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Zineb Fritah, Christophe Drouet, Fabrice Salles, Olivier Marsan, Maëleonn Aufray. Influence of water on an epoxy/amine–metal interphase: a combined DFT and mixing calorimetry approach. ACS Applied Materials & Interfaces, 2023, 15 (8), pp.11342-11352. 10.1021/acsami.2c22431 . hal-04023569

HAL Id: hal-04023569

<https://hal.science/hal-04023569v1>

Submitted on 10 Mar 2023

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Influence of water on epoxy/amine-metal interphase: a combined DFT and mixing calorimetry approach

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Abstract

Epoxy-amine systems are ubiquitous in the field of industrial thermosetting polymers, often used in moist atmosphere. In addition, previous studies showed amine-metal interaction through the formation of an interphase, with the formation of surface complexes that may involve the formation of water molecules. However, to date the impact of water on epoxy/amine-metal interphase was not specifically addressed. In this work, we examined for the first time the role of this potential 4th component by way of a dual experimental/computational approach. The effect of water on the glass transition temperature of obtained polymers was quantified. The *in situ* formation of DETA-Al-water interphase was followed by mixing calorimetry. The DETA-water interaction was highly exothermic, and the underlying mechanism was discussed on the basis of DETA hydration, which was confirmed by DFT and Monte Carlo simulations. Taking into account pre-existing interaction between DETA molecules allowed to model all experimental data. Comparison of experimental and calculated IR spectra contributed to validate the simulation parameters used. Our findings indicate that the presence of water may noticeably affect epoxy-amine-based systems: mixing calorimetry and computational modeling appear as particularly adapted tools for the comprehension of such complex systems.

Keywords

Epoxy-amine systems, water, interphase, calorimetry, DFT simulations, adhesion

Introduction

Epoxy resins are widely used as polymer materials in many fields such as adhesives, paints and sealants, and are extensively encountered in aeronautics, building, and many other strategic domains. They are obtained by polymerization of molecules exposing epoxide functions with a second monomer that is frequently a (poly)amine. In these applications, a metal substrate is often involved. Previous studies showed that, according to the nature of the metal, the properties of epoxy-based systems are significantly modified¹⁻³. Polymerization on metal substrates, with various polymers was indeed found to involve the formation of an interphase, leading to noticeable modifications of the properties of the final materials, e.g. in terms of thermal and mechanical behavior⁴⁻⁸.

In this context, the reaction between amine monomers and metal substrates – which are likely (hydr)oxidized – was shown to be the main contributor to the modification of epoxy-based systems properties, by impacting the characteristics of the interphase. Several studies showed that, upon contacting the amine monomer with metal substrates, metal cations were present in the organic phase: organometallic complexes are formed during this interaction, as was indicated by indirect methods such as FTIR or X-ray Photoelectron Spectroscopy (XPS)^{1,9-12}. Our recent work allowed confirming these results by way of an innovative *in situ* approach based on mixing calorimetry. Using DiEthyleneTriAmine (DETA) as a usual amine hardener for epoxys, DETA-Al and DETA-Cu interactions were especially analyzed, unveiling important exothermic effects. On the contrary, contact between the epoxide monomer (Diglycidyl Ether Bisphenol A, DGEBA) and the metal was found to be endothermic, thus pointing to a less favorable process. These findings unveiled the power of the mixing calorimetry technique to explore and study the formation of this kind of

interphase *in situ*², by directly measuring enthalpies of interaction. The latter can be linked to other properties of the system, like the chelation power of metal cations for aminated molecules, which may allow comparing the stability of various systems.

Mercier *et al.* explored the interaction between (hydr)oxidized metal substrates and one of the simplest molecule with two amine functions, namely DiEthylAmine (DEA)¹³. They proposed a mechanism in two steps, with first the formation of an amine-metal surface complex, that was reported in several studies^{5,12,14}, and then its dissociation from the metal surface to form a chelate in the amine solution¹³. In our recent work, DETA and aluminum were used as model system, and possible chelate configurations were studied, for the first time, by a numerical approach based on the Density Functional Theory (DFT)¹⁵ simulations, allowing comparisons with experimental results and the identification of more probable amine-metal complexes.

Beside the direct interaction between the amine molecule and the surface metal ions, the mechanism suggested by Mercier *et al.* would also involve the formation of water molecules, which have not yet attracted much attention. Also, in the industrial environment, epoxy-amine systems polymerize in moist atmospheric air. Water could then play a significant role in the polymerization reaction when epoxy-based systems are applied on metal substrates after the polymerization¹⁶. Absorption of water by polymers in general is a known phenomenon called plasticization that was studied by both an experimental¹⁷⁻¹⁹ and computational^{16,20,21} approach. On the contrary, only few studies addressed the impact of adding water during polymerization on the properties of final glued systems (e.g.²²), and the link to the interphase formation was rather disregarded. A recent computational work by DFT investigated the interaction of an epoxy polymer and an alumina surface, whether as such or wet – alumina surface in contact with an increased amount of water molecules. The authors reported differences between interfacial

energies in these two kinds of systems ²³, thus pointing out the importance of studying the impact of the potential presence of water molecules at the interphase. In addition, many studies based on Molecular Dynamics simulations have been performed to capture the description of the interphase between epoxy and metal surfaces. The implication of different kinds of interactions (electrostatic, hydrogen bonds, van der Waals interactions) have been thus shown and the influence of both the metal sites nature and the surface state has been evidenced ²⁴. To go further, reactive force fields have been developed to reproduce the creation of bonds between the solid and the amine and prove the implication of N in interaction with the metal site ²⁵. Recent studies have illustrated the complex role of water in the interphase which can enhance the interaction between epoxy and metal surfaces and analyze the opposite behavior of the systems in presence of goethite or hematite ²⁶.

Water molecules could play the role of fourth reactant in epoxy/amine-metal systems, but have not yet received dedicated attention. This is the objective of the present contribution, with the aim of exploring the impact of water in the DGEBA-DETA-Al system, by a dual approach combining experiments (*in situ* mixing calorimetry and DSC) and DFT calculations. By exploring the effects of H₂O molecules on the various components, this work envisions to bring light on the modification of interfacial properties, and suggest possible mechanistic hypotheses, with the view to highlight the impact of water on epoxy-based systems' properties of relevance to the industrial field.

2. Materials and methods

2.1. Materials

In this work, Bisphenol A diglycidyl ether – DGEBA – also known under the commercial name DER 331 (Sigma Aldrich, Molecular Weight: 340.41 g/mol) was used as epoxy resin, containing 2 terminal epoxide functions. Polymerization was undergone by addition in stoichiometric proportions of diethylenetriamine – DETA – used as triamine hardener (Sigma Aldrich, Molecular Weight: 103.17 g/mol) and exhibiting 5 protons arising from 2 primary amines and 1 secondary amine. **Figure S1** reports the chemical formula of the DGEBA and DETA monomers employed in this study.

With the view to determine experimentally the pK_a values of the DETA precursor, titration of a solution of DETA (0.01 mol/L) was undergone by pH follow up, first using a solution of hydrochloric acid (1.20 mol/L) and then MilliQ water [®] – the latter being used as soft provider of H_3O^+ ions, allowing to consider the acid-base couple H_3O^+/H_2O . The determination of the pK_a values was undergone by the tangent method.

