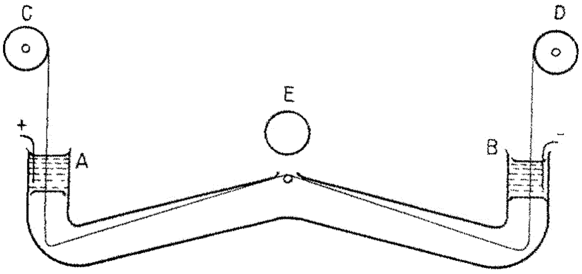

Fig. 1. Migration on a paper strip [6]. A, B – electrolysis compartments filled with NaCl solution; C, D – glass rods; E – Geiger–Müller detector. The tube is filled with carbon tetrachloride.

A similar experiment was carried out to measure the relative mobilities of lithium isotopes [7]. This element has only two stable isotopes, ^{6}Li and ^{7}Li. Their abundance in natural salts is 7.5 and 92.5%, respectively. The paper ribbon was now impregnated with a solution of ammonium nitrate (10%). Moreover, in this case the relative mass difference was large enough and the use of a moving strip was not necessary. The analysis of the lithium spot was carried out by the isotopic dilution technique using a mass spectrometer specially built by Chemla in his laboratory. With the same experimental device, the ^{22}Na and ^{24}Na migration was measured again. The following results were obtained: $\mu_{\mathrm{Na22-Na24}} = -0.023$ and $\mu_{\mathrm{Li6-Li7}} = -0.024$. As expected, due to the solvation process, the values were much smaller than the values predicted by the kinetic theory.

As pointed out in the introduction, to avoid the perturbing solvation effect, Klemm studied the electromigration in the solid state. He was able to show that in an AgCl crystal the heavy isotope, ^{109}Ag, was enriched toward the anode. Using radioactive tracers, Chemla studied the diffusion of various ions in NaCl and KCl monocrystals [8, 9]. The chlorides of radioactive elements were deposited by sublimation at the surface of the crystals. An electrical field was applied by pressing the crystal between two platinum electrodes. According to the experiments, the device was maintained at a temperature ranging from 570 to 750 °C. After a few hours the crystal was cut in sections of 33 µm with a microtome. In general, the measured mass effects were quite close to the theoretical value; for example in NaCl $\mu_{\mathrm{Na22-Na24}} = -0.46$. However, notwithstanding this interesting value, migration did not appear as a valuable technique to produce separated isotopes due to the low conductivity at solid state.

2.3. Ionic Migration in Fused Salts

Following the successful enrichment in 1947 of lithium and potassium in their fused chlorides [4], many experimental papers have appeared on ionic migration in fused salts [10]. Since then, the process has been applied to other isotope mixtures. The melt electrolysis was generally carried out in a counter-current flow device. The anodic and cathodic compartments were connected through a tube filled with an inert material, such as a fine grain zirconium powder.

A simple and efficient method, analogous to the electrophoresis on paper, was proposed to obtain a rapid determination of the isotope effect [11, 12]. The porous support needed to avoid convection mixing was an asbestos strip calcined beforehand and then immersed in a molten salt, generally a mixture $NaNO_3-KNO_3$; the strip (50 × 1.5 cm, thickness 0.3 mm) was introduced into an electrically heated glass tubing (Fig. 2). The impregnation was 25 mg/cm^2. For an applied voltage of 700 V, the current was 100 mA at 300 °C. An advantage of the technique was the short duration of the experiment, which lasted a few hours. The ribbon was cut in 5 mm slices to determine the migration distance of the studied isotopes.

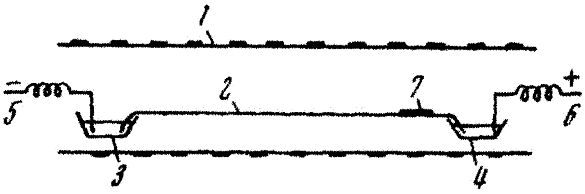

Fig. 2. Migration on an asbestos strip [11]. 1 – electrical furnace; 2 – asbestos strip; 3, 4 – electrolysis compartments filled with fused salt; 5, 6 – conducting electrodes; 7 – isotope spot.

