Theoretical Study of Lithium-Fluoride and Lithium-Chloride Ion Pairs in Aqueous Solution. An SCF-CNDO/2 Approach Including Continuum Solvent Effects

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Abstract

SCF-CNDO/2 calculations, including solvent effects via an extended version of the Generalized Born Formula (GBF), have been performed for $LiX(H_2O)$ species ($n = 1, 2; X = $ F, Cl). Several minima in the free energy surface, representing intimate and solvent-separated ion pair structures, have been analyzed. Qualitative results show a preferential stabilization of the intimate forms with respect to the solvent-separated ones. The results are discussed on the basis of a convenient partition of the total solute-solvent free energy. The interaction of the ionic species with the bulk solvent neglected in previous studies appears to be responsible for the preferential stability of the intimate forms.

Introduction

The importance of ion pairs in solvolysis and exchange reactions has long been stressed [1–3]. Two kinds of ion pairs have been recognized in Winstein's work: an intimate ion pair, which consists of two ions in contact in the same solvent cage, and a solvent-separated ion pair, consisting of a pair of ions in separate, but adjacent, solvent cages.

From a theoretical point of view, the structure of these species and the strength of their interaction have been studied by analyzing the energy surface using both, semiempirical and ab initio techniques [4–6]. The main concern in these works has been the description of the solvent role in the formation and stability of ion pairs by explicitly considering a number of solvent molecules. However, the well known practical limitations of this "supermolecule" approach suggest the necessity of performing semiempirical SCF calculation including continuum (or continuum + discrete) solvent effects. It is worth emphasizing here that, in the present case, the fact of explicitly considering water molecules allows for inclusion of the active participation of the solvent as a proton relay agent in a proton transfer process.

Previous work in this field has shown the necessity of theoretically characterizing the "desolvation" process, which is the previous (and perhaps the key) step in the dynamics of ion pair formation [7–10]. In the present approach, this desolvation potential has been incorporated by considering the steric hindrance effect to solvation on each atomic center, created by the vicinal atoms in the molecule [11, 12]. As a result,

a desolvation barrier is expected to appear in the reaction path, when the free ions come within an overlapping distance. For instance, we have recently studied the proton transfer equilibria in a chain of water molecules in the presence of a strongly polarizable medium in order to determine the influence of both local and dielectric solvent effects on the relative stability of several types of ion pair structures. The continuum solvent effects have been introduced by using a modified version of the generalized Born formula [11]. In the model used, the electrostatic free energy contains the solute-solvent potential interaction energy, which is consistent with a contribution of the solvation enthalpy, plus the solvent self-energy which represents an entropic contribution $-T\Delta S_s^{el}$, formed by the opposite effects of the orientating electric field and the coupling with the thermostat [11, 12]. The temperature dependence is then introduced through the parameter $\varepsilon(T)$, accounting for the orientation polarization of the bulk solvent.

In this work, we present an analysis of the free energy surface for the interaction of lithium fluoride and lithium chloride ion pairs with one and two water molecules, under the effect of a strongly polarizable medium. Further, we have examined the relative stability between the distinct types of (intimate and solvent-separated) ion pairs present in an aqueous solution of LiF and LiCl.

METHOD OF CALCULATION

Within the continuum approach of solvent effects representation, the total free energy of the solute-solvent system is expressed as

$$A(\varepsilon) = E(1) + \Delta A_S(\varepsilon) \tag{1}$$

where ε is the bulk dielectric constant of the solvent, $E(1)$ is the total energy of the isolated solute, and $\Delta A_S(\varepsilon)$ represents the free energy variations of the solute-solvent system when the solute, in a frozen nuclear and electronic configuration, is isothermically inserted into the solvent. One of the most simple formulations to compute the quantity $\Delta A_S(\varepsilon)$ in molecular systems is the well known GBF [9–12]. In this approach, the solvation energy of any molecular system (ionic or neutral) is built up as a sum of Born-like contributions of each partially charged atomic center. For instance, within a CNDO/2-like approach, it is expressed as a function of the one particle density matrix P, as follows:

$$\Delta A_S(\varepsilon, P) = \frac{1}{2} \sum_A Q_A(P) [V_R(\varepsilon, P)]_A \tag{2}$$

where $Q_A(P) = Z_A - \sum_\nu P_{\nu\nu}$ is the net atomic charge on atom A and $[V_R(\varepsilon, P)]_A$ is the reaction field (RF) potential acting on the atomic center A of the solute. The basic quantity in this formalism is the RF potential which is obtained from a set of polarization charges induced in the dielectric medium [12]. These polarization charges are related to the net atomic charges by the expression

$$Q_A^{pol}(\varepsilon, P) = -\left[1 - \frac{1}{\varepsilon}\right] Q_A(P) \tag{3}$$