When mentioned in the text, aluminum powder (Acros) and water (MilliQ [®], resistance of 18.2 M Ω) were used as additional reactants. Prior to use, the aluminum powder has been treated in boiling water for 1h30 and dried for 16h in an oven at 100°C. This process allows obtaining a reproducible surface state (essential for calorimetry experiments), which was also found to promote the surface hydroxylation with boehmite structure ².

2.2. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was used to determine the glass transition temperature (T_g) of polymers obtained after curing in different conditions, as explained in the text, typically involving the addition of water at the time of initiating the polymerization. The latter was operated by contacting the reactants (DGEBA, DETA, \pm water) at RT for 3h followed by a curing step at 140°C for 1h30. In this work, polymerization was carried out both in the absence of aluminum (to prepared “bulk” polymeric pieces) and on Al plates (1050 alloy) to prepare polymeric “films”. In this case, the film thickness was fixed to *ca.* 300 μm using corresponding wedges on both sides of the plate and rolling a glass stick on the wedges to obtain a thin layer of monomers mixture.

DSC experiments were carried out under nitrogen gas flow on a DSC 204 Phoenix Series (NETZSCH, Selb, Germany) apparatus coupled with a TASC 414/4 controller. Cured polymer samples (10–20 mg, with the accuracy of ± 0.01 mg) were weighed in aluminum capsules and heated twice from -80 °C to 180 °C, at a heating rate of $+30$ °C/min. The T_g value was measured during the second run using the Proteus® Software. Both the “onset” and “endset” temperatures associated with the beginning and the end of the glass transition phenomenon, respectively, were identified. Calibration of the DSC apparatus was performed with various metals (In, Hg, Sn, Bi, CsCl, and Zn) to assess melting temperatures via 2 subsequent runs at $+30$ °C/min.

2.3. Mixing calorimetry

Mixing calorimetry was used to assess *in situ* the enthalpy of interaction when contacting components of the DGEBA/DETA/Al/water system at a constant temperature of 40°C, using a Setaram C80 calorimeter equipped with Calvet 3D thermopiles and two-compartment Hastelloy® mixing cells, as described elsewhere ². The heat flow corresponding to the reaction occurring in

the calorimeter cell was recorded over time taking. An empty calorimeter cell served as reference. After temperature equilibration of the calorimeter, contact between the reactants from the two compartments of the measuring cell was operated by rupturing the separating Teflon® membrane. In this work, DETA (1.5 g) or DGEBA (2.4 g) was placed in the upper compartment of the cell, and aluminum powder (100 mg) was positioned in the lower compartment. In order to examine the possible effect of water, MilliQ water (5 mg to 2.1 g) was added to either the upper or lower compartment, as indicated in the text. To complement the study, the DETA/water interaction, exempt of aluminum, was also investigated.

For each calorimetry run, the raw enthalpy of interaction was reached upon integration of the heat flow = $f(t)$ signal. A “blank” experiment was systematically run after return of the baseline to its stabilized value to account for a possible slight asymmetry of the calorimeter cells. The obtained enthalpy ΔH_{blank} was subtracted from the raw enthalpy measured to assess the corrected reaction enthalpy ($\Delta_{\text{R}}H$) that was followed throughout this study. Calibration of the heat flow signal was regularly verified by reference dissolution experiments of dried potassium chloride (KCl, Merck) in water under similar experimental conditions (heat flow resolution: 0.10 μW , temperature accuracy: $\pm 0.1^\circ\text{C}$).

2.4. Computational modeling

In this study, computational methods using density functional theory (DFT) simulations implemented in DMol³ ²⁷ were used to complement the experimental approach for exploring the role of water in the DETA/water system. The main goal was to optimize the geometry of several molecular structures involving these components, in order to provide the plausible geometry of the molecules. The aim of these calculations is to verify our hypotheses concerning the nature of

interaction between water molecules and DETA monomers. In this view, DETA was considered with different global charges (from -3 to +3) to probe the relative stability of the different forms in interaction with water and compare simulated outcomes to the experimental results. Besides, this approach allowed for the determination of the Fermi level and some physical and chemical properties of the systems studied such as partial charges and energy values giving access to the reactivity when combined as reaction energy. Geometry optimizations were carried out on the molecular models using 3 different density functionals: the GGA PBE²⁸ and GGA PW91²⁹ considering polarization functions on hydrogen atoms (DNP) and B3LYP³⁰ containing a dispersion term. Convergence of the calculations was reached when variations became lower than 10^{-5} Ha for energy, 0.002 Ha/Å for maximal force and 0.005 Å for maximal displacement.

The simulation study of the DETA/water interaction was carried out in an incremental way. After optimizing the geometry of DETA, one water molecule was first added and all possible initial configurations were considered by adding the H₂O molecule at the vicinity of each amino group. In the simulation, we allowed H and O atoms from the water molecule to interact (via H bonding) with the nitrogen or hydrogen atoms of the amino groups. Based on the energy of all systems, the most stable configuration system was selected for adding a second H₂O molecule, and this same approach was then used incrementally up to 8 water molecules, starting each time from the most stable configuration.

Once the geometry optimization is reached, the vibrational description of the chemical bonds from the Hessian matrix³¹ allows us to predict the theoretical infrared spectra which can be compared with experimental data. It should be noted that, due to the simplification of the polymers for DGEBA (number of monomers smaller in calculations compared to experiments in particular), the simplification of solvent (a small number of water is considered), a shift for frequencies is

expected. However, the comparison between experiments and DFT calculations should allow us to identify the vibrational bands and then validate the interactions in play in the system. In order to investigate the plausible organization and complete the understanding of the interactions between amine, epoxy and water, Monte Carlo simulations have been performed using Sorption code available in Materials Studio³². From the optimized structures obtained from the above-mentioned DFT calculations, the partial charges were calculated following the Mulliken scheme proposed in DMol³ and allow us to determine the electrostatic part of the energy. The choice of the Mulliken charges have been guided by the good reproduction of hydrogen bonds between water and DETA consistent with DFT results. The van der Waals interactions were calculated using the Lennard Jones parameters issued from UFF (Universal Force Field³³) for DETA and DGEBA and TIP4P-2005 for water. These force fields were then combined following the Lorentz-Berthelot rules. For these calculations, we proposed to fix the number of each species with constant unit cell volume (cubic unit cell with a length of 20Å) and temperature (300K). We thus investigated different loadings in order to investigate the interactions only between water and DETA (30 DETA + 30 H₂O; 10 DETA + 40 H₂O) and the mixtures between the three species at two different loadings to investigate the impact of the concentration of DETA and DGEBA (20 DETA + 10 H₂O + 2 DGEBA; 10 DETA + 30 H₂O + 5 DGEBA). Monte Carlo calculations consisted in 5 million steps of equilibration and 2 million steps for production. The electrostatic interactions were computed using the Ewald summation³⁴, while the short-range contributions were determined using a cut-off for Lennard-Jones parameters fixed at 10Å.

2.5. Fourier Transformed Infrared (FTIR) spectroscopy

The infrared spectrometer used is FTIR Nicolet iS50 model. Some DETA/water mixtures were prepared to be analyzed by infrared spectroscopy in the ATR mode. Spectra were obtained in the mid-IR region, from 400 cm^{-1} to 4000 cm^{-1} with a resolution of 4 cm^{-1} . Acquisitions were carried out with 64 accumulated scans. The proportions of components used in these mixtures can be defined by the molar ratio $\frac{n_{DETA}}{n_{water}}$. In order to correlate these experiments to the mixing calorimetry and computational data, this ratio was varied in this study, as explained in the text, between 0 and 8.

