Potential of interaction between the lithium cation and the sulfo group of an aromatic polyamide

Yu. K. Tovbin* and N. F. Vasyutkin

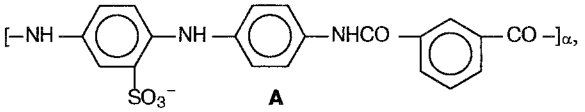
L. Ya. Karpov Institute of Physical Chemistry,
10 ul. Vorontsovo Pole, 103064 Moscow, Russian Federation.
Fax: +7 (095) 975 2450

A three-dimensional potential for the interaction between the lithium cation and the sulfo group of an aromatic polyamide including both the Lennard—Jones and Coulomb contributions was constructed. The Coulomb contribution was calculated using the semiempirical quantum-chemical MNDO method. The potentials accounting for the changes in the electron densities at the cation and the sulfo group and neglecting these changes (the atom—atom approximation) and the corresponding energy profiles of the migration of the lithium cation in a perfectly dry membrane were compared.

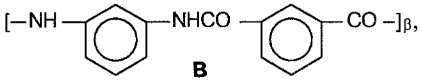
Key words: potential, cation, quantum-chemical calculation, MNDO method, membrane.

An understanding of the processes of the transport of alkali metal cations through ion-exchange membranes requires knowledge of the microstructure of cation-transport paths and the elementary events occurring in cation transfer between the ionic groups. Currently, experimental data on the study of the microstructure of polyamide membranes[1,2] and a theoretical description of the membrane transport[3] are available. However, the experimental data have not been interpreted quantitatively at the level of elementary events that accomplish the transport process. The use of conventional molecular dynamics, Monte Carlo, or cluster methods presents difficulties because these methods are based on atom—atom approximation including Lennard—Jones and Coulomb contributions and are incapable of accounting for the nonadditivity of interparticle interactions in the Li—SO_3 system.[4]

The aim of this work was to obtain the energetic and electronic characteristics of the detachment of the lithium ion from the ionic sulfo group of a polyamide membrane using the semiempirical quantum-chemical SCF MO LCAO method in the MNDO approximation. The calculated geometries, electron densities, and energetics of the system make it possible to construct the interparticle potential of the interaction between Li and atoms of the polymer, which accounts for the anisotropy of the potential energy surface in the surroundings of the sulfo group and the nonadditivity of the interactions between these atoms. This potential can subsequently be used in theoretical calculations. As an example, the potential obtained was used for calculation of the energy profile of cation migration in the amorphous part of a perfectly dry polyamide membrane. The energy profiles were compared with those calculated in the atom—atom approximation.



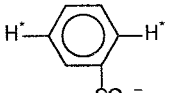
A



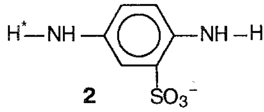
B

A polyamide membrane consists of two copolymers: ion-conductive copolymer **A** (fraction α = 100—30 %) and non-ion-conductive copolymer **B** (fraction β = 0—70 %). Quantum-chemical calculations were performed for a fragment of the chain containing the SO_3 group. This fragment was chosen because of a relative stability of the calculated parameters (geometry, charges, and energies) upon increasing the size of the fragment. In the calculations, the coordinates of the terminal atoms were fixed for maintaining the total length of the copolymer unchanged.

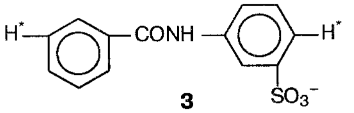
The following fragments were considered (the atoms with fixed coordinates are marked with asterisks):



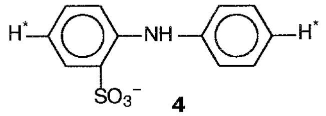
1



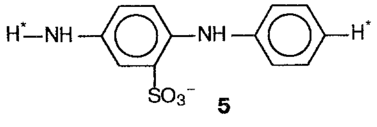
2



3



4



5

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1237—1240, July, 1995.

