



The motion of an ion in a synthetic molecular ion channel

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ABSTRACT

A molecular dynamics investigation is conducted on the passive transport of Na^+ ions through a synthetic channel in aqueous NaCl medium, the channel consisting of fourteen 15-crown-5 rings rigidly linked in a stacked configuration. The investigation studies the entry and exit of Na^+ ions by applied electric fields; the Cl^- ions are not admitted because of the channel's unfavourable axial electrostatic potential for anions, and the water molecules are too large to enter. The Na^+ ions exhibit damped oscillatory dynamics, for which frequencies and damping parameters are calculated, and possible applications of the system are discussed.

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1. Introduction

Syntheses of nanochemical molecular systems have resulted in the creation of interesting mechanical devices [1] and may soon create ones sharing features of living cells. Since synthetic materials may well have lower complexities than those of the biological systems which they model, it is hoped that an analysis of the kinetics and energetics of ion transport through a simple molecular ion channel that is designed for such a study may contribute to an understanding of ion migration in biological systems. These systems might include the transport of Na^+ and Cl^- ions through protein channels across the membrane of a biological cell, for which a complete structural, kinetic and thermodynamic description is currently beyond the capability of theory and simulation.

In this work a molecular dynamics (MD) investigation will be conducted in which ions are transported through a synthetic, structurally simple molecular channel (Fig. 1) consisting of fourteen stacked 15-crown-ether-5 rings (15-CE-5) in which each CE ring is covalently bonded to a similar one on either side of it in a stacked configuration. A previous work considered a two-dimensional lattice consisting of several 'floppy' channels in which the stacked rings were mutually linked by methylene (CH_2) groups, mounted in a bilayer membrane [2,3]. With the channels connecting two salt solutions it was shown that they allowed the passage of cations, anions and solvent molecules between the layers, but that the Na^+ ions showed significantly greater mobility than the Cl^- ions. Water molecules, which were also admitted, played a role

in the migration of the ionic species. In a subsequent work [4] the channel was made rigid by a 'bracket' consisting of an amine segment $-\text{CH}_2-\text{NH}-\text{CH}_2-$ linking the CEs at 10 points on each ring rather than five as for the methylenes. When this rigid channel bridged the two aqueous LiF solutions across the membrane, it acted as a 'cation trap', admitting passage to only the Li^+ cations from the salt layers. It was concluded that its ability to enter the channels and its subsequent motion were principally of electrostatic origin, for while the cations could do this, the solvent water molecules and even the F^- ions (whose radius is smaller than that of Na^+) failed to do so. There was also a suggestion that the Li^+ would undergo an oscillatory motion in the channel, a feature that will be investigated in this work.

2. The molecular system

2.1. The ion transporter channel

As the channel in this investigation is a solute in an aqueous electrolyte solution it is rendered hydrophilic by OH on one carbon atom of each amine linking segment which becomes $-\text{CH}-\text{NH}-\text{COH}-$ as shown in Fig. 1a. Both C atoms are bonded to a CE ring on either side of the unit (or to just one if they are terminal rings, the remaining site being occupied by a H atom). The structure is thus characterised by two adjacent rings constituting the basic unit that repeats along the length of the channel. The smaller one is the $(\text{O}-\text{C}-\text{C})_5$ segments with a diameter 4.10–6.10 Å; the larger has the five 'bracket' segments $[-\text{CH}-\text{NH}-\text{C}(\text{OH})-]_5$ whose diameter is 7.62–9.24 Å (but these segments are not mutually linked). The ion transporter is thus a molecular channel with overall length