3. Results and discussion

3.1. Influence of addition of water on the epoxy thermal properties

Epoxy/amine-metal systems have been the object of numerous studies aiming to understand the effect of metal on epoxy/amine polymerization. The particular amine-metal interaction was then shown to be the largest contributor to an interphase formation in these systems^{1,2,5,11,13}. Mercier *et al.* proposed a mechanism to explain the formation of such interphases, which implied one molecule with amine functions and the metallic surface (partially (hydr)oxidized). Upon amine-metal contact, this mechanism suggests the formation of amine-metal surface complexes that may, in a second step, detach from the surface and form solubilized chelates in the liquid amine monomer. The qualitative and quantitative data obtained in our recent works^{2,15} were in good agreement with this mechanistic approach: they allowed us to follow *in situ* the formation of amine-metal chelates (e.g. DETA/Al) leading to the epoxy/amine-metal interphase in the final bonding system, access to the associated enthalpy of interaction by way of mixing microcalorimetry, and propose first simplified chelate conformations via DFT calculations.

The interaction mechanism considered by Mercier *et al.* involve however also the formation of water molecules¹³, which may act as another component in the amine-metal system, but which did not receive special attention so far. The main goal of this study is thus to understand the potential impact of water on the epoxy polymerization and more specifically on the epoxy thermal properties as measured by DSC experiments.

Table 1 reports the glass transition temperature (T_g) measured by DSC for two types of samples, in the presence or absence of aluminum. Polymerized samples obtained in the presence of aluminum (Al 1050 alloy previously boehmited as described in² were prepared in the form of

films (Table 1) of about 300 μm of thickness. Polymers prepared in the absence of Al were prepared as bulk samples. In all cases, an increasing amount of water was added in the starting mixture to examine the possible effect on T_g . In order to discuss the obtained results, the T_g reported in this work consistently refer to the onset values. It can first be noted that the highest value of T_g was reached for samples polymerized without water, leading respectively to 47 $^{\circ}\text{C}$ for the film sample and 146 $^{\circ}\text{C}$ for the bulk. The lower value of T_g obtained for the film, *i.e.* in the presence of Al, can be linked to monomer(s)/Al interaction as was previously reported ¹¹ (with T_g numerical values that may vary from one work to another depending on parameters such as the surface treatment of the metal substrates used). In particular, the amine/metal (in this case DETA/Al) interaction has to be considered, as we previously showed ².

Table 1: Glass transition temperature (T_g) of films of DGEBA/DETA/water polymers on boehmited Al 1050 alloy, and of bulks of DGEBA/DETA/water polymers (in the absence of Al).

N°	Type of sample	Thickness (μm)	$n_{\text{water}}/n_{\text{DETA}}$	T_g ($^{\circ}\text{C}$)
1	Films	233 ± 12	0	47
2		347 ± 19	0.5	42
3		213 ± 5	2	37
4	Bulks		0	146
5			0.5	124
6			2	27

Based on Table 1 results, it may be inferred that the T_g values measured were clearly impacted by water addition. In the case of bulk samples, a very significant and gradual drop of T_g was evidenced from 146 °C down to 27 °C for molar $n_{\text{water}}/n_{\text{DETA}}$ ratios ranging from 0 to 2, evidencing the direct role of H₂O in the polymerization reaction³⁵. These findings are likely related to the creation of a set of hydrogen bonds involving water molecules^{18,19,36,37}, thereby limiting the formation of the polymer network. Although to a lower extent compared to bulks (for $n_{\text{water}}/n_{\text{DETA}} = 2$, the decrease of T_g was only of 10 °C compared to the case of bulks where a difference of about 120°C was noticed), the T_g value of films was also affected by the presence of water. This noticeable difference of behavior between bulk and film T_g values can be explained by the presence or absence of the aluminum substrate which seems to contribute to the stabilization of the interphase area (which exhibits a typical thickness of around 300 μm as demonstrated previously)¹¹. In this interphase area, when a metal substrate is present, amine-metal surface complexes are formed^{12,13}. Water molecules may then exert an effect on the formation/stability of such amine-metal complexes, thus affecting the thermal properties of the final polymers. With the view to examine in depth the role of water when a metal substrate is present (here in the form of Al powder), we have carried out in the following a dual experimental (essentially via mixing calorimetry) and computational exploration (DFT and Monte Carlo simulation).

3.2. Influence of water on the DETA/Al interaction

In order to investigate from a thermodynamic point of view the potential role of water in the amine-metal interaction, a series of mixing calorimetry experiments was carried out by adding increasing water contents in either the DETA or the Al compartment of the calorimetry cell. For these experiments, the amounts of DETA and of aluminum powder were kept constant,

respectively equal to 1.5 g and 100 mg, and the only variable was the amount of incorporated water in either the upper or lower compartment of the calorimeter cell (**Figure S2**).

In a first stage, DETA was contacted with water during the calorimetry setup, thus prior to heat flow recording, and the {DETA-water} mixture was allowed to react with the Al powder after temperature equilibration and upon rupture of the membrane.

Figure 1 (black curve, ■ symbols) reports the evolution of the corresponding enthalpy of reaction, $\Delta_R H$, as a function of the water content. A proportionality relationship between the enthalpy of reaction and the $n_{\text{water}}/n_{\text{DETA}}$ molar ratio was observed, with a slightly negative slope of -0.1 kJ/mol H_2O (raw value: -142.41 ± 0.03 J/mol) for 1.5 g DETA. The order of magnitude of this value remains rather low, unveiling a situation where the addition of water has only a limited effect on the heat of interaction between {DETA-water} and Al. In other words, the enthalpy value remains close to the value found for the DETA/Al system exempt of water (= ordinate at origin of this black curve) for $m_{\text{Al}} = 100$ mg, meaning that aluminum interaction with water, if any, is not noticeably energetic. To confirm this point, we have in parallel run a set of experiments to follow the Al-water reaction (**Figure S3**). Note however that, in the absence of water, this DETA/Al interaction as presented earlier ² becomes preponderant.

