Theor Chim Acta (1992) 82: 435–457

Theoretica Chimica Acta

Theoretical study of the association of glycine molecules on ionic crystals NaCl, KI, LiF in aqueous solution

Application to the modification of growth habit

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Received August 13, 1990/Accepted October 22, 1991

Summary. The adsorption of glycine on different crystals (namely NaCl, KI, LiF) is studied in an isolated state and in water by methods of theoretical chemistry in view of determining the preferential adsorption sites, the modifications of adsorbing crystal properties, and the role played by the electronic structure of the adsorbed molecule, by the solvent and by the parametric concordance on various sites of the structure.

Key words: Glycine adsorption – NaCl – KI – LiF

1. Introduction

It is well known [1] that crystals growing in the presence of some foreign substances can exhibit a growth habit which is different from the equilibrium form. For instance, phenomenologic or thermodynamic studies of the crystallization of NaCl in the presence of glycine, and in aqueous solution, shows that it is possible to change progressively the habit (100) of NaCl to habit (110) when the percentage of glycine increases [2, 3]. A study of this phenomenon as a function of pH shows that the effect is maximal in the vicinity of the isoelectric point ($pH = 5.7$), i.e., when glycine molecules are exclusively zwitterionic ($H_3N^+{-}CH_2{-}COO^-$). Thus, the authors of Refs. [2, 3] conclude that this ion is essentially responsible for the habit modification.

Moreover, the good fit between the cell parameter of NaCl and that of glycine crystal (CO = 5.465 Å) has been referred to [4] in order to elucidate the fixation of these ions on the lattice: Effectively, if glycine yields to the appearance of the form (110) on NaCl crystal, conversely, NaCl yields to the appearance of the form (100) on glycine crystal. However, in such an adsorption there is a great number of unoccupied sites close to face (110) of NaCl (see Fig. 1); thus this mechanism is not very probable.

In order to explain the appearance of (110) faces the authors of Refs. [2, 3] concluded that glycine chains necessarily must be formed along the (100) edges of the ⟨110⟩ faces. The unceasingly renewed adsorption along these steps would provoke the gradual disappearance of ⟨100⟩ faces.

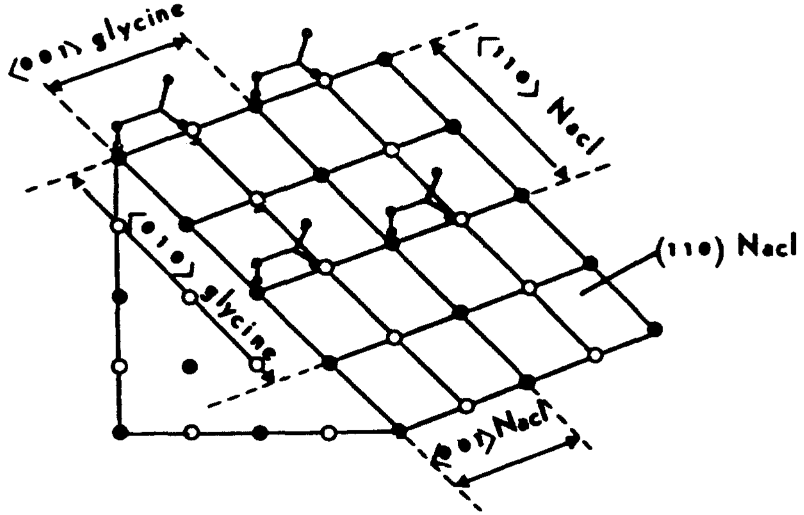


Fig. 1. Adsorption of glycine as it proceeds from epitaxial relations between {110} of crystal NaCl and {100} of glycine

Our study is aimed at determining the role played by the electronic structure of the adsorbed molecule, and that played by the parametric concordance, on various sites of the structure. Thus, in order to determine the factors which play a prevailing role in this phenomenon, it appeared to be of great interest to examine very carefully the energies at work in the NaCl crystallization process, in water, in the presence of glycine.

Previous calculations [5] have been done first in an isolated state (without water), then simulating the solvent by some discrete water molecules. The purpose of this work is to take the solvent into account with a more elaborate method in order to get both qualitative and quantitative results, but also to show that such a treatment of the problem is valid and even allows us to obtain additional information with regard to conventional approaches.

2. Method

The complete treatment of adsorption of glycine zwitterion on M^+X^- crystal where M^+ stands for the cation (Li^+, Na^+, K^+) and X^- for the anion (F^-, Cl^-, I^-), in *sursatured* water solution, is based upon the thermodynamic diagram described in Fig. 2.

Therefore the calculation will include the following stages:

- the calculation of the adsorption energy of an isolated molecule on the crystal surface (ΔE_{ads}) and of the glycine dimerization energy (ΔE_{di}),
- the calculation of the solvation internal energy (ΔE_{solv}), which includes, for instance, the desolvations of glycine and crystal MX.

Thus, the total adsorption reaction in liquid water phase:

$$[MX]_l + [\mathrm{gly}(\mathit{trans})]_l \rightarrow [MX \cdots \mathrm{gly\ II}]_l \qquad \Delta E_{tot} \tag{1}$$

may be decomposed into several steps:

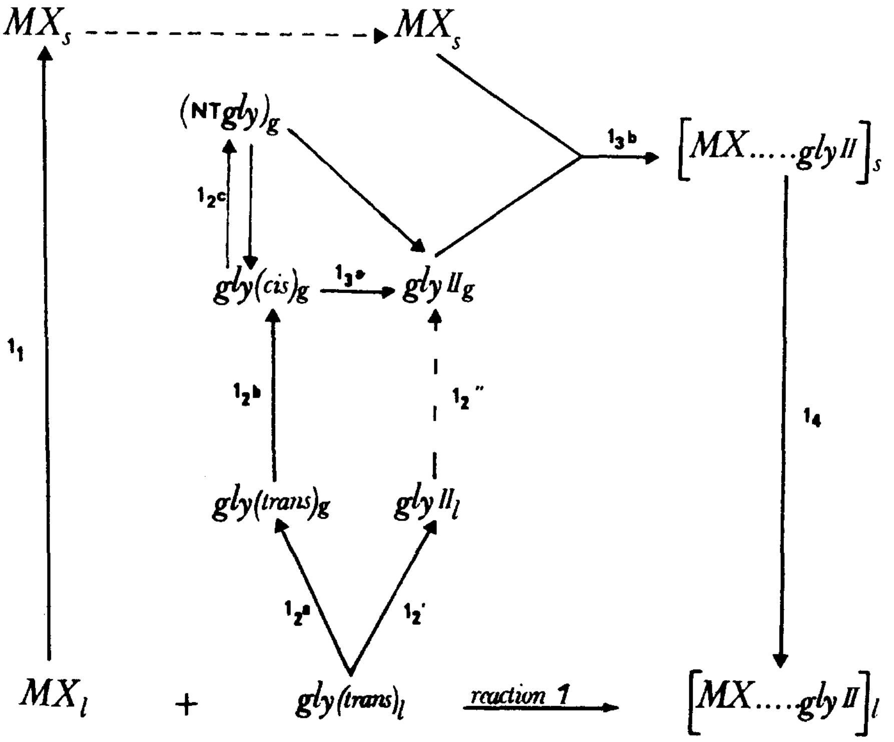


Fig. 2. Thermodynamic scheme for association of glycine zwitterion in various conformations: gly(*cis*), gly(*trans*), and gly II, on MX crystal (M standing for the cation and X for the anion). Subscripts *s*, *l*, and *g* indicate solid, liquid, and gas phase, respectively

2.1. Crystal desolvation

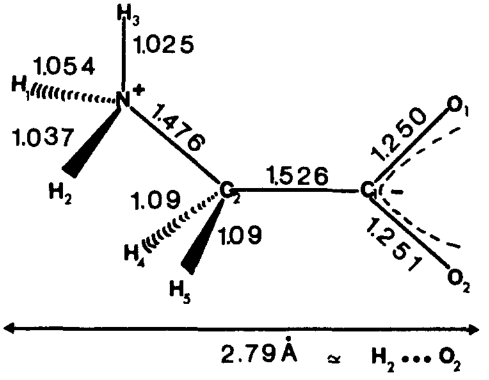
$$\mathrm{MX}_l \rightarrow \mathrm{MX}_s \qquad -\Delta E_{\mathrm{solv}}(\mathrm{MX}) \tag{1_1}$$