The RF potential is then derived from $Q_A^{pol}(\varepsilon, P)$ according to

$$[V_R(\varepsilon, P)]_A = \sum_B Q_B^{pol}(\varepsilon, P)\gamma_{AB} \qquad (4)$$

where γ_{AB} is the Coulomb integral between the atomic centers A and B, representing the solute-solvent interaction [12].

An extension of the GBF has been recently presented [11–13]. The modifications introduced allow the steric hindrance effect upon solvation on each atomic center to be taken into account. The procedure consists of defining an effective polarization charge distribution in the following way:

$$Q_{pol}^i(\varepsilon, P) = -\left(1 - \frac{1}{\varepsilon}\right)[1 - f_B]Q_B(P) \qquad (5)$$

and

$$Q_{pol}^e(\varepsilon, P) = -\left(1 - \frac{1}{\varepsilon}\right)f_B Q_B(P) \qquad (6)$$

where f_B is a parameter characterizing the neighborhood of the center B. The definitions (5) and (6) entail

$$\lim_{\varepsilon \to \infty}[Q_{pol}^i(\varepsilon, P) + Q_{pol}^e(\varepsilon, P) + Q(P)]_A = 0 \qquad (7)$$

so that the electroneutrality of the whole solute is guaranteed.

The RF potential at the center A is now a sum of two terms:

$$[V_R(\varepsilon, P)]_A = [V_R^i(\varepsilon, P)]_A + [V_R^e(\varepsilon, P)]_A = \sum_B [Q_{pol}^i(\varepsilon, P)]_B \gamma_{AB}^i + \sum_B [Q_{pol}^e(\varepsilon, P)]_B \gamma_{AB}^e \qquad (8)$$

where we have introduced the interaction integrals defined by

$$\gamma_{AB}^i = [1 - f_A]\gamma_{AB} \qquad (9)$$

and

$$\gamma_{AB}^e = f_A \gamma_{AB} \qquad (10)$$

The electrostatic solute-solvent interaction energy may be written as

$$E_{\Sigma-S}(\varepsilon, P) = \sum_A Q_A(P)[V_R^i(\varepsilon, P) + V_R^e(\varepsilon, P)]_A \qquad (11)$$

and consequently, the free energy of solvation $\Delta A_S(\varepsilon, P)$, is given by

$$\Delta A_S(\varepsilon, P) = -\frac{1}{2}\left[1 - \frac{1}{\varepsilon}\right]\sum_A \sum_B Q_A(P)Q_B(P)[1 - (f_A + f_B - 2f_A f_B)]\gamma_{AB} \qquad (12)$$

A convenient (empirical) choice for f_B is the following [11]

$$f_B = \frac{1}{2} \sum_{A \neq B} S_{AB} \tag{13}$$

where S_{AB} is the overlap integral between the $2S$ atomic orbitals of the centers A and B ($1S$ orbital in the case of hydrogen). As a result, Eq. (12) may be rewritten as

$$\Delta A_S(\varepsilon, P) = -\frac{1}{2}\left(1 - \frac{1}{\varepsilon}\right) \sum_A \sum_B Q_A(P) Q_B(P) [1 - F_{AB}(S)] \gamma_{AB} \tag{14}$$

with $F_{AB}(S)$, a function depending only on the overlap S_{AB} matrix. It immediately follows that Eq. (14) contains a first term which is the GBF and a corrective term depending on the neighborhood factors. If we assume that $f_B \leqq 1$, $\forall_B$, we obtain $F_{AB}(S) \geqq 0$ and as a result, the corrective term displays an opposite sign to that of the standard GBF: it may be interpreted as a desolvation contribution:

$$\Delta A_{\text{desol}}(\varepsilon, P) = -\frac{1}{2}\left(1 - \frac{1}{\varepsilon}\right) \sum_A \sum_B Q_A(P) Q_B(P) F_{AB}(S) \gamma_{AB} \tag{15}$$