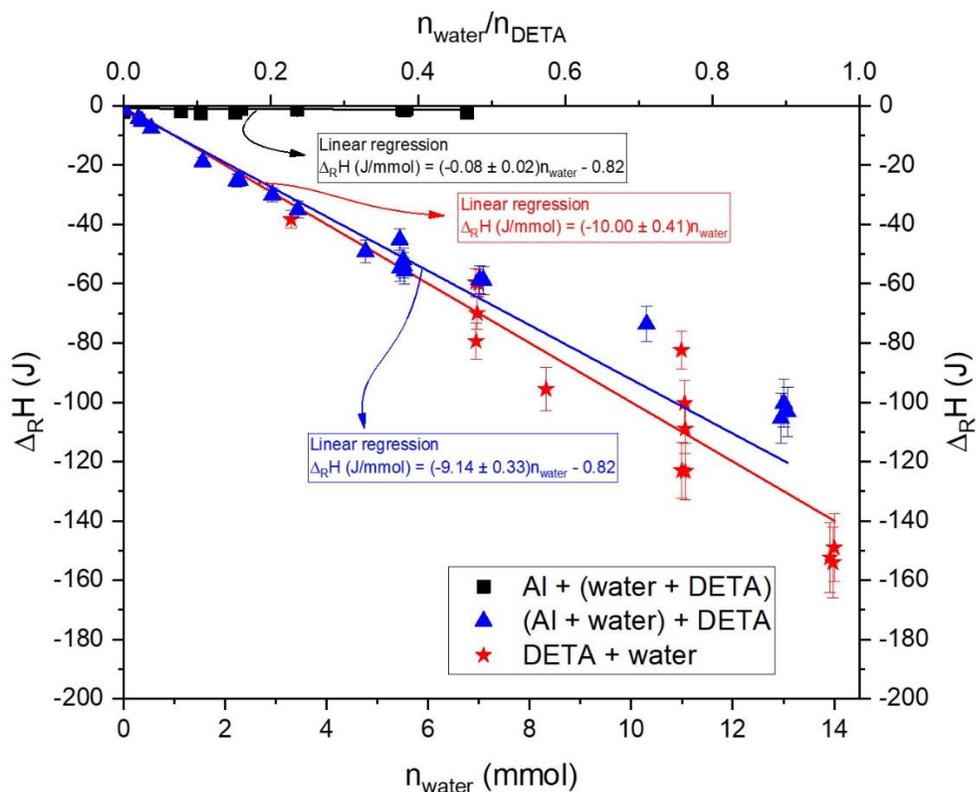


Figure 1: Enthalpies of reaction $\Delta_R H$ between DETA, water and aluminum powder, as a function of the molar ratio $n_{\text{water}}/n_{\text{DETA}}$.

In a second stage, the water was added to the Al (hydr)oxidized powder at the time of the calorimetry setup, and the equilibrated {Al-water} mixture was allowed to interact with pure DETA after rupturing the Teflon® membrane separating the two compartments of the calorimeter cell, leading to the blue curve (**Figure 1**, ▲ symbols). In contrast to the preceding case, a significantly more negative slope, about 100 times, was noticed in these conditions reaching -9.98 ± 0.02 kJ/mol H₂O (for 1.5 g DETA). These findings thus evidence the highly exothermic character of the {Al-water} + DETA interaction.

Comparing the two curves allows hypothesizing that contact between DETA and H₂O molecules may contribute by an important exothermic effect, which will be examined in the next section.

3.3. Investigation of the DETA-water interaction: experimental and computational approaches

Previous studies by DSC or molecular dynamics were run on polymerized systems formed from epoxide monomers and amine hardeners, and have suggested that the (polar) water molecules could interact with the non-binding doublet of nitrogen atoms from the amine component in epoxy-based networks^{16,37,38}. However, to date, no mixing calorimetry study nor direct enthalpy measurements, allowing us to confirm this kind of interactions when amines and epoxide are put in contact, have been reported to the best of our knowledge. Therefore, in the next series of experiments, the DETA-water interaction, in the absence of aluminum, was scrutinized (up to $n_{\text{water}}/n_{\text{DETA}} = 1$) by following the effect of an increasing amount of water contacted with 1.5 g DETA (**Figure 1**, ★ symbols). The data shows again a highly exothermic trend, with a slope (within the propagated uncertainties) similar to the one observed in the previous case corresponding to the {Al-water} + DETA interaction. It strongly suggests that the presence of aluminum in such conditions has almost no detectable effect on the measured heat of interaction.

The above findings thus demonstrate the existence of a strong exothermic event occurring when DETA molecules are contacted with water (independently on the copresence of Al). It thus appears relevant at this stage to further examine the possible mode of interaction between aminated molecules such as DETA and circulating water molecules.

To explore the origin of this strong exothermic effect, the acid-base character of DETA could first be questioned. Indeed, this triaminated molecule exhibits, in its neutral form, two primary (-NH₂) and one secondary (-NH-) amino groups. In aqueous medium, these amino groups are susceptible to get protonated or remain neutral dependently on the pH. Although some pK_a values

may be found in the literature for DETA^{39,40}, a discrepancy occurs among these sets of data. With the view to clarify this point, a pH-based titration was undergone here from an aqueous solution of DETA. First, HCl was used as titrating agent to probe the wide 0.5-12 pH range, and then H₂O was used as a weak provider of H₃O⁺ to scrutinize with more details the 11-12 pH domain (**Figure 2**). These experiments allowed us to refine the pK_a values of DETA in aqueous medium, leading to pK_{a1} = 11.9 ± 0.1, pK_{a2} = 9.6 ± 0.1, and pK_{a3} = 8.8 ± 0.2. Taking into account the generally easier protonation of secondary amines, it appears reasonable to attribute pK_{a1} to the protonation of the secondary amine, and the two other (rather close) pK_{a2} and pK_{a3} to the protonation of the two primary amines. These results point out in particular that the highest pK_a value involving DETA is pK_{a1} = 11.9. Yet, pH measurements made after calorimetry experiments indicated a final pH systematically close to ~14, and thus significantly more alkaline than pH = 11.9. Consequently, if the DETA-water interaction occurring in the calorimeter is considered in first approximation as an “aqueous medium”, these findings indicate that the DETA molecule could not lead to protonated forms and should remain neutral. In other words, if considered as a “regular” aqueous reactant, DETA should not modify its speciation in these conditions, which rules out the possibility of an acid-base reaction to explain the exothermic effect observed.

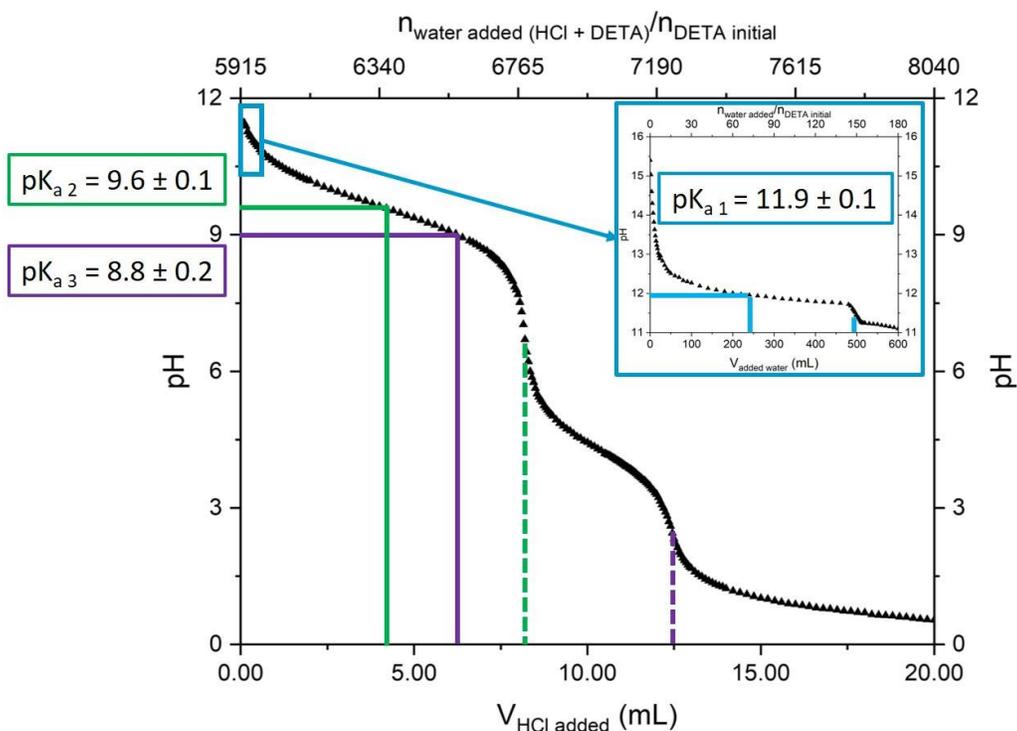


Figure 2: Titration of a DETA solution (0.01 M) by a HCl solution (1.20 M) by pH monitoring. Inlet: zoom in the pH range 11-16 via DETA titration with water.