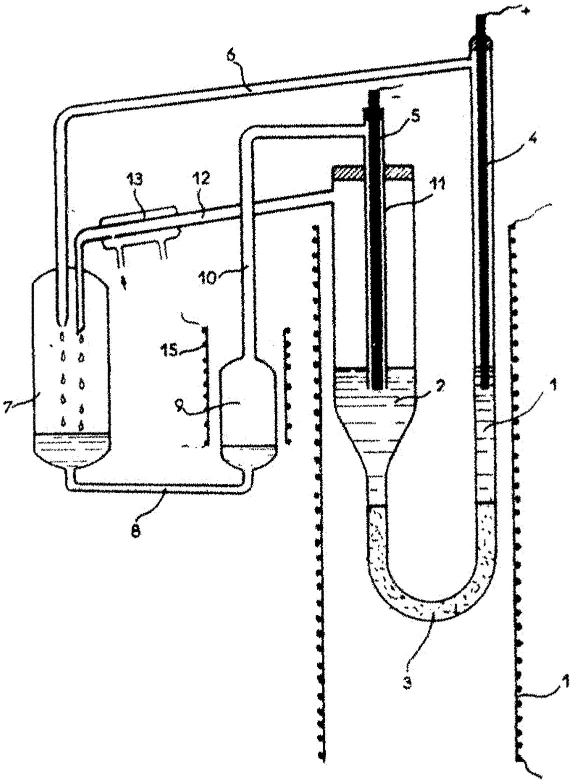

Fig. 3. Counter-current device for the production of separated lithium isotopes in LiBr – KBr mixture [18]. 1 – anodic compartment; 2 – cathodic compartment; 3 – diaphragm; 4, 5 – graphite electrodes; 6 – anodic bromine outlet; 7 – bromine tank; 8 – junction tubing; 9 – boiler; 10, 11 – inlet tubings; 12 – cathodic bromine outlet; 13 – condenser; 14 – electrical furnace.

As expected, these set of experiments showed that fused salts were a more favourable medium to produce separated isotopes. For example, the mass effects for the ^{22}Na and ^{24}Na couple were, $\mu_{\mathrm{Na22-Na24}} = -0.023$, in aqueous solutions, and $\mu_{\mathrm{Na22-Na24}} = -0.11$, in fused $NaNO_3-KNO_3$. Nevertheless, these values remain smaller than those obtained in crystals.

2.4. Production of Separated Isotopes

The only techniques suitable for a practicable separation are counter-current processes in which the elementary effect is repeated many times in a continuous manner [13 – 15]. The isotopic ions migrating in the electric field move counter-current to the supporting medium; then the ions can be allowed to move over a very large distance, although the whole

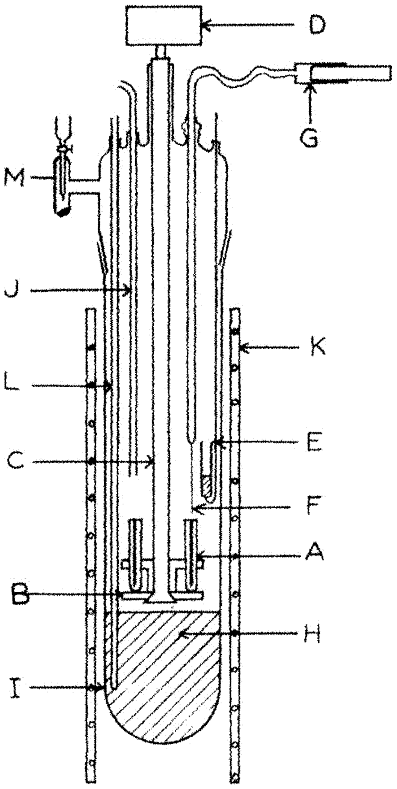

Fig. 4. Diffusion apparatus [23]. A – silica capillary, B – aluminium basket, C – Pyrex rod, D – micro-motor, E – salt with tracers, F – Pyrex needle, G – syringe, H – salt bath, I – Pyrex container, J – argon inlet, K – electrical furnace, L – thermocouple, M – preparation of N_2O_5 atmosphere, HNO_3 on P_2O_5.

process takes place over short distances. Of course, this procedure cannot be used with materials in the solid state although they exhibit a favourable separation coefficient. It may be used with aqueous solutions, but the efficiency remains very low. So, most of the experiments were carried out using fused salts.

A special effort was devoted to the separation of lithium isotopes. Indeed, the light isotope ^{6}Li is valuable as the source material for the production of tritium and as an absorber of neutrons in nuclear fusion reactions. ^{7}Li is used as a part of the molten lithium fluoride in molten salt reactors.