1066-5285/95/4407-1190$12.50

Table 1. Geometric parameters and charges on atoms for the fragments of the polyamide membrane*

Fragment	Angle/deg		Bond length/Å		Charge/a.u.					
	C—C—S	C—S—Li	C—S	S—Li	Q_C	Q_S	$Q_{O(1)}$	$Q_{O(2)}$	$Q_{O(3)}$	Q_{Li}
1	122.0	115.0	1.78	3.31	−0.387	1.715	−0.769	−0.721	−0.723	0.642
2	120.0	114.0	1.79	3.31	−0.372	1.732	−0.773	−0.703	−0.725	0.638
3	122.5	115.0	1.78	3.31	−0.390	1.718	−0.768	−0.721	−0.721	0.646
4	118.8	116.0	1.78	3.31	−0.458	1.717	−0.766	−0.735	−0.722	0.640
5	118.8	116.0	1.78	3.31	−0.457	1.717	−0.764	−0.733	−0.721	0.642

* The coordinates of lithium atoms are specified with reference to fixed C and S atoms, because the coordinates of oxygen atoms vary significantly upon displacing lithium atoms.

The geometric parameters and atomic charges of the above-mentioned fragments are listed in Table 1.

The largest differences are observed in the first three fragments. For fragment **5**, the parameters are virtually identical to the corresponding parameters of fragment **4**, and therefore, these parameters are used in all subsequent calculations.

The interaction potential for Li—SO_3 in the polyamide membrane was constructed similarly to that for the perfluorinated sulfocationite membrane.[4] The energy of the detachment of the Li^+ cation from the SO_3^- group along the selected directions ("rays") was calculated by the MNDO method (the AMPAC program). The position of Li was specified by a set of internal coordinates (R, α, φ), where R is the distance between Li and S, α is the C—S—Li angle, and φ is the dihedral angle between the C—C—S and C—S—Li planes. By analogy with the salts of sulfonic acids, the O—Li bond actually exists in the given system. In the calculations of the potential under study, the positions of the atoms of the sulfo group were optimized at each of the fixed S—Li distances, and the O—Li bond length was varied within the optimization. The parameter R was varied from 2.0 to 5.0 Å with steps of 0.3 Å. The angles are given in Table 2.

The potential constructed is three-dimensional; it is represented by a table containing the binding energies of Li with SO_3, the charges of all atoms of the fragment, and the displacement coordinates of the atoms of the SO_3 group relative to the nearest C atom of the benzene ring. The cubic spline interpolation according to the algorithm from Ref. 5 was used for the calculation of intermediate values.

Table 2. Dihedral angles between the C—C—S and C—S—Li planes

N*	α	β	N*	α	β
1	90	−90	8	120	90
2	120	−90	9	150	90
3	150	−90	10	90	180
4	90	0	11	120	180
5	120	0	12	150	180
6	150	0	13	180	—
7	90	90			

* N is the ray number.

Figure 1 presents the results of calculations of (*a*) the charge on the lithium cation Q and (*b*) the binding energies ΔE for the 13 specified rays. Note that for a polyamide membrane, Q and ΔE show a stronger dependence on the number of the ray N (a higher spread) than for a perfluorinated sulfocationite membrane, which is due to the effect of a nearby benzene ring.

The anisotropy of the potential energy surface in the surrounding of the sulfo group is conveniently illustrated in Fig. 2, which presents the angular dependences of the potential for Li—SO_3. The intermediate values of