As expected, this desolvation term disappears when the distance between the atomic centers involved becomes larger than the overlapping ones (i.e., when $f_B = 0$, $\forall_B$). It is interesting to note that from Eqs. (9), (10), and (13) we obtain:

$$\gamma_{AB}^i \geqslant \gamma_{AB}^e \tag{16}$$

which implies that $[Q_{\text{pol}}^i(P)]_B$ is closer to the B center than $[Q_{\text{pol}}^e(P)]_B$. In other words, $[Q_{\text{pol}}^i(P)]_B$ may be considered as an "internal" charge polarization where $[Q_{\text{pol}}^e(P)]_B$ is an "external" one. We then may conclude that the desolvation process appears to be the consequence of a polarization charge transfer from the integral region of the solvent towards the bulk region [12].

Finally, the effective Fock operator compatible with the solvation free energy given by Eq. (14) is obtained from [12]

$$\hat{F}(\varepsilon, P) = \hat{F}(1, P) + \frac{1}{2}\left[\frac{\partial E_{\Sigma - s}}{\partial P}\right] = \hat{F}(1, P) - \hat{V}_R(\varepsilon, P) \tag{17}$$

where $\hat{F}(1, P)$ is the Frock operator of the isolated solute and

$$\hat{V}_R(\varepsilon, P) = -\left[\sum_A Z_S \left(\frac{\partial V_R}{\partial P}\right)_A - \text{Tr}\, P\left(\frac{\partial V_R}{\partial P}\right)_A\right] \tag{18}$$

with $V_R(\varepsilon, P)$ given by Eq. (8).

Results and Discussion

We have studied the energetics of several types of Li-F and Li-Cl ion pairs in water, in order to investigate both the specific interaction with one and two water molecules and the effect of the bulk solvent regarded as a continuum. Following the nomenclature used by Gupta and Rao [14], three types of ion pairs structures have been considered: (a) the hydrated cage pairs (or intimate ion pair) $H_2O \ldots Li^+\text{-}F^-$

and $H_2O \ldots Li^+-Cl^-$; (b) the extended-cage pair (or one-solvent separated ion pair) $F^- \ldots H_2O \ldots Li^+$ and $Cl^- \ldots H_2O \ldots Li^+$; and (c) the two-solvent-separated ion pair $F^- \ldots H_2O \ldots H_2O \ldots Li^+$ and $Cl^- \ldots H_2O \ldots H_2O \ldots Li^+$. In the first case, based on a previous study [14], and considering the well known preferential ability of cations (compared to anions) to bind water molecules [15, 16], the structures dentated to anion (i.e., $H_2O \ldots F^- - Li^+$ and $H_2O \ldots Cl^- - Li^+$), have been neglected. The preferential hydration in solution of cations compared to anions has also been confirmed, for both LiF and LiCl, by the RF calculations: for LiF, the hydration energy difference is about 35 Kcal/mol in favor of the structure associated to the cation whereas for LiCl, a hydration energy difference of about 40 Kcal/mol is obtained. The one and two-solvent-separated ion pair structures were generated by transferring all the intervening protons in a planar molecular arrangement, according to Figure 1. The geometries with their corresponding geometrical parameters are also displayed in Figure 1. The choice of these geometries is based on previous studies concerning hydrogen bond on closely related molecular systems. For instance, ab initio calculations on $(FHOH)^-$ ion reported by Diercksen and Kraemer [17] suggested that a linear hydrogen bonded structure was the most stable one. CNDO/2 calculations performed on several hydrogen bonded systems by Schuster [18] also showed that the shape of the potential curves is not appreciably affected by a mode-rate change of the fixed geometrical quantities. These previous results suggest that calculations on different hydrogen bonded systems, using standard geometries, may be successfully compared without approaching the absolute minimum of the energy surface. In order to represent in the simplest way the proton potential curves (PPC), we have defined the reduced coordinate $Z = r_{O-H'}-(1/2)R_{AB}$, where $r_{O-H'}$ is the distance between the donor and the atom and the proton, and R_{AB} is
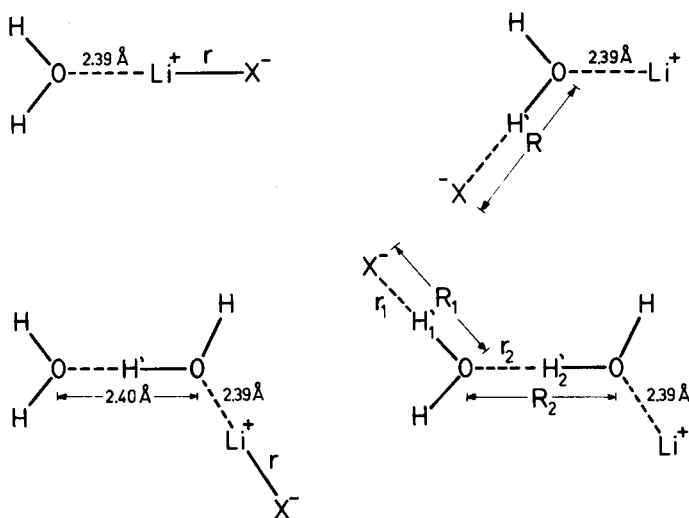