An interesting way was provided by migration in lithium chloride or bromide [16, 17]. However, some difficulties appeared when the laboratory technique was to be extended toward a large scale production of separated isotopes. At high temperature, the salt melts are very corrosive, and it was not possible to maintain the migration process for a long enough time to achieve a high enrichment.

A well-known procedure to obtain a salt bath at lower temperatures is to use a eutectic mixture. At first glance, this idea seems to be quite unrealistic: indeed, the counter-current technique, which is efficient to separate isotopes having very similar physicochemical properties, should first rapidly separate the two components of the salt mixture. However, an attempt was carried out to study the separation of lithium isotopes in a eutectic mixture LiBr – KBr [18, 19]. The result was very surprising. After a few hours, the salt composition in the glass tubing reached a constant value close to the eutectic composition. No separation between lithium and potassium was observed, but the isotope separation still continued with a progressive ^{7}Li enrichment in the anodic compartment whereas the proportion of ^{6}Li increased on the cathodic side. Moreover, not only the lithium isotopes separated, but it was observed that the potassium isotopes separated as well, the heavy isotope concentrated also in the anodic compartment and the lighter one toward the cathode.

This unexpected behaviour opened the way toward a more practicable design for the production of separated isotopes. An apparatus with an automatic recycling of the bromine was built with large glass tubing (Fig. 3). This apparatus was able to work properly for about one month. With this procedure, a few grams of nearly pure ^{7}Li were produced.

2.5. The Chemla Effect

The strange failure of the counter-current technique to separate the components of a salt mixture was not restricted to the mixture LiBr – KBr, but was also obtained with the mixture LiBr – NaBr. Moreover, this behaviour was not specific to the bromide salts. It was rapidly shown that a similar effect occurred in the mixture $LiNO_3 - KNO_3$ [20].

These results encouraged a lot of experiments which showed that this effect was fairly common in binary molten salt systems consisting of two monovalent cations with a common anion. It was even observed in a system with a common cation: $LiCl - LiNO_3$ [21]. This important phenomenon was named the Chemla effect [22].

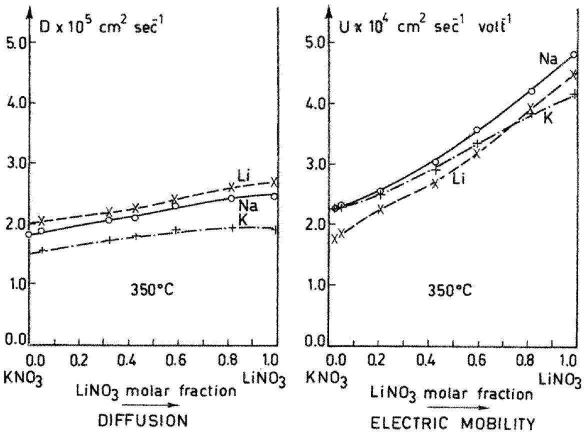

Fig. 5. Ionic diffusion coefficients and electrical mobilities, $LiNO_3 - KNO_3$ mixtures [20].

This behaviour is in contradiction with the classical theory of the particle motion in liquid state, and its interpretation was of crucial importance to reach a better understanding of the nature of ionic liquids. Of course, it was evident that, at the constant composition (called the critical composition) reached during the countercurrent experiments, the two cations have exactly the same mobility.

The stable situation concerning the concentration of the mixture components implies that, in mixtures rich in heavier cations, the mobility of the heavier cation should be larger than that of the lighter one; the reverse should be obtained on the other side of the critical composition. To check this assumption, measurements of ionic mobilities were carried out by Chemla's group. In order to obtain an accurate determination of the ionic motion, the capillary technique (Fig. 4) was used to measure the aptitude of ions to move in the melt. The self-diffusion coefficient of the different components of the salt mixture was accurately measured [23, 24]. The self- (or tracer) diffusion of the potassium and sodium ions were measured using radioactive tracers, ^{42}K (period 12.4 hours), ^{22}Na (period: 2.6 years), and the stable isotope ^{6}Li. In nitrate melts, the diffusion of the anions was followed by $^{15}NO_3^-$. The concentration of stable isotopes was determined by use of the isotopic dilution technique.