2.2. Glycine solvation

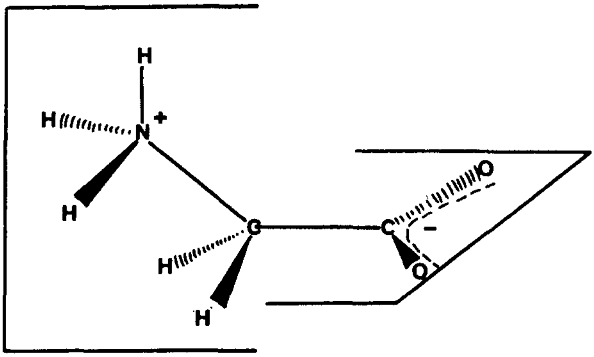
From a strict point of view, concerning the solvation of glycine, one has to consider that the most stable form of glycine is the neutral one ($H_2N{-}CH_2{-}COOH$) in gas phase, and the zwitterion form ($H_3N^+{-}CH_2{-}COO^-$) in water solution at pH = 5.7. Furthermore, the zwitterion form may assume several conformations: *cis* (0, 0) which is the most stable one when isolated (Fig. 3, geometry I), and *trans* (60, 0) which is the most stable one in water (in this geometry, the hydrogens of NH_3^+ group are rotated by 60° with regard to the (0, 0) geometry). (In the notation (φ, ψ), φ indicates rotation along the $C_2{-}N_1$ bond, and ψ along the $C_1{-}C_2$ bond.)

Thus, the total solvation internal energy of glycine:

$$[\mathrm{gly}(\mathit{trans})]_l \rightarrow [NT\,\mathrm{gly}]_g \qquad \Delta E_{\mathrm{solv}}(\mathrm{gly}) \tag{1_2}$$



Geometry I



Geometry II

Fig. 3. Two different geometries of glycine zwitterion. Geometry I concerns two possible conformations: *cis* (0, 0) and *trans* (60, 0) but geometry II refers to only one *twisted* (0, 90) conformation. In the notation (φ, ψ), φ indicates rotation along C_2–N_1 bond, and ψ along C_1–C_2 bond

may be decomposed into the following steps:

$$[\mathrm{gly}(\mathit{trans})]_l \rightarrow [\mathrm{gly}(\mathit{trans})]_g \qquad -\Delta E_{\mathrm{solv}}[\mathrm{gly}(\mathit{trans})] \qquad (1_2\mathrm{a})$$

$$[\mathrm{gly}(\mathit{trans})]_g \rightarrow [\mathrm{gly}(\mathit{cis})]_g \qquad \Delta E(\mathit{trans} \rightarrow \mathit{cis}) \qquad (1_2\mathrm{b})$$

$$[\mathrm{gly}(\mathit{cis})]_g \rightarrow [NT\ \mathrm{gly}]_g \qquad \Delta E_{\mathrm{PT}} \qquad (1_2\mathrm{c})$$

Since we are interested in the adsorption of glycine zwitterion on different MX crystals, we do not have to consider Eq. (1_2c); thus we do not calculate the proton transfer energy (ΔE_{PT}), as the diagram of Fig. 2 clearly shows.

2.3. Adsorption of glycine zwitterion on MX *crystal*

According to the results obtained by Julg et al. [5], the conformation adopted by glycine zwitterion during the adsorption on MX crystals (the *twisted* one (0, 90), denoted geometry II in Fig. 3) is characterized by a 90° rotation of the NH_3

group around the C_3-C_4 axis. Thus, the adsorption reaction of glycine zwitterion on MX crystal:

$$(\mathrm{MX})_s + [\mathrm{gly}(cis)]_g \rightarrow [\mathrm{MX} \cdots \mathrm{gly\ II}]_s \tag{1_3}$$

may be decomposed into:

$$[\mathrm{gly}(cis)]_g \rightarrow (\mathrm{gly\ II})_g \qquad \Delta Ecis \rightarrow \mathrm{II} \tag{1_3a}$$

$$(\mathrm{MX})_s + (\mathrm{gly\ II})_g \rightarrow [\mathrm{MX} \cdots \mathrm{gly\ II}]_s \qquad \Delta E_{\mathrm{ads}} \tag{1_3b}$$

2.4. Solvation of [MX · · · gly II] *complex*

This part of the energy refers to the reaction:

$$[\mathrm{MX} \cdots \mathrm{gly\ II}]_s \rightarrow [\mathrm{MX} \cdots \mathrm{gly\ II}]_l \qquad \Delta E_{\mathrm{solv}}[\mathrm{MX} \cdots \mathrm{gly\ II}] \tag{1_4}$$

In order to evaluate the total internal energy, ΔE_{tot}, of Eq. (1), we must take all preceding energies into account. Thus, this term may be written as follows:

$$\Delta E_{\mathrm{tot}} = -\Delta E_{\mathrm{solv}}(\mathrm{MX}) - \Delta E_{\mathrm{solv}}[\mathrm{gly}(trans)] + \Delta E_{trans \rightarrow cis} + \Delta E_{cis \rightarrow \mathrm{II}} + \Delta E_{\mathrm{ads}} + \Delta E_{\mathrm{solv}}[\mathrm{MX} \cdots \mathrm{gly\ II}] \tag{2}$$

If we call Δ the sum of internal energies due to solvation and conformation changes of glycine, namely:

$$\Delta = -\Delta E_{\mathrm{solv}}[\mathrm{gly}(trans)] + \Delta E_{trans \rightarrow cis} + \Delta E_{cis \rightarrow \mathrm{II}} \tag{3}$$

we get the total energy of Eq. (1):

$$\Delta E_{\mathrm{tot}} = -\Delta E_{\mathrm{solv}}(\mathrm{MX}) + \Delta + \Delta E_{\mathrm{ads}} + \Delta E_{\mathrm{solv}}[\mathrm{MX} \cdots \mathrm{gly\ II}] \tag{4}$$

From a preliminary study, the value of Δ has been calculated as 68.64 kcal/mol. (For more details about these results see Appendix I.)

But we may also notice in the diagram shown by Fig. 2 that the energies of Eqs. $(1_2\mathrm{a}) + (1_2\mathrm{b}) + (1_3\mathrm{a})$ and $(1_{2'}) + (1_{2''})$ are equivalent. The hypothetical presence of twisted zwitterion (gly II) in liquid water proceeds from resutls we have obtained when calculating the solvation energy of the three conformations of glycine zwitterion: the energy difference between *trans* and *twisted* conformation, in water, has been evaluated as 0.90 kcal/mol (see Table 8 of Appendix I). It will be noted that this result is in good agreement with calculations of Forner et al. [6], who have also shown the presence of a *twisted* conformation of glycine zwitterion, in water.

As we have explained above, in a second part of this work we studied the adsorption of glycine zwitterion dimer on different MX crystals; in this case the total energy given by Eq. (4) becomes:

$$\Delta E_{\mathrm{tot}} = -\Delta E_{\mathrm{solv}}(\mathrm{MX}) + 2\Delta + 2\Delta E_{\mathrm{ads}} + \Delta E_{\mathrm{di}} + \Delta E_{\mathrm{solv}}[\mathrm{MX} \cdots (\mathrm{gly\ II})_2] \tag{5}$$

and refers to the following reaction:

$$\mathrm{MX} + 2\ \mathrm{gly}(trans) \leftrightarrows [\mathrm{MX} \cdots (\mathrm{gly\ II})_2] \tag{6}$$

2.5. Calculation procedures of involved energies

The direct treatment of the (molecule + solvent + crystal) system is, of course, impossible to perform. So the treatment of our problem necessitates first the simulation of the ionic crystal, then a choice of an adequate method for the calculation of adsorption, solvation, and dimerization energies.

2.5.1. Simulation of an ionic crystal. It has been shown [7] that the electric potential created at any point of the surface of infinite ionic crystal may be calculated, in a satisfying way, when the infinite crystal is simulated by a finite number of point charges located at the sites of the ions in the natural crystal (for instance, cube for NaCl crystal). A recent study [8] concerning the simulation of the actual structure by these point charges proves the validity of the procedure: the authors discuss the convergence of the potential and that of the electric field versus the size of crystal. It appears that limitation of point charges to a few hundred leads to a very low error of the electrostatic potential (5×10^{-8} u.a.).

In this work, three different adsorption sites have been considered, namely: the ideal plane (100), the double step $(110)_2$, and the kink $(111)_2$. Figure 4 gives a schematic representation of the active part in adsorption for these three sites. According to results obtained by the author of [9], these three sites have been simulated by: 196, 238, and 244 point charges for the ideal plane, the double step, and the kink, respectively.