Explanation of the strong exothermic character of the DETA-water interaction measured by calorimetry thus cannot be based on “regular” aqueous medium considerations. In contrast, since DETA remains largely predominant throughout the calorimetry experiments, it should probably be instead considered as an “organic” medium, with water acting as a “perturbation” agent. In order to examine further this phenomenon, and investigate the possible speciation of DETA in such an “organic” medium, DFT calculations were carried out. With the view to explore the widest panel of possible speciation, DETA was considered with various charges ranging from -3 to +3 by either proton departure(s) or proton fixation(s) upon interaction with water, thus generating H_3O^+ or OH^- ions as secondary species (**Figure S4**). These calculations were performed using 4 different functionals, with different levels of consideration of dispersion effects. Results indicate

systematically that neutral DETA is more stable than its protonated or deprotonated forms. Furthermore, as few differences were obtained as a function of the functionals considered in the calculations (except for B3LYP), we carried out the other calculations only with GGA PBE.

The above findings thus strongly suggest that in all cases, the DETA molecule likely keeps its neutral form upon interacting with water, including in the calorimeter conditions where DETA remains largely predominant. Thus, again, a change in DETA speciation cannot explain the exothermic character observed, even if considering the medium as non-aqueous. The DETA-water interaction should therefore allow heat production via other processes, e.g. involving a network of hydrogen bonds. To further investigate this point, we have extended the experimental range of water addition to the DETA contained in the calorimeter cell until $n_{\text{water}}/n_{\text{DETA}} = 8$. As depicted on **Figure 3**, a rather monotonous evolution of $\Delta_{\text{R}}H$, becoming growingly exothermic, may be evidenced upon addition of water until a value of $n_{\text{water}}/n_{\text{DETA}} \approx 5$ as evidenced by the dotted black line on **Figure 3**, beyond which a clear drop of slope is seen.

To complete this study, DGEBA/water interaction was also examined in a similar way. For these experiments, the amount of DGEBA was constant for all experiments (equal to 2.5 g) while the added water amount was increased (from 66 mg to 265 mg). Contrary to the DETA-water interaction, the DGEBA/water interaction generated an endothermic effect rather than exothermic (denoting an energetically unfavorable process) and with a significantly lower magnitude, around +600 mJ for $n_{\text{water}}/n_{\text{DGEBA}} = 2$. In order to compare this DGEBA/water results to the DETA/water ones, it can be noted that the stoichiometry of the DGEBA/DETA polymer should be considered. The $n_{\text{water}}/n_{\text{DETA}}$ (which is described here between 0 and 5, **Figure 3**) and the $n_{\text{water}}/n_{\text{DGEBA}}$ (between 0 and 2) ratios can thus be compared considering the stoichiometry relation between DETA and

DGEBA monomers. These data show that water essentially interacts with the amine hardener (DETA in this case) of such epoxy-amine-based systems.

The results of **Figure 3** point out a characteristic feature when 5 H₂O molecules are present per DETA molecule. This could remind the 5-fold functionality of this amine (**Figure S1**) exhibiting 5 protons from the 3 amino groups. One hypothesis to explain the DETA-water interaction at this point could thus be found in a hydration phenomenon, assuming that each proton could be associated with one water molecules via H-bonding to the oxygen atom of the water molecule.

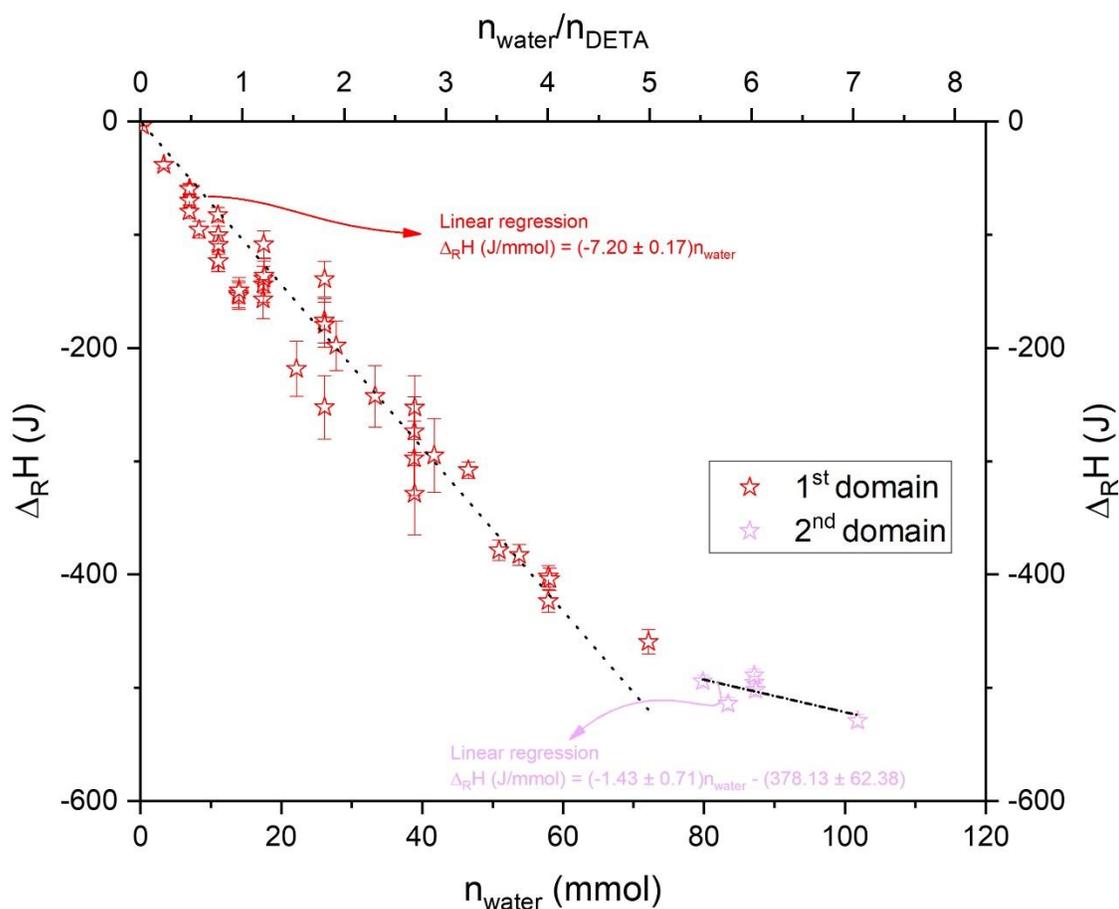


Figure 3: Enthalpy of reaction Δ_{RH} between DETA and water, as a function of the molar ratio $n_{\text{water}}/n_{\text{DETA}}$ in the range 0-8