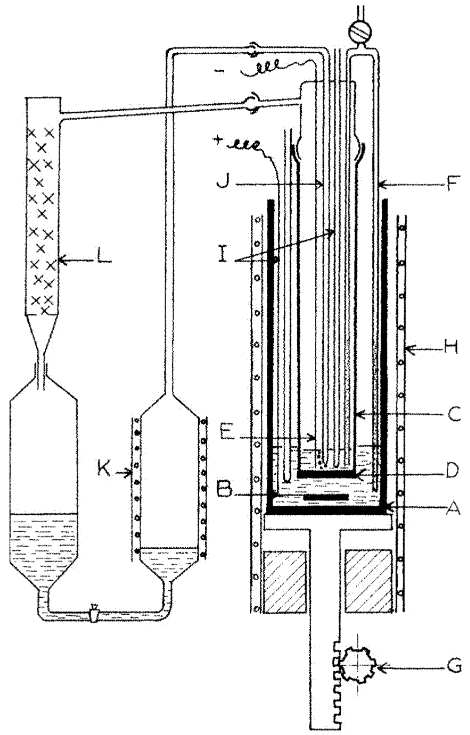

Fig. 6. Apparatus for the measurement of transport numbers [20]. A – Pyrex container, B – platinum sheet, C – Pyrex tube, D – porous plug, E – tantalum wire, F – equilibration tubing, G – device used to equilibrate the salt level in the two compartments, H – electrical furnace, I – thermocouples, J – nitric acid inlet, K – boiler, L – condensation column.

The results were again very surprising: in the whole concentration range of the mixture $LiNO_3 - KNO_3$, the lithium ions moved faster than the potassium ions, in contradiction with the expected crossing (Fig. 5). The accuracy of the experiment left no doubt about this result, the displacements of potassium and lithium were measured simultaneously in the same experiment, and the ratio of the diffusion coefficients was obtained with a great accuracy, around 1%. Of course, it was then suspected that for a given ion i, the diffusion coefficient D_i and the electrical mobility u_i could exhibit a different behaviour, notwithstanding the Nernst–Einstein relation, which states that the ratio D_i/u_i should be constant: $D_i/u_i = k_B T/e_i$ [25] (T is the absolute temperature; k_B Boltzmann's constant, and e_i the charge of the moving ion).

An accurate knowledge of the ionic electrical mobility was needed. It was obtained from the transport coefficients of the melt components measured by the classical Hittorf technique [26]. In order to avoid hydrodynamic flows, the anodic and cathodic compartments were separated by a porous plug, and a special apparatus was built to maintain the same salt level in the two compartments [27, 28] (Fig. 6). The ionic mobilities were deduced from the ionic transport numbers and from the equivalent conductivity Λ of the melt. The results are shown in Figure 5. Now, the Chemla effect was clearly explained: In lithium rich mixtures, the lithium ions moved faster than the potassium ones, and in potassium rich mixtures, the potassium ions moved faster than the lithium ones. The mobility of the lithium ions decreased more rapidly than that of the potassium ions when the potassium concentration was increased.

In order to investigate the system used by Chemla for the isotope separation, the same determinations were carried out in the $LiBr-KBr$ mixtures [29]. The same effect as in nitrate melts was obtained. A more marked crossing was observed, whatever the temperature; the mobility of the lithium ions decreased much more rapidly than that of the potassium ions. However, surprisingly, as already obtained for the nitrate melts, the diffusion measurements did not show any crossing, the lighter ions moved always faster than the heavier ones in the whole concentration range [30].

2.6. Polyionic Displacements

The above observations soon appeared not to be limited to the two systems $LiBr-KBr$ and $LiNO_3-KNO_3$, and the large generality of this behaviour encouraged the scientific community to dig deeper into the mechanism of particle motions in ionic liquids. The first idea put forward came from the surprising deviation from the Nernst–Einstein relation. It was generally assumed that, at least for alkali halides, the ions are fully ionized in crystals or fused crystals. Thus, the charge of the moving alkali ions should be the electron charge e. However, the particle motion in condensed media should take into account the effect of interactions between the particle and its environment. For example, the Debye–Hückel theory indicates that ions moving in a solvent are surrounded by a hydration shell which has a drag effect on the ion motion. This shell arises from the electrostatic interaction between the ion and the dipoles of the solvent molecules; this interaction slows down the ion motion; a similar behaviour must occur in ionic liquids, all the more so since the cation–anion interaction is quite stronger than the ion–dipole interaction. The ion motion can be described as the ion moving surrounded by its ‘hydration shell’. But now the shell is made of charged particles, so the effect of the shell is also to change the apparent charge of the moving particle, $e_i \neq e$.