It may be now noted that our first approximation in the simulation of crystal concerns the finite size of the crystal, but as a second approximation, we have neglected the relaxation of the ions located at the crystal surface. Various experimental [10] and theoretical [11] treatments seem to corroborate this approximation. For instance, the authors of [11] have constructed models which clearly show that non-symmetrical structures (relaxed ones) are changed into symmetrical structures upon adsorption on the crystal surface.

So, in short, in this work the infinite MX crystal is simulated by a rigid structure of finite size, and we do not take the relaxation of superficial ions into account.

Following [12] the distances between nearest neighbors used for the selected ionic crystals are:

$$d(\mathrm{NaCl}) = 2.814\ \text{Å}; \qquad d(\mathrm{KI}) = 3.526\ \text{Å}; \qquad d(\mathrm{LiF}) = 2.01\ \text{Å}$$

2.5.2. Adsorption energy. In order to evaluate the energies of various forms, isolated or adsorbed on the crystal, we have used the values calculated by Julg et al. [5], within a methodology summarized as follows.

Simulating a crystal by a finite number of point charges (as defined in Sect. 2.5.1), the adsorption energy (ΔE_{SCF}) is determined as the difference between the energy of an isolated molecule adsorbed on an ad-site of a crystal surface (E_1), and that of a molecule far away from the surface (E_∞).

$$\Delta E_{\mathrm{SCF}} = E_1 - E_\infty \tag{7}$$

ΔE_{SCF} thus calculated represents the fixation energy of glycine on a lattice of point charges and does not take into account the fact that, in reality, the crystal is built up on finite size and polarizable ions. Consequently, the dispersion-repulsion energy E_{DR} has to be added to ΔE_{SCF} of Eq. (7). According to [5] we have used a semiempirical Lennard-Jones potential in order to evaluate this dispersion-repulsion term.

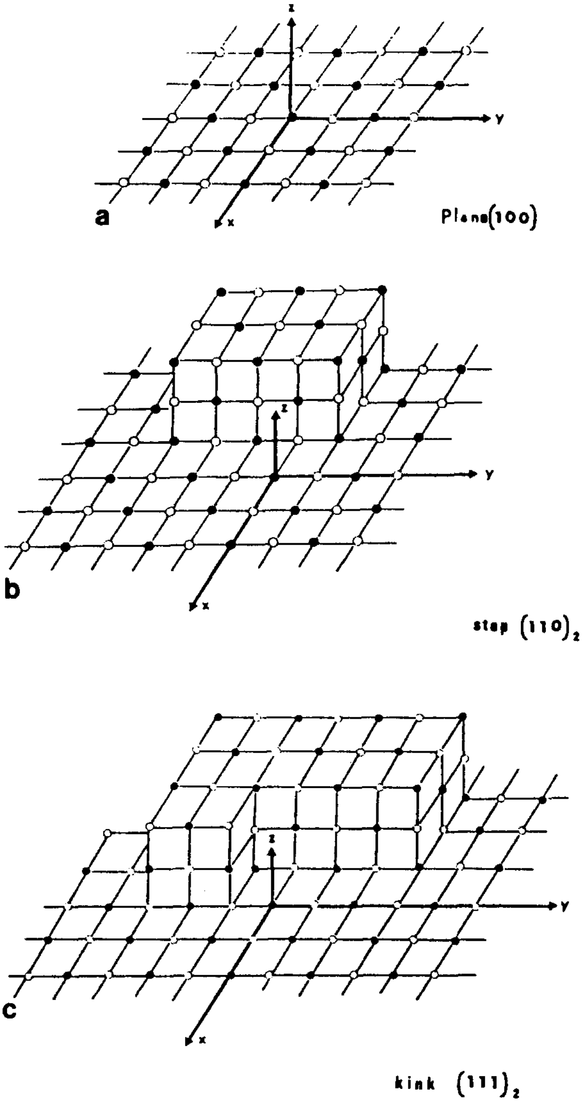


Fig. 4a–c. Orientation used in ad-site (**a**) (100) (**b**) $(110)_2$ (**c**) $(111)_2$

At last, it will be noted, that in these calculations, the possible change of glycine geometry upon the effect of electrostatic field created by the ionic crystal has not been taken into account. Since, some theoretical works [13] have shown that an electric field of 5×10^{10} V/m (0.1 u.a.) changes bond lengths of adsorbate by no more than 0.01 Å, however, the electric field created in the vicinity of NaCl surface does not exceed 10^{10} V/m [9]. So, we have assumed that the adsorbed molecules keep the same geometry as in the isolated state (I or II of Fig. 3).

2.5.3. Glycine dimerization energy (ΔE_{di}). This term, ΔE_{di}, has been calculated in the framework of the *ab-initio* SCF supermolecule model:

$$\Delta E_{\mathrm{di}}^{\mathrm{SCF}} = E_{\mathrm{di}}^{\mathrm{SCF}} - 2E_{\mathrm{m}}^{\mathrm{SCF}} \tag{8}$$

with subscripts *di* and *m* standing for dimer and monomer, respectively.

Furthermore, in order to take correlation effects into account, the dispersion energy ΔE^D (evaluated with Lennard-Jones semiempirical potential) has been added to the term $\Delta E_{\mathrm{di}}^{\mathrm{SCF}}$.

The SCF calculations have been performed within a minimal basis set adapted for interaction energy calculations [14]. We have verified that enlarging this basis set by polarization orbitals (*d* on heavy atoms and *p* on hydrogen atoms) and by diffuse orbitals on anionic oxygens has a very small effect on the quantitative results.

In fact, the results obtained within the minimal and the 6-31G basis set are not very different (all the results are collected in Table 1). Thus, since multipoles used for calculations of ΔE_{solv} (see Sect. 2.2) proceed from this adapted minimal basis, we will also use values of $\Delta E_{\mathrm{di}}^{\mathrm{SCF}}$ obtained within this basis.

Table 1. Glycine SCF. Dimerization energy calculated for two intermolecular distances R_1 and R_2 within different basis set: SZ1(STO-6G), SZ2 (minimal 'adapted basis'), DZ(6-31G)

Basis set	$\Delta_{\mathrm{di}}^{\mathrm{SCF}}(R_1)$	$\Delta_{\mathrm{di}}^{\mathrm{SCF}}(R_2)$
SZ1	−26.59	−14.00
SZ2	−28.56	−15.24
DZ	−25.30	−16.65
SZ(*)	−28.94	−14.62
SZ(**)	−29.21	−14.62
SZ(** + 1)	−30.26	−15.33
DZ(*)	−25.80	−16.14
DZ(+1)	−24.77	−16.66

(*) denotes polarization orbitals *d* only on heavy atoms involved in dimerization process

(**) the second star denotes polarization orbitals *p* on the three H of (NH_3^+) involved in the dimerization

(+) denotes diffuse functions on the two oxygens involved in the dimerization

All values in kcal/mol

2.5.4. Solvation energy ΔE_{solv}. Because of the size of our system it has been appealing to use a continuum model. The well-known principle of such methods rests on the representation of the solute molecule as a charge distribution placed inside a cavity surrounded by a continuous medium standing for the solvent which is characterized by macroscopic properties: dielectric constant, molecular volume, thermal expansion coefficient.

In such a model, the calculation of solvation energy involves:

(a) the calculation of cavitation energy (necessary to create in the solvent the appropriate cavity of the solute).

(b) the calculation of energies corresponding to the introduction of the solute molecule into the cavity, namely: dispersion-repulsion energy, electrostatic energy, solute polarization energy.

We have used a method initially proposed by Huron and Claverie [15] for pure hydrocarbon liquids and have recently improved this technique, particularly in respect of the solute-solvent electrostatic energy [16]. The details of this development are found in [16], here we will just summarize the method.

The choice of the shape of the cavity is of great importance in a continuum model; in the method we have adopted, one uses a volume corresponding to the exact molecular shape of the solute, in practice, made of the union of Van der Waals spheres of the atoms composing it.

(a) Cavitation energy

This is calculated as a sum of contributions from corresponding spherical atomic fragments. All these terms have been evaluated utilizing the Reiss–Pierrotti expression [17–19], based on the scaled particle theory of liquids [17] for spherical cavities.

(b) Introduction of the solute into the cavity

– *Solute-solvent dispersion-repulsion energy* is calculated as a sum of products of energy integrals by calibration constants K_{ij}^D and K_{ij}^R (superscripts D and R stand for dispersion and repulsion, respectively; subscripts i and j refer to atoms belonging to solute and solvent, respectively). All details of this calculation may be found in [15] and [16].