Figure 1. Structure and geometrical parameters for the proton transfer in the processes under study

the distance between the donor and acceptor atoms. Once the PPCs were constructed, the reaction path was defined as the trajectory passing through the minima of the PPC at different intermolecular distances.

In the case of the intimate ion pair structures, an equilibrium distance $R_{O-Li} = 2.39$ Å was found for both Li-F and LiCl complexes. The equilibrium r_{Li-F} and r_{Li-Cl} distances were 2.50 and 2.60 Å, respectively.

The reaction path for the proton transfer process involving one water molecule is shown in Figure 2. In the case of LiCl, an "extended-cage" pair structure $Cl^- \ldots H_2O\text{-}Li^+$, characterized by the distances $R_{O-Cl} = 3.6$ Å and $r_{O-Li} = 2.4$ Å, appears greatly stabilized with respect to the solvated species LiCl and H_2O. This may probably be due to the poor ability of Cl^- to bind a proton in aqueous solution (i.e., probably due to the strong acid character of HCl in water).

In the case of LiF, a very different picture is obtained. An intimate ion pair structure $Li^+\text{-}OH^- \ldots HF$, corresponding to a H-bonded complex appears to be in equilibrium with the corresponding solvated species HF, Li^+, and OH^-. This complex has not been considered in the previous studies by Gupta and Rao [14] and Bertrán and Revetllat [19]. If we consider the fact that these authors have neglected dielectric af-
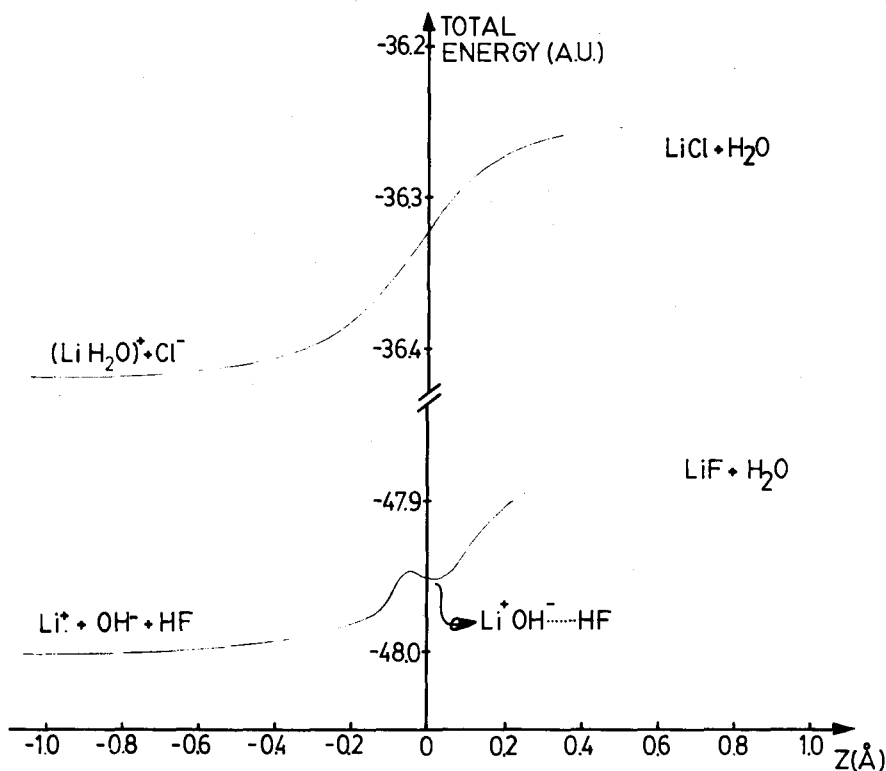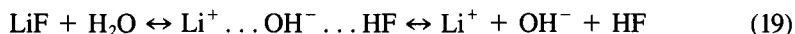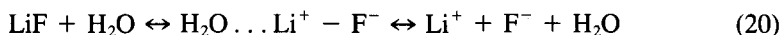