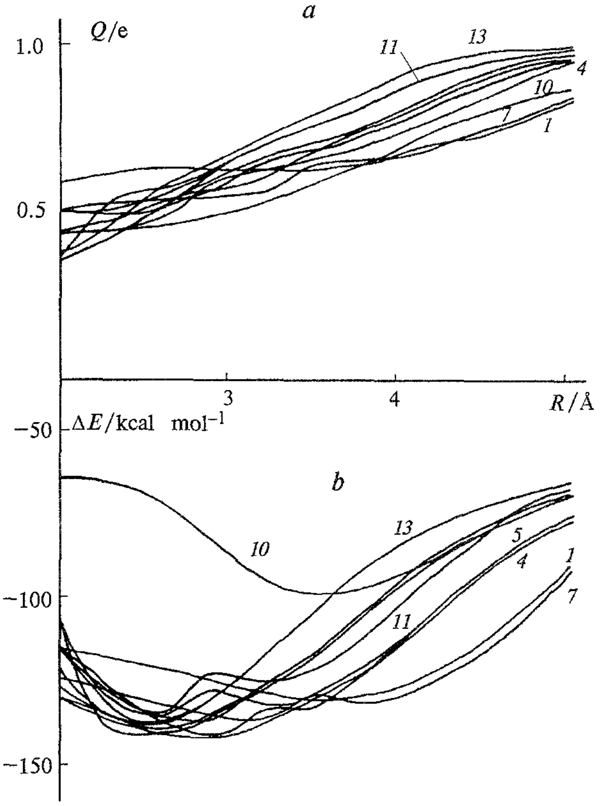


Fig. 1. Results of MNDO calculations for the fragment of the aromatic polyamide: (*a*) charge on the lithium cation; (*b*) binding energy. The numbers at the curves are the ray numbers.

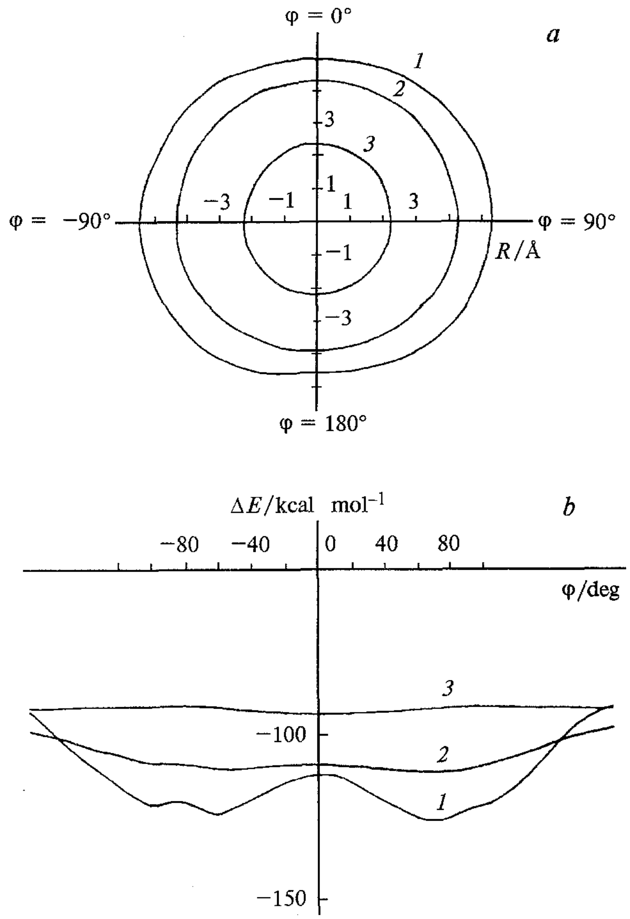


Fig. 2. Sections of the potential energy surfaces in the surroundings of the SO_3 group: (*a*) equipotential lines in the polar coordinates (ΔE = −80 kcal/mol); (*b*) dependences of the energy ΔE on the dihedral angle φ (R_{S-Li} = 4.1 Å); α: (*1*) 90°, (*2*) 120°, and (*3*) 150°.

energy for different angles α and φ were obtained using the interpolation procedure. Figure 2*a* shows equipotential lines in polar coordinates. The distance *R* is plotted on the radius, and the angle φ is used as the polar angle. The three closed curves correspond to different α angles. Deviations from circles indicate that the potential is asymmetric. The maximum deviation occurs at α = 69°. Figure 2*b* gives the dependence of the potential on the dihedral angle φ for three α angles. The largest distortions appear in curve *1* corresponding to the smallest α angle, and the smallest distortions appear in curve *3* corresponding to the largest α angle.

The potential for Li—SO_3 was used in the calculation of the profile of migration of the Li^+ cation in a pore of a polyamide membrane. The pore was modeled by a set of periodically repeated images of the unit cell containing copolymers **A** and **B**. The copolymers were constructed by addition of the lacking atoms with typical bond lengths, angles, and charges corresponding to an infinitely distant cation. The constraint of electric neutrality was imposed on the charges.

The base unit of the polyamide membrane is given in Fig. 3*a*. Figure 3*b* presents the potential profile of the migration of the lithium cation along the polymer. The path of the displacement of the cation was chosen so that it passes as close as possible to the optimum position, but does not intersect the Lennard—Jones spheres of the atoms in the chain. To account for the rigid atomic spheres, the potential was supplemented by the Lennard—Jones term from Ref. 4.