In order to examine in detail this possibility, DFT simulations were carried out by considering one (neutral) DETA molecule surrounded by up to 8 H₂O to cover the experimentally evaluated range (**Table 2**). The different possible configurations are described on **Figure S5**. The calculations were run with the PBE GGA function with the view to evaluate the global energy of the system and its geometry, starting from initial proximity between the oxygen of water and protons from the amino groups for the 5 first H₂O molecules (taking into account the 5-fold proton functionality of DETA). Then, the 3 additional H₂O molecules were placed near the 3 N atoms (bearing non-bonding doublets) of DETA. Note that the global energy obtained corresponds to the energy of each final system considered. In order to discuss the difference of stability between all of these DETA/water configurations, it is necessary to apply in each case an adequate thermodynamic cycle (reported on **Figure S6**) to determine the interaction energy per water molecule. As may be seen in **Table 2** (third column), our simulation results point to favorable water/amine interactions in all scenarios considered, with significantly negative interaction energies. The hypothesis of DETA “hydration” upon contact with water molecules therefore seems appropriate to explain our experimental and calculated findings. It may be remarked in particular that, for the first water molecule, our calculations point to a higher stability of the DETA_1 H₂O system involving the secondary amine rather than a primary amino group (-45.4 versus -7.0 kJ/mol H₂O). Then, no specific trend can be outlined for an increasing number of H₂O molecules, and a mean value around -45 kJ/mol can be considered. In the literature, one study reported enthalpies of solvation of some alkylamine molecules in water ⁴¹, and another paper ⁴² pointed out the relationship between the length of the alkyl chain in these aminated molecules and the evolution of the exothermic effect. Although DETA was not considered in these studies and exhibits a chemical composition more complex than alkylamines, the order of magnitude reported

for the corresponding solvation enthalpies (between -46 kJ/mol for the shortest amine molecule – methylamine – and -66 kJ/mol for 1-hexylamine ⁴¹) is similar to the one found in the present work.

Table 2: Energy and modes of interaction for DETA_x H₂O systems (with x ranging from 1 to 8)

Modeled system*	Interaction energy (kJ/mol)	Interaction energy (kJ/mol per water molecule)	Modes of interaction
DETA_1 H ₂ O prim	-37.0	-37.0	N _{DETA} -H _{H2O}
DETA_1 H ₂ O sec	-45.4	-45.4	
DETA_2 H ₂ O prim	-84.7	-42.3	
DETA_2 H ₂ O prim&sec	-86.0	-43.0	
DETA_3 H ₂ O	-132.2	-44.1	
DETA_4 H ₂ O_2	-195.6	-48.9	N _{DETA} -H _{H2O} H _{DETA} -O _{H2O} H _{H2O} -O _{H2O}
DETA_4 H ₂ O_3	-191.7	-47.9	
DETA_5 H ₂ O_A	-244.9	-49.0	
DETA_5 H ₂ O_B	-220.8	-44.2	
DETA_5 H ₂ O_C	-213.8	-42.8	
DETA_5 H ₂ O_D	-217.8	-43.6	
DETA_6 H ₂ O	-268.2	-44.7	
DETA_7 H ₂ O	-290.2	-41.5	
DETA_8 H ₂ O	-315.3	-45.0	

*see **Figure S5** for detailed configurations

A deeper analysis of these results may also allow identifying the preferred reaction sites of DETA for water molecules and related modes of interaction, which have been added to **Table 2**. For the DETA_x H₂O systems up to 3 H₂O, only one type of hydrogen bond seems to be generated, namely N–H between the N atoms of DETA and an H atom of water. Beyond x = 3, the supplementary water molecules are involved in additional H–O hydrogen bonds formed between protons from amino groups of DETA and the oxygen of H₂O. Also, the formation of H–O bonds among H₂O molecules themselves was noticed for x ≥ 4.

In order to approach one step further “real” experimental conditions (which start from pure liquid DETA) encountered in calorimetry, it is possible to increase the complexity of the systems considered in the DFT modeling. To this aim, second runs of calculations have been performed by integrating the fact that such a solvation phenomenon likely necessitates the separation of adjacent DETA molecules (and thus the weakening the H-bonding network among DETA molecules) so as to allow water “intercalation”. For these calculations aiming more realistic outcomes, we have thus considered adding a second molecule of DETA in the configurations previously studied. Two possible scenarios have been explored, starting from either two isolated DETA molecules or from a pre-existing {DETA-DETA} interacting network. These DFT simulations were made for x from 0 up to 5, as no convergence was found beyond this value due to the flat energy landscape involving hydrogen bonds. **Figure S7a** summarizes the different {DETA-DETA/water} configurations along with the obtained interaction energies. With the intention of examining these scenarios, the only difference is in the thermodynamic cycles which have to be considered (see **Figure S7b** for an example of thermodynamic cycle in the case of pre-existing {DETA-DETA} interactions, and **Figure S7c** for an example starting from two isolated DETA molecules). It may be noted that, according to the values obtained, it is energetically more favorable to start from 2

isolated DETA than two DETA in interaction for all configurations, suggesting that it is more difficult – less thermodynamically favorable – to break bonds between two DETA chains to develop new bonds with water molecules. However, in real experimental conditions, the pure DETA used as reagent most likely involves pre-existing interactions between adjacent molecules. Thus, in the rest of the study, the configurations involving two adjacent DETA molecules was considered.

As for the simplistic {DETA_x H₂O} systems mentioned previously (see **Table 2**), the interaction energies obtained per water molecule for all the {DETA_x H₂O_DETA} configurations (**Figure S7a**) are again of the same order of magnitude, around -55 kJ/mol, and close to the one reported for amine hydration ⁴².

A deeper analysis of the results can be made by examining one by one the different scenarios for an increasing number of H₂O intercalated molecules, as depicted in **Figure S8** and described in the following.

For {DETA_x H₂O_DETA} with x = 1, three calculations were performed by considering water interaction between either the primary or secondary facing amino (**Figure S8**). The case where H₂O would interact with one primary amine of the first DETA molecule and the secondary amine from the second DETA molecules was clearly found to lead to the least stable configuration (interaction energy -2.7 kJ/mol H₂O). Indeed, in this case, the water molecule stays close to one DETA chain while the other DETA molecules separates from the {DETA_H₂O} system, thus approaching the simplified scenario with a single DETA molecule discussed on **Figure S5**. The other two configurations (between only facing primary or only secondary amines) thus appear much more probable, with respectively -43.5 and -55.6 kJ/mol H₂O. The latter being more negative thus suggests that intercalation of 1 H₂O between 2 DETA would be favored between the two

secondary amines, which agrees also with our conclusions drawn from the simplified scenario discussed above with a single DETA molecule. In such {DETA_1 H₂O_DETA} systems, three modes of H-bonding interaction are observed. For {DETA_1 H₂O prim_DETA}, two hydrogen bonds are developed between the H₂O and DETA, namely N_{DETA prim}-H_{H2O} and H_{DETA prim}-O_{H2O}. In contrast, the {DETA_1 H₂O sec_DETA} and {DETA_1 H₂O prim&sec_DETA} configurations only developed one of these two types of H-bonds, respectively N_{DETA prim}-H_{H2O} only and H_{DETAprim}-O_{H2O} only.

For x = 2, it can be noted that the configuration leading to the highest stability appears to be {DETA_2 H₂O prim&sec_DETA} involving the primary and secondary amines. Two modes of interaction can then be outlined, namely N_{DETA sec}-H_{H2O} and a bridging H₂O molecule connecting to the two primary amines through its H atoms.