– *Solute-solvent electrostatic energy.* Using the charging parameter method [20], it has been shown [21, 22, 16] that the *electrostatic free energy* ΔF^{el} is given by:

$$\Delta F^{\text{el}} = \tfrac{1}{2}\langle U_{\text{s-sv}}^{\text{el}} \rangle \tag{9}$$

where $\langle U_{\text{s-sv}}^{\text{el}} \rangle$ is the mean solute-solvent electrostatic interactions energy. Once ΔF^{el} is obtained, one gets ΔE^{el} (solute-solvent electrostatic energy) by the standard relation:

$$\Delta E^{\text{el}} = \Delta F^{\text{el}} - T\frac{\partial(\Delta F^{\text{el}})}{\partial T} \tag{10}$$

In a continuum model $\langle U_{\text{s-sv}}^{\text{el}} \rangle$ of Eq. (9) is evaluated in terms of the reaction potential ψ_1 of the solvent fully polarized by the solute fully charged. ψ_1 is the statistical average of the electrostatic potential created by all the solvent molecules. In practice, ψ_1 is calculated within the framework of a dielectric electrostatic model (see Ref. [16]); in Appendix II, we just give a brief description of the method.

Finally in this section, we want to notice that using thermodynamic consideration and relations [9], we can obtain the electrostatic part of the solvent reorganization energy [16]:

$$\Delta U_{\text{reorg}}^{\text{el}} = \Delta E^{\text{el}} - 2\Delta F^{\text{el}} \tag{11}$$

– *Solute polarization energy.* Once again using the charging parameter method [20], the polarization part of the solvation free enthalpy is calculated as:

$$\Delta F^{\text{pol}} = \sum_{i=1}^{N} \tfrac{1}{2}\alpha_i \left|\mathscr{E}_i'(\vec{r_i})\right|^2 = \langle U_{\text{s-sv}}^{\text{pol}} \rangle \tag{12}$$

where α_i is the polarizability of the i^{th} atom of the solute, and $\mathscr{E}_i'(\vec{r_i})$ is the reaction field created at point $\vec{r_i}$ (see Appendix II).

Then, ΔE^{pol} is again evaluated by Gibbs–Helmholtz relations. Here we only deal with solvation internal energy ΔE_{solv} (and its components). We do not take into account those terms due to the compression of the gas, from the gas phase to the liquid phase, i.e., the classical term:

$$P(V_g - V_l)RT \tag{13}$$

– In such a model, the size of the cavity is of great importance. When dealing with nonpolar molecules solvated in a nonpolar solvent, the van der Waals radius of each atom is multiplied by a factor λ, calibrated in such a way that the calculated volume is equal to the experimental molal volume of the solute, at infinite dilution. When calculating polar or charged solute in a polar solvent (water, for instance), the situation is a little more complicated. In fact, the macroscopic dielectric constant does not give a perfect representation of the statistical behavior of solvent molecules, in the immediate vicinity of the solute. In fact, this model should not give the solvation sites, i.e., the sites of the solute molecule that interact very strongly with the solvent. In such a situation we can adopt the systematic approach defined by Millero et al. [23]:

$$V^{\circ} = V^{\circ}(\text{int}) + V^{\circ}(\text{elect}) \tag{14}$$

where $V^{\circ}(\text{int})$ is the intrinsic partial molal volume of the solute and $V^{\circ}(\text{elect})$ is the electrostriction partial molal volume due to the hydration of the amino acid.

(1) $V^{\circ}(\text{int})$ can be calculated by:

$$V^{\circ}(\text{int}) = (0.7/0.634)V^{\circ}\,\text{cryst} \tag{15}$$

where 0.7 is the packing density for molecules in organic crystal [24] and 0.634 is the packing density for random packing spheres (for more details see [23]). For glycine zwitterion, the factor λ has been fitted in order to obtain $V^{\circ}(\text{int})$ given by Eq. (15): $\lambda = 1.15$.

(2) In order to obtain $V^{\circ}(\text{elect})$ of Eq. [14], we have adopted the systematic approach proposed by Claverie et al. [16]: these authors have adopted the formulae of Whallay [25] for a sphere containing charges, dipoles, and quadrupoles embedded in a dielectric medium, for a cavity built from the union of van der Waals spheres (see Eqs. (65–66) in [16]); the electrostatic volume change ΔV_{elec} of the system has been obtained by differentiating ΔG with respect to the pressure. Once ΔV_{elec} is calculated, it is possible to obtain the modified van der Waals radius for each atom of the solute (see Eqs. (67–73) in [16]). Following this process, the partial molal volume of glycine zwitterion, at infinite dilution in water, has been calculated as 45 cm^3, which is in good agreement with the experimental value: 43 ± 1 cm^3 [23]. Furthermore, our calculated modified van der Waals radii seem to be in a rather good agreement with the ones determinated by Bonnacorsi et al. [26].

3. Results

First, let us recall that previous calculations [5] have shown that, in an isolated state, the conformation of glycine zwitterion giving the preferential adsorption varies following the adsorption site: these authors have found (for each MX crystal) a *cis* conformation (geometry I, Fig. 3) on ideal plane (100) and a *twisted* one (geometry II, Fig. 4) on double step $(110)_2$ and kink $(111)_2$.

But, in this project we are concerned with adsorption phenomena in water; thus, because of the strong destabilization of the *cis* conformation in aqueous solution (see Appendix I), we only deal with the *twisted* conformation of glycine zwitterion.

3.1. Adsorption energy of one glycine molecule on MX *crystal*

All quantities necessary for the calculation of the total adsorption energy, ΔE_{tot}, of one glycine zwitterion on different MX crystals in water [namely $\Delta E_{\text{solv(MX)}}$, Δ, ΔE_{ads}, $\Delta E_{\text{solv}}(\text{MX} \cdots \text{gly II})$] are collected in Table 2.

From the values indicated in this table, it emerges essentially that:

(a) *In an isolated state*, adsorption energy of glycine on different crystals is negative, thus this process is favorable.

Furthermore, we notice that LiF crystal stands out against KI and NaCl crystals effectively, only double step $(110)_2$ is favored in adsorption on LiF crystal, whereas both kink and double step are favored in adsorption on KI and NaCl crystals. We can explain these results when considering steric hindrance: effectively the distance $\text{Li}^+ \cdots \text{F}^-$ (2.01 Å) is too short in regard to glycine dimensions (2.79 Å), while the $\text{Na}^+ \cdots \text{Cl}^-$ distance (2.814 Å) is in good order of magnitude.

Finally, our results clearly show that parametric concordance between the crystal lattice and the adsorbed molecules plays an important role in adsorption, but it is not the essential one. So, this 2D-lattice coincidence is obviously a necessary, but not sufficient condition to explain the modification of habit $\{100\} \rightarrow \{110\}$, of NaCl, owing to the fact that KI, which has a longer interionic distance than NaCl (3.526 Å instead of 2.814 Å), gives similar results. Hence, we must conclude that other factors do exist, in particular the solvation and the dimerization of glycine zwitterions, neglected in this isolated state.

(b) *In water solution*, the complex $[\text{MX} \cdots \text{gly II}]$ is unfavored with regards to the two separate entities, namely MX crystal and glycine zwitterion, whatever the crystal MX or the selected adsorption site (100), $(110)_2$, $(111)_2$ may be.

Effectively, on one hand, we get:

$$\Delta(\Delta E_{\text{solv}}) = \Delta E_{\text{solv}}(\text{MX} \cdots \text{gly II}) - \Delta E_{\text{solv}}(\text{MX}) - \Delta > 0 \qquad (16)$$

On the other hand, though the adsorption energy E_{ads} is favorable, its absolute value is smaller than $\Delta(\Delta E_{\text{solv}})$ leading to a positive total energy ΔE_{tot} (Eq. (4)). The destabilization of a complex in water with regard to the molecule partners is a very well-known phenomenon, which proceeds from the desolvation of molecular parts which interact in the complex formation.