Figure 2. Reaction path profile for the proton transfer in the system $H_2O \ldots LiX$ ($X = F, Cl$). $\varepsilon = 78.5$.

fects, it could be probable that the stabilization of such a complex mainly arises from its interaction with the bulk solvent. It is also interesting to notice, from Figure 2, that when the solvated species Li^+-OH^- and HF become within an overlapping distance, a desolvation barrier of about 10.6 Kcal/mol appears in the reaction path at a distance $R_{O-F} \simeq 3.0$ Å. Further, in connection with this problem, we may speculate that a probable mechanism for the dissociation of LiF in water could be written as:

$$LiF + H_2O \leftrightarrow Li^+ \ldots OH^- \ldots HF \leftrightarrow Li^+ + OH^- + HF \qquad (19)$$

instead of

$$LiF + H_2O \leftrightarrow H_2O \ldots Li^+ - F^- \leftrightarrow Li^+ + F^- + H_2O \qquad (20)$$

as recently proposed [19]. Also, mechanism (19) is more consistent with the well-known weak acid behavior of HF in water. On the contrary, the formation of such a complex in the case of LiCl, appears to be highly improbable due to the strong acidity displayed by HCl in water.

The reaction path for the proton transfer process involving two water molecules is shown in Figure 3. Again, in the case of Li-Cl, a solvent separated ion pair structure: $Cl^- \ldots (H_2O)_2 \ldots Li^+$, characterized by the distances $R_{O-O'} = 2.40$ Å and $R_{O-Cl} \simeq 4.90$ Å appears greatly stabilized with respect to the solvated species Cl^-, Li^+ and $2(H_2O)$. However, when this structure is compared with the intimate ion pair structure $(H_2O)_2 \ldots Li^+ \ldots Cl^-$, a significant stabilization energy is observed in favor of the latter. It is important to stress here that the relative stabilization energies appear systematically overestimated. This is a well known shortcoming of the CNDO/2 procedure [14]. However, for the purpose of *qualitatively* comparing the chemical behavior of LiF and LiCl in water in the H-bond region, the results obtained allow us to describe the gross features that discriminate between the stabilization of the different chemical species in solution. It should be stressed that the dissociation step itself and the proton potential curves, especially in the region of free ions, cannot be fully described in quantitative terms by these kind of SCF calculations.

In the case of LiF, the effect of a second water molecule entails the stabilization of a solvent-separated $FH \ldots (H_2O)) \ldots OH^-$-$Li^+$ ion pair. By comparing Figures 2 and 3, it may be seen that the second water molecule also confers a more ionic character to the H-bonded complex.