To illustrate this mechanism, it has been proposed [20] to calculate the statistical proportion of the ion displacements attributed to ‘free’ ions and to ‘group motions’ such as that of anion–cation pairs $[AC]^0$ or more generally of groups such as $[A_xC_y]^{(y-x)+}$. The calculation was performed based on the deviations from the Nernst–Einstein relation by using the diffusion coefficients and the ionic mobilities deduced from the Hittorf experiments, called external mobilities (measured with respect to the wall of the container). This description, known as the polyionic model, has the advantage of providing a simple illustration of the charged particle motion in an ionic environment. An example of the results for the nitrate system is given in Table 1.

Some points should be emphasized. Firstly, the pair proportion (or associate motion) increases strongly from potassium to lithium; this effect illustrates the influence of the electrostatic interactions, which depends directly on the size of the ion: the smaller the ion the larger the anion–cation interaction.

Secondly, the potassium ions do not attract the anions very much. Thus, in potassium rich mixtures, the anions are more available for associate cations than in lithium rich mixtures; this behaviour explains the Chemla effect: the proportion of associated motion increases when the salt mixture becomes potassium rich, this trend is much more marked for the smaller ions (lithium) than for the larger ones (potassium).

Thirdly, the association effect depends also on the structure of the melt. As the temperature increases the quasi-lattice structure vanishes and the particles of opposite sign tend to associate more freely, the liquid structure approaches that of the gaseous state, which is mainly made of neutral anion–cation pairs. On the other side, at low temperature, the association should decrease, the particles remaining in their own quasi-lattice; it is well known that in crystals the particle motion nearly obeys the Nernst–Einstein equation, showing that the associated motions remain small. This tendency is illustrated by the results in Table 1, which show that the proportion of free-motion particles increases for decreasing temperature. This trend explains the shift in the concentration of the mobility crossing-point as the temperature varies. A similar calculation was done for the bromide mixtures and led to the same conclusions.

Table 1. Percentage of the particle motions (see text) in $LiNO_3-KNO_3$ melts with traces of $NaNO_3$ [20].

°C	Composition mol%	Potassium K^+	KNO_3	$K_2NO_3^+$	$K(NO_3)_2^-$	$LiKNO_3^+$	Lithium Li^+	$LiNO_3$	$Li_2NO_3^+$	$Li(NO_3)_2^-$	$LiKNO_3^+$	Sodium Na^+	$NaNO_3$	$NaMNO_3^+$	$Na(NO_3)_2^-$
350	KNO_3 94.2 $LiNO_3$ 5.8	51	19	13	3	1	22	46	0	16	16	43	30	17	10
	KNO_3 79.4 $LiNO_3$ 20.6	57	21	9	1	3	21	43	6	12	12	45	29	18	8
	KNO_3 57.0 $LiNO_3$ 43.0	63	17	7	0	6	23	38	11	10	7	48	24	22	6
	KNO_3 40.6 $LiNO_3$ 59.4	64	16	7	0	6	28	39	10	7	5	53	24	18	5
	KNO_3 18.5 $LiNO_3$ 81.5	74	7	6	0	7	31	35	15	2	2	61	20	16	3
	KNO_3 0.7 $LiNO_3$ 99.3	90	0	0	0	10	36	19	22	2	0	75	4	20	1
280	KNO_3 57.0 $LiNO_3$ 43.0	68	7	10	1	4	25	26	15	13	6	50	17	27	5
	KNO_3 0.7 $LiNO_3$ 99.3	97	0	0	0	3	42	20	18	2	0	80	8	10	2

M = Li or K

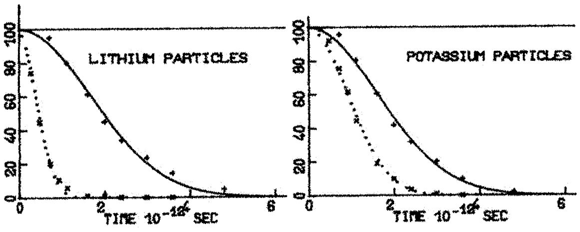

Fig. 7. Time evolution of the percentage of ions remaining in a shell around a moving ion; LiCl – KCl eutectic, 1570 K, solid line with, dotted line without Coulomb forces [35].

3. Molecular Dynamics Calculations

3.1. Simple Ionic Salts, Alkali Halides

The experimental observations previously described encouraged the scientific community to dig more deeply into the intimate mechanism of particle motion in purely ionic media. To obtain a more concise view of the transport properties in ionic liquids, the idea germinated to calculate ab initio the properties of a collection of charged particles. However, at least for alkali halides, the Coulomb interactions are the dominant forces acting on the particles. The effect of these long range forces can be easily taken into account by the method described by Ewald [31]. The particle notion was deduced from the integration of Newton's equation step by step in a computer program.