For x = 3, all of the above-mentioned interactions are developed, i.e. N_{DETA sec}-H_{H2O} and H_{DETAprim}-O_{H2O}, N_{DETA prim}-H_{H2O} and a bridging H₂O with primary amines, as illustrated in **Figure 4**.

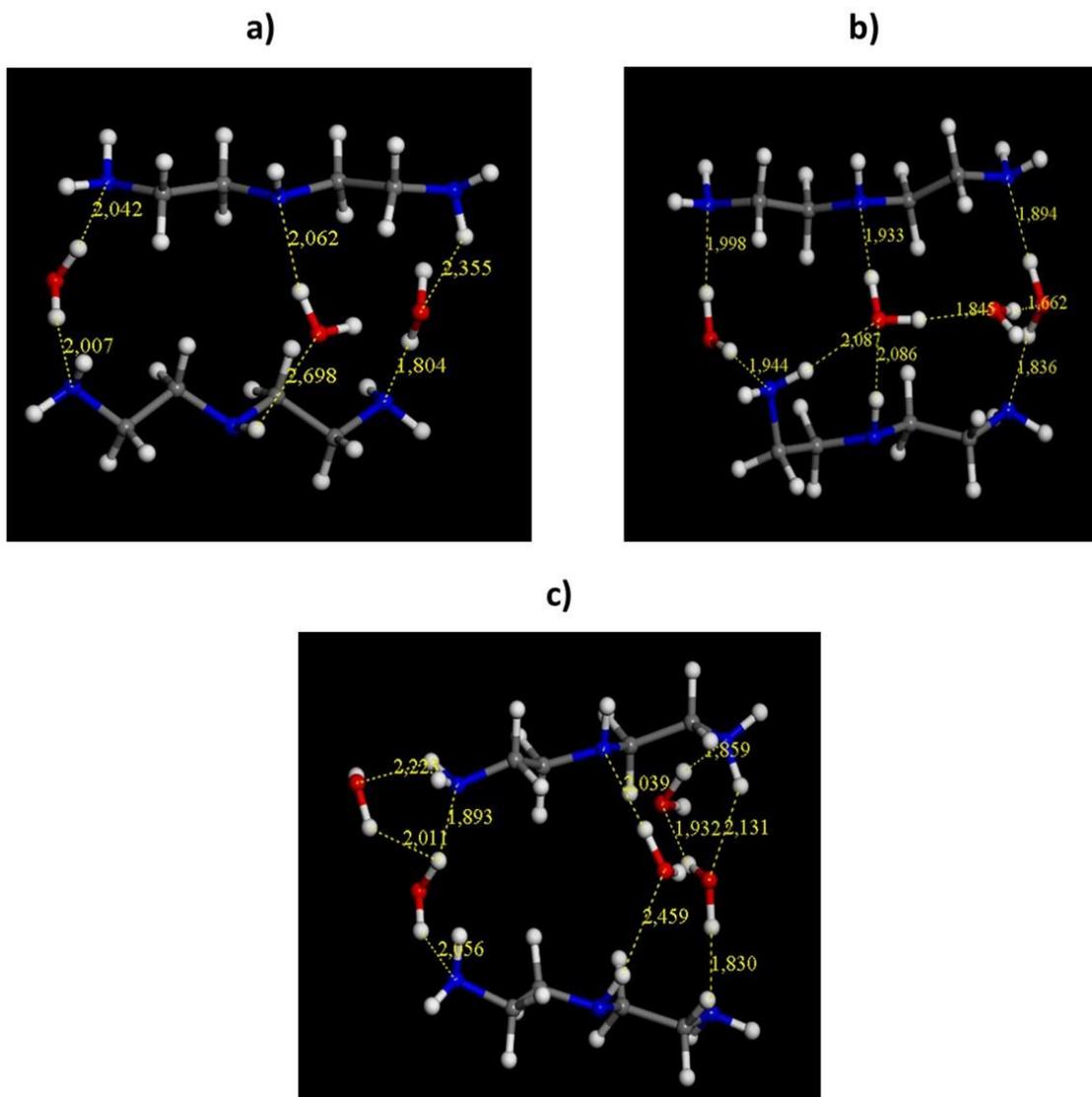


Figure 4: Representation of the most stable final configurations for {DETA-x H₂O-DETA} with x = 3(a), 4(b) and 5(c) after DFT calculations; red balls correspond to the oxygen atoms; blue balls correspond to the nitrogen atoms; white balls correspond to the hydrogen atoms.

For x = 4, calculations were performed starting from this {DETA_3 H₂O_DETA} result and adding one H₂O molecule. Three scenarios were considered (**Figure S8**), and the most stable

configuration was obtained for the fourth H₂O interacting with 2 other H₂O molecules plus the formation of a new hydrogen bridge with the two secondary amines.

Finally, for $x = 5$, we added two water molecules to the {DETA_3 H₂O_DETA} system, initially positioned near two primary amines from the same DETA molecule. After computation (at convergence), these two additional H₂O molecules moved closer to the pre-existing bridging H₂O molecules to develop further H- bonds for increased stability of the system.

All of the above results therefore allow better understanding the type of interaction that may occur between DETA and H₂O molecules, which generated a strong exothermic effect quantified by mixing calorimetry and directly related to the H₂O/DETA molar ratio, especially from 1 to 5 H₂O per DETA molecule (see **Figure 3**). Our calculations strongly suggest the incremental formation of a network of hydrogen bonds that is bound to generate stabilizing conditions as inferred by the negative interaction energies involved. Despite more negative mean energy values accessed from DFT, around -55 kJ/mol H₂O, they remain of the same general order as the experimentally measured enthalpy -7.2 kJ/mol H₂O; especially keeping in mind that DFT calculations are carried out at 0K and with a restricted number of DETA and H₂O molecules to model the {DETA_H₂O} system.

In order to further validate the coherence of these calculations, using the GGA PBE function, with regard to experimental results, the infrared (IR) spectrum of DETA was computed from our DFT data and compared to the experimental reference spectrum of the DETA specimen used in calorimetry. As may be seen in **Figure 5**, the calculated IR features considering “isolated” DETA (black curve) led to a general pattern in good agreement with the experimental reference spectrum (red curve), thus confirming the validity of the DFT parameters used in this work and evidencing the consistency of the theoretical results compared to experiments. It may also be noticed that an

even better concordance in the 3300-3600 cm^{-1} region can be accessed between simulated and experimental IR spectra, by considering the DETA-DETA system (implying an existing network of H-bonds between DETA molecules) as described in **Figure S7**. This spectral region corresponds to the N–H stretching vibration of amino groups (whether from primary or secondary amines), which is indeed prone to be modulated by H-bonds among adjacent DETA molecules.