Finally, in order to discuss the relative stability of the different ion pair structures found, we propose to analyze the different contributions to the total solute-solvent free energy by using the partition of the total energy proposed by Constanciel [20] and applied in a previous study by us [11]:

$$A(\varepsilon, P) = \text{Tr} P \overline{H}(P) + \frac{1}{2} \sum_A \sum_B Q_A(P) Q_B(P) \gamma_{AB}$$

$$+ \frac{1}{2} \sum_A \sum_B Z_A Z_B (\Gamma_{AB} - \gamma_{AB}) \qquad (21)$$

In this expression, the first term represents an effective electronic energy in the strongly polarizable medium approximation [11, 19]; the second term is a net charge
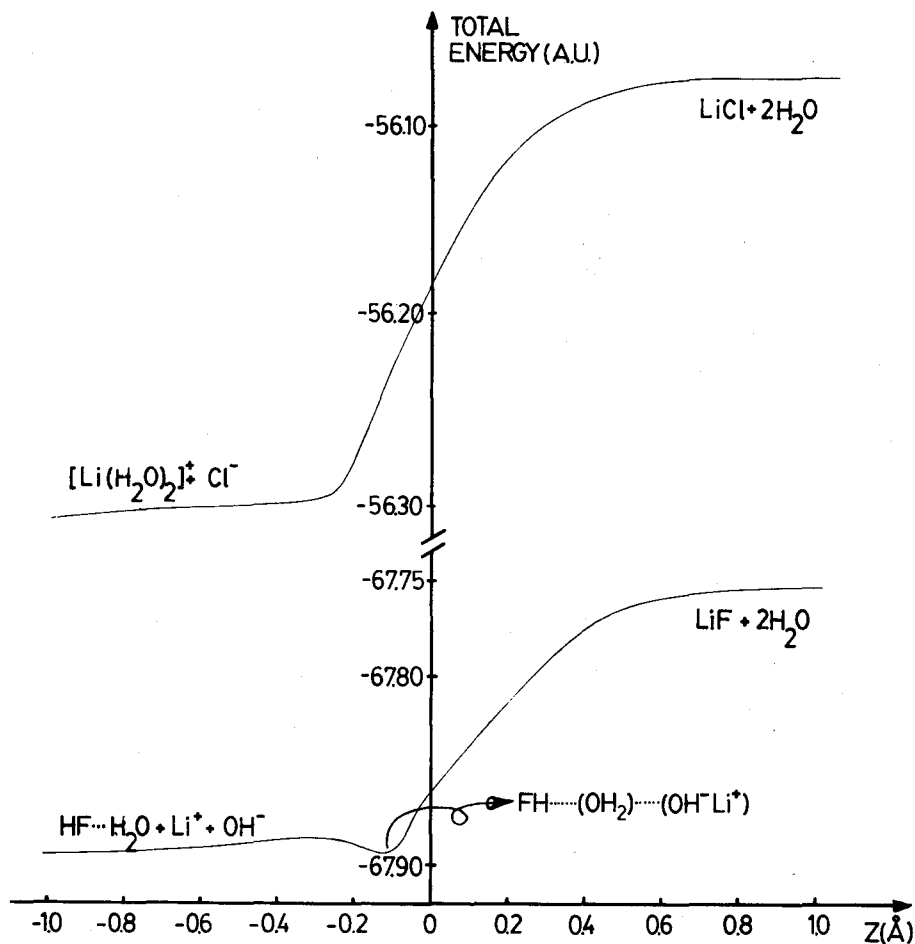
Figure 3. Reaction path profile for the proton transfer in the system $(H_2O)_2 \ldots LiX$
$(X = F, Cl)$. $\varepsilon = 78.5$

interaction term (which vanishes for $\varepsilon \to \infty$); and the third one represents a steric hindrance destabilizing contribution. The results are displayed in Table I.

It may be observed (in the case of LiF) that the preferential stability of the intimate ion pair structures arises mainly from the electronic contribution to the total solute-solvent free energy. The contribution coming from the steric hindrance effect displays the opposite trend, but it is not strong enough to produce the inversion of the observed order.

From these considerations, we may conclude that the stabilization of the intimate forms is related to the polarization charge distribution created in both cases: for the solvent-separated ion pair structure, the internal water molecules induce a weak polarization of the medium while for the intimate structure, a stronger reaction field potential is generated on each atomic center.

TABLE I. Relevant contributions to the total solute-solvent free energy (a.u.).