In order to understand this phenomenon:

- we have analyzed ΔE_{solv} in terms of its different contributions: ΔE^{cav} (cavitation), $\Delta E^{\text{D.R.}}$ (dispersion-repulsion), ΔE^{el} (electrostatic), ΔE^{pol} (polarization). For each term ΔE^X (X = Cav, D.R., el. or pol.), we have calculated the energetic balance $\Delta(\Delta E^X)$, which has the following expression:

$$\Delta(\Delta E^X) = \Delta E^X(\text{MX} \cdots \text{gly II}) - \Delta E^X(\text{MX}) - \Delta E^X(\text{gly II}) \qquad (17)$$

The corresponding values are listed in Table 3 (for sake of brevity, we only give values obtained for MX = NaCl, since the values calculated for MX = KI are very similar). It clearly appears that the destabilization of adsorption complex principally proceeds from ΔE^{el}.

- we carried out a more refined analysis of ΔE^{el} in terms of $\langle U^{\text{el}}_{\text{s-sv}} \rangle$ and $\Delta U^{\text{el}}_{\text{reorg}}$ (solute-solvent mean electrostatic energy and solvent reorganization energy, respectively).

Table 2. Association [MX ··· gly II] in water, total energy of reaction: ΔE_{tot}

Crystal	Site	$-\Delta E_{solv}(MX)$	$-\Delta$	$\Delta E_{solv}(MX \cdots \text{gly II})$	$\Delta(\Delta E_{solv})$	ΔE_{ads}	ΔE_{tot}	z_{min} (Å)
	(100)	+221.14	+68.64	−250.47	+29.31	− 3.82	+25.49	2.9
LiF	$(110)_2$	+284.91	+68.64	−319.75	+33.80	−19.32	+14.48	2.9
	$(111)_2$	+310.59	+68.64	−307.25	+71.98	− 0.48	+71.50	2.9
	(100)	+190.16	+68.64	−228.63	+30.17	− 6.11	+24.06	3.05
NaCl	$(110)_2$	+234.90	+68.64	−257.91	+45.63	−15.28	+30.35	3.05
	$(111)_2$	+252.42	+68.64	−258.90	+62.16	−20.41	+41.75	3.05
	(100)	+205.19	+68.64	−242.01	+31.81	− 8.19	+23.62	3.12
KI	$(110)_2$	+251.30	+68.64	−272.15	+47.79	−17.96	+29.83	3.12
	$(111)_2$	+257.21	+68.64	−274.48	+51.37	−26.56	+24.81	3.12

All the values (in kcal/mol) are defined in Sect. 2 [Eqs. (1_1), (3), (1_4), (1_{3b})] for $\Delta E_{solv}(MX)$, Δ, $\Delta E_{solv}(MX \cdots \text{gly II})$ and ΔE_{ads}, respectively. $\Delta(\Delta E_{solv}) = \Delta E_{solv}(MX \cdots \text{gly II}) - (\Delta E_{solv}(MX) + \Delta)$

z_{min} is the distance between the surface and the adsorbate (in Å)

Table 3. Decomposition of ΔE_{solv} into its different components ΔE^X for various sites on the NaCl crystal

Site	Association	ΔE^{Cav}	ΔE^{DR}	ΔE^{el}	ΔE^{pol}	ΔE_{solv}
(100)	MX ··· gly II	20.98	−67.57	−176.74	−5.30	−228.63
	MX	20.76	−58.21	−150.52	−2.18	−190.15
	gly	1.38	−4.94	−55.44	−8.12	−67.12
	$\Delta(\Delta E^X)$	−1.16	−4.42	29.22	5.00	28.64
$(110)_2$	MX ··· gly II	23.52	−73.11	−203.60	−4.71	−257.90
	MX	23.67	−67.72	−187.99	−2.86	−234.90
	gly	1.38	−4.94	−55.44	−8.12	−67.12
	$\Delta(\Delta E^X)$	−1.53	−0.45	39.83	6.27	44.12
$(111)_2$	MX ··· gly II	23.85	−73.34	−204.55	−4.86	−258.90
	MX	24.00	−69.45	−203.66	−3.31	−252.42
	gly	1.38	−4.94	−55.44	−8.12	−67.12
	$\Delta(\Delta E^X)$	−1.53	1.05	54.55	6.57	60.64

For definition of $\Delta(\Delta E^X)$ see Sect. 3.1 Eq. (17)

Once again, for these two terms, we have evaluated the energetic balance defined as follows:

$$\Delta_{\text{s-sv}} = \langle U^{\text{el}}_{\text{s-sv}} \rangle (\text{MX} \cdots \text{gly II}) - \langle U^{\text{el}}_{\text{s-sv}} \rangle (\text{MX}) - \langle U^{\text{el}}_{\text{s-sv}} \rangle (\text{gly II}) \tag{18}$$

$$\Delta_{\text{reorg}} = \Delta U^{\text{el}}_{\text{reorg}} (\text{MX} \cdots \text{gly II}) - \Delta U^{\text{el}}_{\text{reorg}} (\text{MX}) - \Delta U^{\text{el}}_{\text{reorg}} (\text{gly II}) \tag{19}$$

From values indicated in Table 4, it appears that the loss of solute-solvent energy is not counterbalanced by a gain in solvent reorganization energy. Thus, water molecules interact more strongly with glycine zwitterion than between themselves.

Table 4. Decomposition of ΔE^{el} into 'solute-solvent' mean interaction energy $\langle U^{\text{el}}_{\text{s-sv}} \rangle$ and solvent reorganization energy $\langle U^{\text{el}}_{\text{reorg}} \rangle_{\text{s}}$

	Association	(100)	$(110)_2$	$(111)_2$
$\langle U^{\text{el}}_{\text{s-sv}} \rangle$	MX ··· gly II	−245.74	−276.78	−276.48
	MX	−201.24	−251.83	−269.08
	gly	−102.38	−102.38	−102.38
$\Delta_{\text{s-sv}}$		57.88	77.43	94.98
$\langle U^{\text{el}}_{\text{reorg}} \rangle_{\text{s}}$	MX ··· gly II	69.00	73.18	71.93
	MX	50.72	63.84	65.42
	gly	46.94	46.94	46.94
Δ_{reorg}		−28.66	−37.60	−40.43
ΔE^{el}		29.22	39.83	54.55

$\Delta_{\text{s-sv}}$ and Δ_{reorg} are defined in Eq. (18) and Eq. (19) of Section 3.1, respectively
Values (in kcal/mol) are given for MX = NaCl

This has been verified from some preliminary calculations we have done (within a discrete model: 60 water molecules surrounding glycine zwitterion). From our results, in agreement with previous ones [5, 27], there are at least 6 water molecules strongly bound to glycine zwitterion (3 to NH_3^+ group and 3 to COO^- group) (see Fig. 5), and the glycine zwitterion-water interaction energy thus calculated (see Table 5) are stronger than the water-water interaction energy (5.39 kcal/mol).

Furthermore, from the calculated values of Δ_{reorg} (Eq. (19)), we can get an estimation of the number of water molecules (N_w) which have been removed from both glycine zwitterion and crystal surface upon complex formation and which then reassociate by hydrogen bonds with other water molecules of the solution: this can be done by taking as *mean* electrostatic interaction energy a value of 6.0 ± 0.5 kcal/mol (value obtained within our "adapted" minimal basis set). Our evaluation of N_w (see Table 6) is in a good agreement with a qualitative estimation given by Julg et al. [5]: Effectively, these authors (taking as an example, adsorption of glycine zwitterion on ideal plane (100) of NaCl crystal, see Fig. 6) have considered that during the complex formation: (a) owing to the size of a water molecule with regards to $Na^+ \cdots Cl^-$ distance, one water molecule

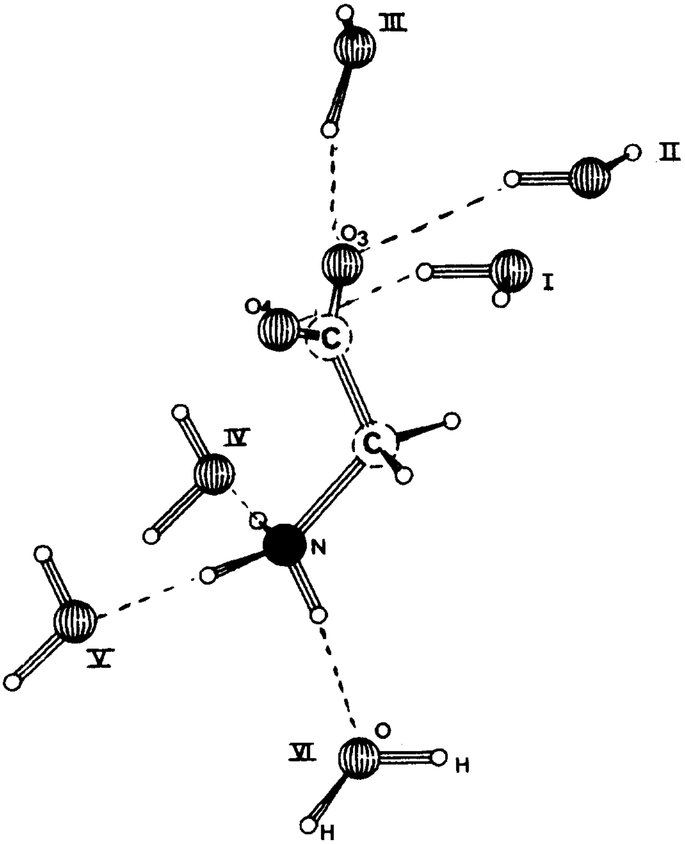


Fig. 5. Structure of [gly II, $6H_2O$] complex in aqueous solution

Table 5. Interaction energy ΔE_{int} and its components between glycine zwitterion and the six 'strongest bound' water molecules