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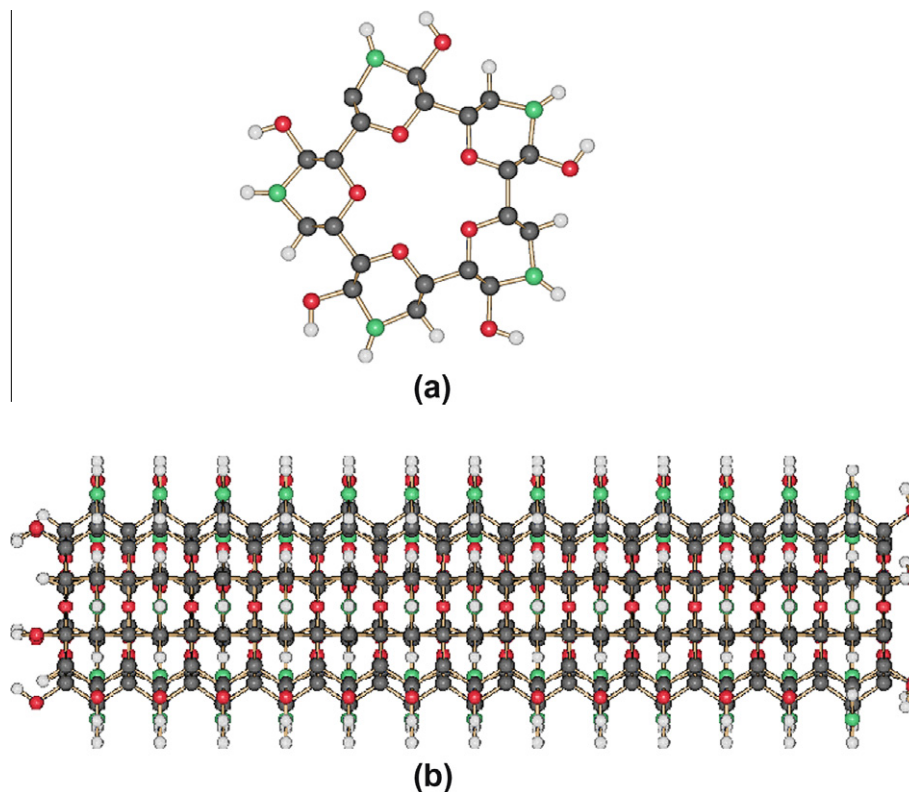


Fig. 1. The molecular channel containing fourteen stacked 15-crown ether-5 rings viewed (a) along, and (b) perpendicular, to the axis.

35.75 Å and consists of alternating narrow and wide rings which Fig. 1b shows to define 13 molecular chambers or cavities, with a repeat distance of 2.5 Å.

2.2. Molecular dynamics

Structural geometries were taken from literature values of diffraction and computed quantities on model compounds [5], Refs. in [4,2,3]. Partial atomic charges were obtained from Restricted Hartree–Fock (RHF) calculations performed by the Gaussian package [6] using 6-311 basis sets supplemented by (2*p*, 2*d*, 3*d* and 3*f*) polarisation functions, on model molecules consisting of a pair of (CH–NH–HOC)-linked 5-CE-15 rings, hydrogenated where necessary. The resulting charges were compared with those obtained from calculations on smaller molecules on which Møller–Plesset (MP2) corrections had been performed. (These were acetic acid CH₃COOH and dimethylamine H₃C–NH–CH₃.) The consistency between the latter and the RHF results was deemed to be sufficient to accept the RHF charges without reviewing their values other than those resulting from the minor adjustments involved in dehydrogenating the 2-ring model molecules that had been deployed as models for the quantum calculations. The problem of atomic charges was discussed in an earlier work [4,3].

Molecular dynamics (MD) calculations were performed using DL_POLY [7] under constant volume–temperature and also constant pressure–temperature conditions (Evans NVT and Hoover NPT thermostats). Simulations of several hundred thousand to a million time-steps, where a time-step was 1 femtosecond (10^{–15} s), were first performed to ensure that the MD system had achieved thermal and dynamic equilibrium, while the running times for the migrations of the ions in the channel were much shorter. The simulation box consisted of a 36 × 36 × 75 Å cell containing the 685-atom channel (Fig. 1) in an aqueous solution of

various molarities (0–5 M) in NaCl, about 3500 water molecules and a varying number of ions depending on the salt concentration.

The bond and non-bond atom-pair interactions were DREIDING (6–12) atomistic potentials [8] except those for the ions, for which those of Åquist [9] were used for Na⁺, and those of Lee and Rasaiah [10] for Cl[–]. As the use of these potentials, together with those of Berendsen’s SPC model [11] successfully simulate the solvation of the ions by the water molecules no additional electronic polarisation effects were allowed for (which would be inconsistent with the use of the atomistic potential described). Potential functions for heteroatomic pairs were calculated by the geometric-mean rule. Constant DREIDING values were used for all bonded atom pairs (bonds) and atom triads (bond angles).

3. Results

3.1. Axial electrostatic potential

When the channel is made rigid by the amine ‘clamping’ structural unit described in Section 1, the principal factor governing the entry of the ions into the channel and their subsequent trajectories is the electrostatic potential along the axis of the channel [4]. As a result, while the deformable channel in the phospholipid membrane [2] distorts to transport the anions and solvent, the rigid channel was found to admit Li⁺ cations but water molecules from the bulk solution, and even the smallest halide ion F[–], were denied entry [4]. (Even when the F[–] ion was inserted in a channel cavity it could not be displaced by more than 0.5 Å by strong electric fields.)

Fig. 2 shows profiles of the channel’s axial electrostatic potential plotted for the 35 Å channel length plus 20 Å on either side. The two curves are the potentials for the isolated channel and for that when contributions are included from the aqueous medium consisting of water molecules and ions in a 0.1 M NaCl solution. Despite the particles’ translations and reorientations in the bulk

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