Complex	Total energy	Electronic effective energy	Steric hindrance term
$H_2O \ldots Li^+ \ldots F^-$	−47.9938	−48.2805	0.2867
$FH \ldots OH^- \ldots Li^+$	−47.9377	−48.1017	0.1640
$H_2O \ldots Li^+ \ldots Cl^-$	−36.4788	−36.5597	0.0809
$Cl^- \ldots (H_2O) \ldots Li^+$	−36.4172	−36.6475	0.2303
$(H_2O)_2 \ldots Li^+ \ldots F^-$	−67.9387	−68.3470	0.4083
$FH \ldots H_2O \ldots OH^- \ldots Li^+$	−67.8988	−68.2021	0.3033
$(H_2O)_2 \ldots Li^+ \ldots Cl^-$	−56.4086	−56.5273	0.1187
$Cl^- \ldots (H_2O)_2 \ldots Li^+$	−56.0775	−56.2109	0.1334

As a result, the solvation energy of the intimate structures becomes greater than the corresponding solvent-separated one. These conclusions are consistent with the previous ones obtained in the study of water polymers [11].

For LiCl, when one water molecule is considered, it may be observed that the preferential stabilization of the intimate structure is governed by the steric hindrance contribution, since the electronic energy displays an opposite trend (see Table I). The inversion of the steric hindrance effect, in passing from LiF to LiCl, could be related to the differences in the ionic radii of F^- and Cl^-.

Concluding Remarks

We have analyzed the relative stability of a series of ion pair structures present in aqueous solutions of LiF and LiCl. The partition of the total solute-solvent free energy allowed us to recognize relevant contributions governing the equilibria between the different species in solution. In all of the cases examined, the intimate ion pair structures were found to be more stable than the corresponding solvent-separated ones.

These results are in opposition with those recently reported for LiF in water [19]. As a general conclusion, we suggest that the interaction of the ionic species with the bulk solvent may be responsible for the preferential stability of the intimate forms. Finally, it has been shown that in the present case, the solvent participates not only as a stabilizer agent, but mainly as an active reagent where the principal role is the proton transfer relay in a proton transfer reaction: the differences between the chemical behavior of LiF and LiCl in water appears to be governed by their different acid-base equilibria in aqueous solution.

Acknowledgments

Bibliography

[1] W. Winstein and R. G. Robinson, J. Am. Chem. Soc. **80**, 169 (1958).

[2] J. D. Simon and K. S. Peters, J. Am. Chem. Soc.**104**, 6542 (1982).

[3] C. Decoret, J. Royer, and J. J. Dannenberg, J. Org. Chem. **46**, 4074 (1981).

[4] P. Cremaschi, A. Gamba, and M. Simonetta, J. Chem. Soc., Perkin Trans. II 162 (1977).

[5] A. Gamba, M. Simonetta, G. Suffritti, I. Szele, and H. Zollinger, J. Chem. Soc., Perkin Trans. II 493 (1980).

[6] A. Bongini, G. Cainelli, G. Cardillo, P. Palmieri, and A. Umani-Ronchi, J. Organometal. Chem. **110**, 1 (1976).

[7] E. Grunwald, Anal. Chem. **26**, 1696 (1954).

[8] J. T. Denison and J. B. Ramsey, J. Am. Chem. Soc. **77**, 2615 (1955).

[9] G. Klopman and P. Andreozzi, Theor. Chim. Acta (Berlin) **55**, 77 (1980).

[10] R. Constanciel and R. Contreras, C. R. Acad. Sci. (Paris) **296**, 417 (1983).

[11] R. Contreras and J. S. Gómez-Jeria, J. Phys. Chem.**88**, 1905 (1984).

[12] R. Constanciel and R. Contreras, Theor. Chem. Acta (Berlin) **65**, 1 (1984).

[13] R. Contreras and A. Aizman, Int. J. Quant. Chem.**27**, 293 (1985).

[14] A. Gupta and C. N. Rao, J. Phys. Chem. **77**, 2888 (1973).

[15] R. M. Noyes, J. Am. Chem. Soc. **84**, 513 (1962).

[16] R. H. Stokes, J. Am. Chem. Soc. **86**, 979 (1964).

[17] G. H. F. Diercksen and W. P. Kraemer, Chem. Phys. Lett. **5**, 570 (1970).

[18] P. Schuster, Int. J. Quant. Chem. **3**, 851 (1969).

[19] J. A. Revetllat and J. Bertrán, Gazz. Chim. Ital.**108**, 149 (1978).

[20] R. Constanciel, Theor. Chim. Acta (Berlin) **54**, 123 (1980).