The interaction potential between the lithium cation and the sulfo group was considered within two approximations: atom—atom (curve *2*) with fixed charges (infinitely distant lithium) and with varying charges (curve *1*). At large distances, the two potentials are the same and correspond to the conventional atom—atom approximation. As expected, the interaction between Li and the SO_3 group makes the largest contribution. The two potentials differ only in the vicinity of the sulfo group. When charge redistribution in this region is taken

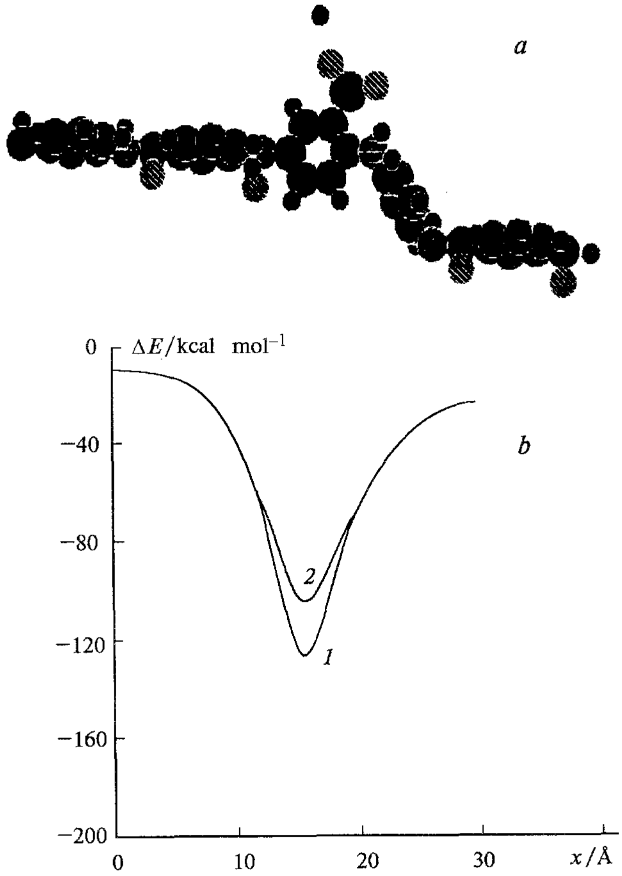


Fig. 3. Potential energy of the migration of the lithium cation in a polyamide membrane (*1*) involving the electrostatic contribution obtained by quantum-chemical calculations and (*2*) within the conventional atom—atom approximation.

into account, the potential minimum becomes deeper by 25 %.

Thus, on the basis of the MNDO quantum-chemical calculations, the three-dimensional potential of the interaction between the Li^+ cation and the atoms of the polyamide membrane, which accounts for the nonadditivity of interparticle interactions, was constructed. This potential was used for the calculation of the profile of migration of Li along the channel of the membrane. It was demonstrated that charge redistribution should be taken into account in the systems containing charged particles.

This work was supported by the Russian Foundation for Basic Research (Project No. 93-03-4205).

References

1. S. F. Timashev, *Fizikokhimiya membrannykh protsessov* [*Physics and Chemistry of Membrane Processes*], Khimiya, Moscow, 1988 (in Russian).
2. Yu. E. Kirsh, I. V. Malkina, Yu. A. Fedotov, N. A. Yanul', S. S. Gitis, S. A. Smirnov, and S. F. Timashev, *Vysokomol. Soedin.*, 1993, **35A**, 320 [*Polym. Sci.*, 1993, **35A**, 360 (Engl. Transl.)].
3. Yu. E. Kirsh and S. F. Timashev, *Zh. Fiz. Khim.*, 1991, **65**, 2469 [*Russ. J. Phys. Chem.*, 1991, **65**, 1304 (Engl. Transl.)].
4. N. F. Vasyutkin and Yu. K. Tovbin, *Vysokomol. Soedin.*, 1993, **35A**, 1600 [*Polym. Sci.*, 1993, **35A**, 1336 (Engl. Transl.)].
5. V. S. Ladygin, Preprint of M. V. Keldysh Institute of Applied Mathematics, Academy of Sciences of USSR, 1991, No. 25.

Received December 7, 1994