Water molecules	E^{el}	E^{pol}	E^{rep}	E^{disp}	ΔE_{int}
I	−6.74	−0.67	3.67	−3.65	−7.39
II	−6.68	−0.68	3.57	−3.60	−6.44
III	−5.45	−0.89	3.69	−3.69	−6.34
IV	−13.07	−1.88	3.79	−3.04	−14.20
V	−13.50	−2.64	5.42	−4.52	−15.24
VI	−12.90	−2.46	4.49	−4.06	−14.93

Superscripts *el*, *pol*, *rep*, *disp* stand for electrostatic, polarization, repulsion, dispersion, respectively
The numbering of water molecules corresponds to the one given in Fig. 5
All values in kcal/mol

Table 6. Estimation of the number of water molecules (N_w) which reorganize themselves upon complex [MX · · · gly II] formation

Site / Crystal	(100)	$(110)_2$	$(111)_2$
LiF	$\simeq 5$	$\simeq 5$	$\simeq 4$
NaCl	$\simeq 5$	$\simeq 6$	$\simeq 7$
KI	$\simeq 5$	$\simeq 7$	$\simeq 7$

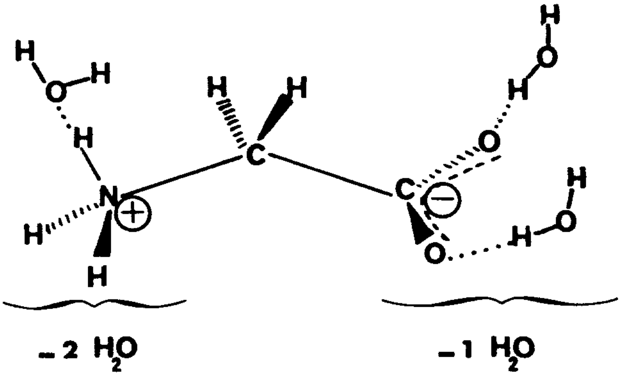


Fig. 6. Structure of solvated gly II, adsorbed on ideal plane (100) of crystal NaCl

is removed from NaCl surface (b) three water molecules are removed from glycine zwitterion.

It is interesting to notice that the value of $\Delta_{\text{s.sv}}$ [Eq. (18)] (see Table 4) also practically corroborates our estimation of N_w when: (a) looking at Fig. 6 and Table 5 and (b) taking for NaCl···H_2O interaction energy the values evaluated by Julg et al. [5]: 10 kcal/mol.

3.2. Adsorption of two glycine zwitterions on MX *crystal*

Once one glycine zwitterion is adsorbed on the crystal surface, the second one has to be located on the structure at the optimal position previously obtained in order to minimize its adsorption energy.

Now, the distance between two adsorbed glycine zwitterions is of great importance with regards to the interaction energy between themselves.

In order that active chains be formed, it is necessary that the monomers, located at their optimal position on the surface, present an attractive interaction (distance between the extremities of the molecule as short as possible, and without overlap). In other terms, an approximate equality between the size of the molecule and the anion-cation distance is required.

Thus simple energetic and geometric considerations clearly show that such an association is impossible on LiF crystal: the LiF distance (2.01 Å) is too short and the monomers of glycine would interpenetrate. In a same way, for reason of steric hindrance, such an association between two glycine zwitterions is impossible in a kink $(111)_2$ of a crystal MX. Thus, in this work, we will just consider the ideal plane (100) and the double step $(110)_2$ of NaCl and KI structures.

A preliminary study has shown that the $Na^+ \cdots Cl^-$ distance (2.81 Å) quite perfectly corresponds to the optimal distance between two glycine zwitterions forming a dimer, while the $K^+ \cdots I^-$ distance (3.526 Å) is really too large to bring the sufficient gain in energy required for an associative interaction [5].

Table 7 summarizes the energetic balances, ΔE_{tot}, calculated for the association of two glycine zwitterions on MX crystal (NaCl or KI). From the values indicated in Table 7, it emerges that:

(1) The interaction energy between the two zwitterions is more important on NaCl crystal than on KI substrate (−39.46 kcal/mol versus −16.13 kcal/mol). This result is in good agreement with the authors of Ref. [5].

(2) For the two concerned crystals, the total energy of Eq. (6), ΔE_{tot} (see Eq. (5)) is again positive. But we may notice that:

(a) ΔE_{tot} increases when a second glycine is adsorbed on the KI surface: in that case, Eq. (6) is more unfavorable than Eq. (1).

(b) Reverse results are obtained with NaCl crystal; the difference in energy ΔE_{tot} for Eqs. (1) and (6) is: 2.69 kcal/mol and 13.61 kcal/mol, respectively for the ideal plane (100) and double step $(110)_2$.

Thus, these values allow us to hope that, with an increase of the number of glycine zwitterions adsorbed on NaCl surface, in aqueous solution, the reaction will become more favorable ($\Delta E_{tot} < 0$).

Table 7. Association of $[MX \cdots (gly\ II)_2]$ in water
Total energy, ΔE_{tot}, of Eq. (6). All values in kcal/mol

Crystal MX	Site	$-\Delta E_{solv}(MX)$	2Δ	$\Delta E_{solv}[MX \cdots (gly\ II)_2]$	$\Delta(\Delta E_{solv})$	$2\Delta E_{ads}$	ΔE_{di}	ΔE_{tot}
NaCl	(100)	+190.16	+137.28	−254.39	+73.05	−12.22	−39.46	+21.37
	$(110)_2$	+234.90	+137.28	−286.42	+85.76	−30.56	−39.46	+15.74
KI	(100)	+205.19	+137.28	−273.61	+68.86	−16.38	−16.13	+36.35
	$(110)_2$	+251.30	+137.28	−290.08	+98.50	−35.92	−16.13	+46.45

We may try to give a rough approximation of the minimal number of monomers necessary to be adsorbed on the NaCl surface. In order to form an active chain, i.e., to get a balance $\Delta E_{\text{tot}} < 0$.

Effectively, considering the reaction:

$$\text{MX} + n[\text{gly II}] \rightarrow [\text{MX} \cdots (\text{gly II})_n] \tag{20}$$

we get:

$$\Delta E_{\text{tot}} = -\Delta E_{\text{solv}}(\text{MX}) - n\Delta + \Delta E_{\text{solv}}[\text{MX} \cdots (\text{gly II})_n] + n\,\Delta E_{\text{ads}} + (n-1)\,\Delta E_{\text{di}} \tag{21}$$

which may be written as follows:

$$\Delta E_{\text{tot}} = \Delta(\Delta E_{\text{solv}}) + n\Delta E_{\text{ads}} + (n-1)\,\Delta E_{\text{di}} \tag{22}$$

One has to evaluate $\Delta(\Delta E_{\text{solv}})$. But an examination of Tables 2 and 7 shows that this value achieved with $n = 2$ is approximately twice the one obtained with $n = 1$.

Thus, within this assumption we have realized the analytic resolution of the inequation: $\Delta E_{\text{tot}} < 0$, for the sites and substrates mentioned in Table 7.

Our results show that the balance ΔE_{tot} is never negative, whatever the value of n is, concerning KI crystal. Thus, any association of glycine zwitterion is possible on ideal plane or double step of KI structure.

But, concerning NaCl crystal, the resolution of ΔE_{tot} thus gives:

$n > 4$ for an ideal plane (100)

$n > 3$ for a double step $(110)_2$

These values prove the existence of a $[\text{MX} \cdots (\text{gly II})_n]$ complex stabilization on this NaCl structure, and are in agreement with the formation of an active chain of adsorbed glycine zwitterions as concluded by the authors of [2, 5].