With the help of Professor Singer's group at Royal Holloway College [32], we have initiated a program to calculate by the molecular dynamics (MD) technique the behaviour of a set of charged particles [33, 34]. The good agreement between the experimental and calculated properties proved the validity of the model. This tool provided a suitable means for examining the structure of the ionic medium at a microscopic scale and the mechanism of ionic motion at very short times [35]. At a time scale of around 10^{-13} s, it was shown that the particles oscillated in a quasi lattice structure. The oscillating motion rapidly vanished and then, after about $2 \cdot 10^{-12}$ s, the mean square displacement of the ion provided a correct value of the macroscopic (experimental) diffusion coefficient. So we have carefully examined the behaviour of the ions during this crucial lapse of time. For example, the presence of the anions in a shell surrounding a cation was followed (the shell radius corresponds to the first minimum of the anion–cation radial distribution function). At very short time,

Table 2. Cut-off radius; for Li^+: 3.800 Å, for K^+: 4.580 Å; Minimum lifetime of the group motion: $0.176 \cdot 10^{-11}$ s [35].

Number of particles in the group motion	Percentage of particles involved in the motion	Percentage of the different species involved in the motion				Composition of the group motion percentage of the different species			
		Anion	Cation	Li^+	K^+	Anion	Cation	Li^+	K^+
1	46.18	48.15	44.21	42.86	46.11	52.13	47.87	27.07	20.80
2	29.63	29.63	29.63	34.13	23.33	50.00	50.00	33.59	16.41
3*	7.64	6.71	8.56	7.94	9.44	43.94	56.06	30.30	25.76
4	5.09	4.83	5.56	6.35	4.44	45.45	54.55	36.36	18.18
5	5.79	5.56	6.02	4.76	7.78	48.00	52.00	24.00	28.00
6	2.78	2.55	3.01	1.98	4.44	45.83	56.17	20.84	33.33
8	1.85	1.85	1.85	0.78	3.33	50.00	50.00	12.50	37.50
9	1.04	0.93	1.16	1.19	1.11	46.44	55.56	33.34	22.22

*Angles of the triplet configuration (degrees) 112.75, 39.56, 27.69

100% of the ions remained in the shell; whereas at long time the surrounding structure vanished (Fig. 7). After a time long enough to reach the macroscopic mean displacement of the cation ($\approx 2 \cdot 10^{-12}$ s), the anion remaining in the shell were considered as being involved in the motion. The results in Table 2 show that most of the particles moved either freely or coupled with a particle of opposite sign, the paired displacements being more important for the lithium ions than for the potassium ions Thus, everything happens as if the motion described in the polyionic displacement model came from associated species, the life-time of which was around $2 \cdot 10^{-12}$ s, long enough to affect the particle motion, but too short to be considered as long living macroscopic species.

The application of statistical mechanics to the results of computer simulation provided a valuable tool for a better understanding of particle motions in ionic liquids. For example, to illustrate the influence of the Coulomb forces on the particle motion, the behaviour of the same set of particles was examined without the presence of these electrostatic forces. The curves in Figure 7 show clearly that now the influence of the surrounding atmosphere vanished rapidly. The difference was most important for the smallest cation (lithium).

Moreover, the migration isotope effect was studied by varying the mass of the moving particles. It is known that for dilute gases, or to a lesser extent for ionic solids, the transport coefficients are roughly proportional to the reciprocal of the square root of the mass of the moving particles. In ionic liquids, it was shown that at very short times the particle motion can be described by a unique function if the time is scaled as $t/m^{1/2}$. However, this effect, which corresponds to Graham's law, vanished quite abruptly according to a collision–dissipation process [36]; the time evolution of this dissipation is quite well described by the Brownian motion approximation [37]. This mechanism was carefully interpreted in the frame of a perturbation theory, the parameter introduced in this theory being proportional to the reciprocal of the square root of the masses [38].

4. Conclusion

The research work initiated by Professor Klemm for producing separated isotopes by migration in molten salts was the starting point of experiments leading to a better understanding of fused media. The present paper shows his pioneering work concerning the description of ionic motion in liquids. These experiments have open the way to a large number of investigations. Firstly, the Brownian dynamics model was applied to the study of concentrated solutions and, latter, molecular dynamics calculations were extended to the study of various melts of industrial interest (nitrates, fluorides silicate with multivalent cations . . .). These investigations are described in the literature [39, 40].

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