4. Discussion

We want to emphasize that the temperature effect has been taken into consideration in the solvation effect but not for the adsorption process of glycine on the crystal. As a first step of a study of temperature effects on adsorption we limited ourselves to the adsorption on NaCl and will discuss our results in the following. In fact, glycine is adsorbed on the surface of a simple cubic lattice of a solid B: LiF, NaCl, KI. The forces holding the solid (mainly electrostatic forces between positive and negative ions in our case) are much stronger than adsorption forces; thus, the solid is nearly unperturbed by the presence of glycine, it only plays the role of providing a potential field for adsorbed molecules. E_{ads} is a function of x, y, z coordinates where the z axis is taken orthogonal to the surface. Considering adsorption on NaCl crystal, it appears that, at the equilibrium position NH_3^+ and COO^- groups of glycine, respectively, interact with both entities of the crystal Cl^- and Na^+. For a fixed value of z ($z_{\text{min}} = 3.10$ Å), the motion parallel to the surface (in Ox or Oy directions), involves passing over a potential barrier V_0 which is reached when NH_3^+ and COO^- glycine groups are above Na^+ and Cl^- ions of the NaCl crystal. This barrier is very high compared to the thermal energy $RT = 0.6$ kcal/mol, while $V_0 = 27.4$ kcal/mol, 31.7 kcal/mol, and 36.0 kcal/mol when considering plane (100), double step $(100)_2$, and kink $(111)_2$, respectively. Some considerations occur concerning $E_{\text{ads}} = f(z)$ (for x and y coordinates fixed): The dissociation energy which is again high compared to $RT = 0.6$ kcal/mol ($E_{\text{dis}} = 6.11$ kcal/mol, 15.28 kcal/mol and 20.41 kcal/mol, respectively, when considering (100) plane, $(110)_2$ double step, and $(111)_2$ kink). So at 298 K the thermal energy being small compared to the height of V_0 dissociation energy, glycine will be localized in the neighborhood of the potential minima of $E_{\text{ads}} = f(x, y, z)$. In such a localized adsorption, the adsorbed molecule has three vibrational degrees of freedom (replacing three translational degrees in gas phase), i.e., there are three vibrations in x, y, z directions around the minimum with frequencies of ν_x, ν_y, and ν_z. We then write:

$$E_{\text{ads}}(T) = E^0_{\text{ads}} + \sum_{i=1,3} \tfrac{1}{2} N h \nu_i + RT \sum_{i=1,3} (\Theta_i/T)/(e^{\Theta_i/T} - 1) \tag{23}$$

where $\Theta_i = h\nu_i/k$ is the characteristic temperature for vibrations ν_i, $i = 1, 3$ for x, y, z, respectively. The first term of Eq. (23) is the electronic adsorption energy calculated by Eq. (7). The second term represents zero-point vibrational energy and the third one is the temperature contribution to vibrational energy.

- The zeroth point energy has been calculated as 0.175 kcal/mol (plane (100)), 0.410 kcal/mol (double step $(110)_2$), and 0.476 kcal/mol (kink $(111)_2$).

- The third term is equivalent to $3RT = 1.80$ kcal/mol (for $T = 298$ K) for the three situations cited above.

Very similar results have been obtained considering KI and LiF crystals. So in vacuo at 298 K the complex glycine-crystal is stable even when considering thermal effects which are nearly constant for all the complexes we have studied. Furthermore, the effect of temperature on adsorption is negligible with regard to the destabilization of glycine-crystal complex by the solvent (24.6 kcal/mol for glycine adsorbed on plane (100) of NaCl, for instance).

As concerns glycine dimer, we have considered the stretching motion along the *Ox* axis following that this dimer is in vacuo or adsorbed on ClNa crystal (plane (100)). The zeroth point energy has been calculated as 0.15 kcal/mol and 0.17 kcal/mol, respectively. In the same way considering the motion along the *Oz* axis for this dimer, a value of 0.24 kcal/mol has been calculated.

So we think that the temperature effects (which are very small) are similar for all the complexes we have studied and do not change our qualitative results.

5. Conclusion

The parametric concordance alone cannot explain the modification $\{100\} \rightarrow \{110\}$ of the NaCl habit. It appears as being only a necessary condition for the association between glycine zwitterions; effectively, the energy gain obtained by such an association must compensate the energy loss due to the solvent effects.

Our calculations quantitatively and nicely show that NaCl $(110)_2$ can stop growing just for the adsorption of zwitterion building up a 2D crystal of associated glycine and water molecules, and so explain the formation of (110) faces to the detriment of (100) faces.

Figure 7 shows the final state of $(110)_2$ surface structure of crystal NaCl growing in aqueous solution and in the presence of glycine zwitterions.

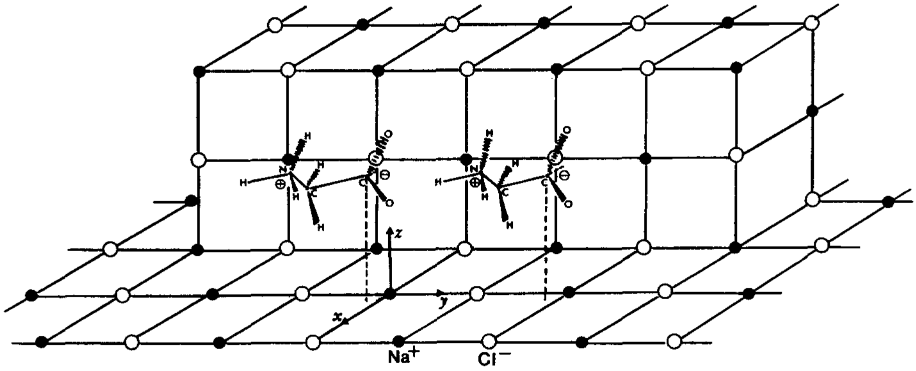


Fig. 7. Final state of $(110)_2$ surface structure corresponding to the case gly II/$(110)_2$ for NaCl crystal (the water molecules are not mentioned) $z = 3.10$ Å

In essence, this work is in good agreement with previous studies [5], but also gives additional information with regard to the treatment of solvation effects. The modification of the growth habit of NaCl is determined by a selective adsorption on well-defined sites of the structure, and the energy involved is essentially governed by two factors, one electrostatic and the other geometric.

This work also gives the solvent reorganization energy, and has allowed us to predict quantitatively the number of water molecules which reorganize upon the formation of [MX · · · gly II] complex; our results in this domain are also in good agreement with the qualitative estimations of the authors of [5].

Acknowledgements. The authors thank Professor A. Julg (Laboratoire de Chimie Théorique, Marseille) for many valuable and stimulating discussions related to this work. They also thank C. Mijoule (Laboratoire de Dynamique des Interactions Moléculaires, Paris) for very helpful discussions concerning temperature effects on the adsorption process and for his collaboration on vibrational energy calculations.

Appendix I

Conformation of glycine zwitterion in an isolated state or in water

The calculation of the preferential conformation of glycine zwitterion has been performed using *SCF method* (within an "adapted" minimal basis set [14] when considering the "isolated state" and *a continuum model* [16] (see Sect. 2.4) in order to take the solvation effects in water into account.

From results listed in Fig. 8 we may say:

- The *cis* (0, 0) conformation (Fig. 3, geometry I) is the most stable one in an "isolated" state and the *trans* one (60, 0), in water.
- The energy difference between *trans* (60, 0) and *twisted* II (0, 90) (Fig. 3, geometry II) conformation in water is very weak 0.9 kcal/mol, so we can expect the presence of these two conformations in water (results in agreement with Ladik et al. [6]).

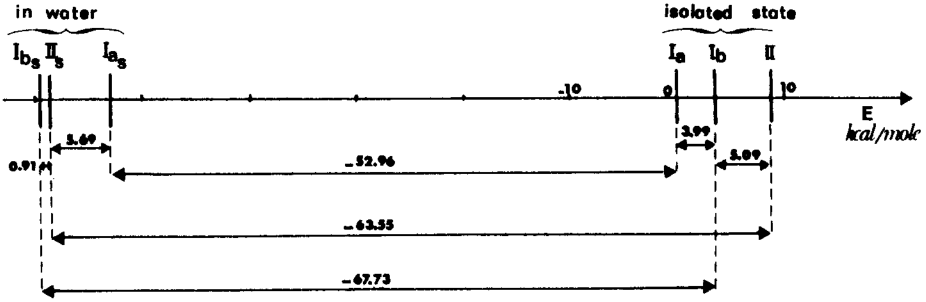


Fig. 8. Energy diagram showing the relative stabilization of the various conformations of glycine zwitterion, in the isolated state (I_a, I_b, and II respectively stand for *cis*, *trans*, and *twisted* conformation), and in water (Ia_s, Ib_s, II_s). The subscript *s* stands for "solvent"

An analysis in terms of solvation energy components has clearly shown that the energy difference between the three conformations mainly proceeds from the electrostatic energy (see Table 8).

A decomposition of ΔE^{el} into $\langle U^{el}_{s\text{-}sv}\rangle$ and $\langle U^{el}_{reorg}\rangle_s$ (see Table 9) clearly shows that the solute-solvent electrostatic interaction energy is stronger for both *trans* (60, 0) and *twisted* (0, 90) conformations than for the *cis* one (0, 0). Furthermore, introduction in the solvent of (60, 0) and (0, 90) conformations leads to a more important reorganization of the solvent than the (0, 0) conformation.

The solvation energy of the *trans* glycine zwitterion has been calculated as: −63.55 kcal/mol (with electrostatic energy representing 76% of this value). It is

Table 8. Energy components of solvation energy, ΔE_{solv}, for the three conformations of glycine zwitterion

Conformation zwitterion	ΔE^{cav}	ΔE^{el}	ΔE^{pol}	ΔE^{DR}	ΔE^{solv}
Ia (*cis*)	1.37	−39.81	−6.21	−8.31	−52.96
Ib (*trans*)	1.38	−50.46	−7.95	−6.52	−63.55
II (*twisted*)	1.38	−55.44	−8.12	−5.55	−67.73

All values in kcal/mol

Table 9. Decomposition of the component ΔE^{el}, given in Table 8, into the solute-solvent electrostatic interaction energy $\langle U^{el}_{s\text{-}sv}\rangle$ and the energy of solvent reorganization $\langle U^{el}_{reorg}\rangle_s$

Conformation zwitterion	$\langle U^{el}_{s\text{-}sv}\rangle$	$\langle U^{el}_{reorg}\rangle_s$	ΔE^{el}
Ia (*cis*)	−73.64	33.83	−39.81
Ib (*trans*)	−93.18	42.72	−50.46
II (*twisted*)	−102.38	46.94	−55.44

All values in kcal/mol

not possible to compare directly this value to experiment since our calculation of solvation energy corresponds to the reaction:

$$[\mathrm{gly}(\mathit{trans})]_l \rightarrow [\mathrm{gly}(\mathit{trans})]_g \qquad \Delta E_{\mathrm{solv}}(\mathrm{gly}(\mathit{trans})) \tag{I.1}$$

whereas experiment gives:

$$[\mathrm{gly}(\mathit{trans})]_l \rightarrow [NT_{\mathrm{gly}}]_g \qquad \Delta E_{\mathrm{solv}}(\mathrm{gly}) \tag{I.2}$$

since it is well known that glycine exists in a neutral form (NT) in the gas phase.

Furthermore, $\Delta E_{\mathrm{solv}}(\mathrm{gly})$ has not been obtained directly: only heat of sublimation (ΔE_{sub}) and heat of solution (ΔE_{solu}) are known: $\Delta E_{\mathrm{sub}} = 23.0 \pm 1$ kcal/mol [28] and $\Delta E_{\mathrm{solu}} = 3.8$ kcal/mol [29].

Thus $\Delta E_{\mathrm{solv}}(\mathrm{gly})$ has been estimated as -19.2 kcal/mol [24].

Regarding the diagram of Fig. 2, in order to get $\Delta E_{\mathrm{solv}}(\mathrm{gly}(\mathit{trans}))$ one has to consider steps (1_2a), (1_2b), and (1_2c). From $\Delta E_{\mathit{trans\text{-}cis}}$ we have evaluated ΔE_{PT} (see Eq. (1_2c)) and recently calculated it in our laboratory as 25 kcal/mol. Thus, we can give an estimation of 50 ± 2 kcal/mol for $\Delta E_{\mathrm{solv}}(\mathrm{gly}(\mathit{trans}))$; therefore our calculated value is rather good with regard to the limitations in the heats of solution, the problem of questionable purity of the material, and to errors associated with heats of solution of hydrated glycine, rather than unhydrated crystals.

Furthermore, we may emphasize that our calculated value for $\Delta E_{\mathrm{solv}}(\mathrm{gly}(\mathit{trans}))$ of -63.55 kcal/mol quite well compares with the ones obtained by Monte-Carlo simulations: -69.00 ± 4 kcal/mol by Alagona et al. [30] and -78.00 ± 13 kcal/mol by Mezei et al. [27]. From an electrostatic point of view our results are also very close to the ones of Bonaccorsi et al. [26].

Appendix II

Calculation of $\langle U^{\mathrm{el}}_{\mathrm{s\text{-}sv}} \rangle$ in a continuum model

Under the influence of the electrostatic field $\vec{\mathcal{E}}^{\circ}$ created by the charge distribution (multipolar in our model) of the solute, the outside dielectric medium is polarized and acquires a dipole moment $\vec{p}$ by unit volume, which produces a reaction potential V' (thus a reaction field $\vec{\mathcal{E}}'$), hence a resulting total potential V and a total electrostatic field $\vec{\mathcal{E}}$:

$$V = V^{\circ} + V' \tag{II.1}$$

$$\vec{\mathcal{E}} = \vec{\mathcal{E}}^{\circ} + \vec{\mathcal{E}}' \tag{II.2}$$

We have used the fact that in a homogeneous dielectric medium, the reaction potential V' created by the dipolar density $\vec{p}$ is equivalent to that of a fictive charge density σ on the surface of the cavity [27, 28].

$$V'(\vec{r}) = \frac{1}{4\pi\varepsilon_0} \iint \frac{\sigma(s)}{(\vec{r} - \vec{s})}\, d\vec{s} \tag{II.3}$$

with:

$$\sigma = \vec{n} \cdot \vec{p} = \frac{1}{4\pi}(\varepsilon - \varepsilon_0)\vec{n} \cdot \vec{\mathcal{E}} \tag{II.4}$$

where $\vec{n}$ is the vector normal to the surface.

ε_0 is the vacuum dielectric permittivity, ε is the permittivity of the solvent, and $\varepsilon/\varepsilon_0$ is the usual dielectric constant.

The calculation of σ is rather complicated and requires lengthy calculations. But in the methodology we have adopted, the calculation of σ becomes very simple because of (a) the multipolar representation of the charge distribution of the solute and (b) the representation of the cavity by union of van der Waals atomic spheres. Thus we can use Kirkwood's formulae [29].

Once σ is calculated, $\langle U^{\mathrm{el}}_{\text{s-sv}} \rangle$ is simply obtained as:

$$\langle U^{\mathrm{el}}_{\text{s-sv}} \rangle = \int_s \sigma(s) V^{\circ}(\vec{s})\, d\vec{s} \tag{II.5}$$

$V^{\circ}(\vec{s})$ being the electrostatic potential created by the solute charge density at the surface point $\vec{s}$.

The reaction field $\mathscr{E}'(\vec{r}_i)$ entering in Eq. (12) of Sect. 2.4 is simply calculated as the electric field created by the charge surface density $\sigma(s)$:

$$\mathscr{E}'(\vec{r}_i) = \iint_s \sigma(s) \left(\frac{\vec{r}}{r^3} \right) d\vec{s} \tag{II.6}$$

In our methodology, the charge distribution of the solute is represented by *ab initio* (within an appropriate basis set [14]) multipoles (up to quadrupoles) located on atoms and bonds, calculated by a procedure defined by Vigne-Maeder et al. [34]. The crystal is represented by a finite number of point charges located at sites of the ion in the natural crystal. We may wonder whether this model is compatible to the one used to calculate adsorption energy (Eq. (7)). In fact, the question is: does the localized discontinuous SCF change distribution represent the continuous SCF charge distribution as concerns the electrostatic energy? The answer is "*yes*" as shown in [35]. Furthermore, it has been shown [36] that the multipole model (up to quadrupoles) reproduces the electric field with a fairly high precision both in magnitude and in orientation in water dimer at 3 Å; at longer distances the differences become negligible. In this present work we have verified the electrostatic part of the adsorption energy by using (a) Eq. (7) and (b) by the finding that multipole distribution does not differ by more than 2%.

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