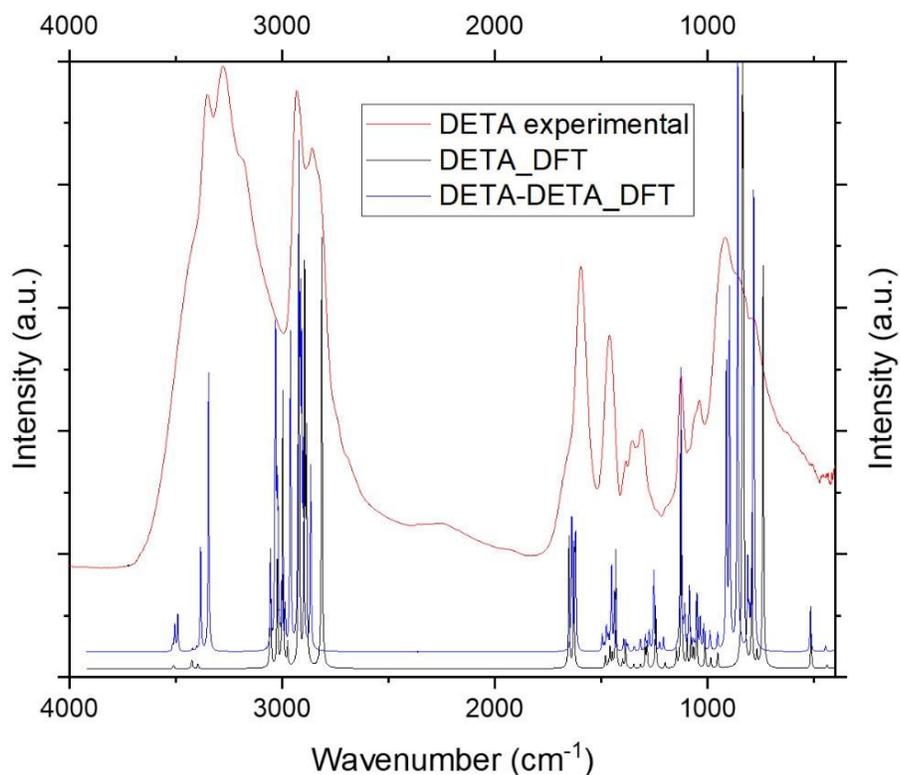


Figure 5: Experimental (red curve) and computed infrared spectra of the DETA molecule: DETA considered alone (black curve) or DETA in interaction with a second DETA molecule (blue curve)

In order to probe a more complete system, Monte Carlo simulations allowed us to take into account more atoms. We therefore investigated {DETA- H_2O } and {DETA- H_2O -DGEBA} systems. Using the procedure presented in Materials and Methods, it is possible to extract the

plausible configuration corresponding to the lowest energy. In the case of {DETA-H₂O} systems, Monte Carlo simulations show that a large amount of water molecules compared to DETA (see **Figure 6-a**) imposes to the DETA to interact with strong hydrogen bonds (similar distances ranging from 1.9 to 2.2 Å for both H₂O-H₂O and H₂O-DETA while DETA-DETA interaction is lower (distances of 2.3-2.7 Å) according to Monte Carlo simulations). However, in the case of a low amount of water and large amount of DETA, the situation is different. Indeed, water molecules interact with some DETA molecules but prefer to interact with other water molecules, while DETA molecules interact with each other (see **Figure 6-b**). Furthermore, according to Monte Carlo simulations and in good agreement with our DFT calculations, water interaction occurs mainly on the secondary amine of DETA (as observed at low loading of DETA).

When we consider the complete system, in the presence of DGEBA (see **Figure 7**), strong interactions between water molecules, between water molecules and DGEBA, and between DGEBA and DETA can be observed. However, the density of presence shows that groups of interacting molecules are formed (clustering tendency).

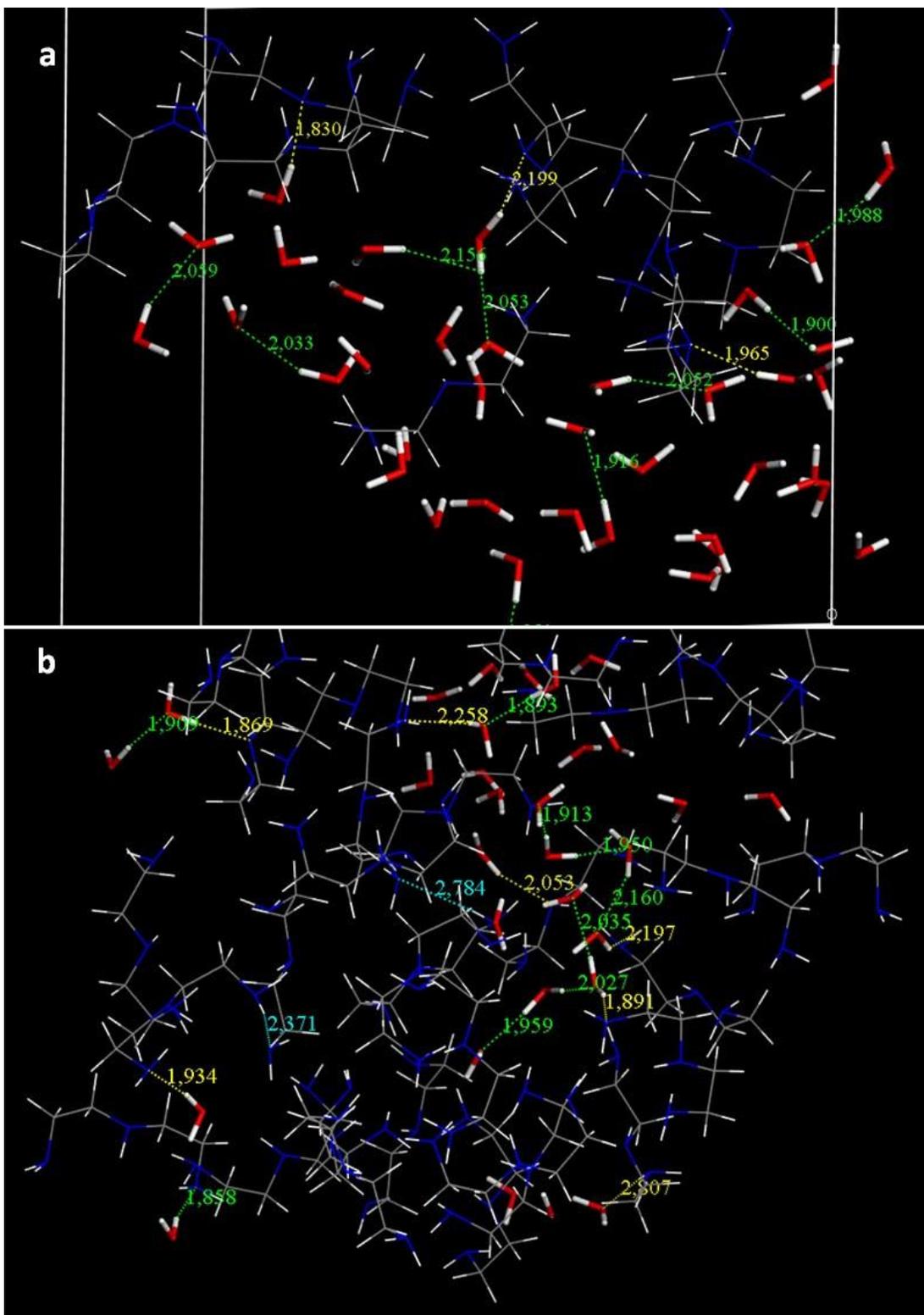


Figure 6: Configurations extracted from Monte Carlo simulations for {DETA-H₂O} systems at low concentration (a) and large concentration (b) of amines. The atoms are represented in color:

white = H, blue = N, grey = C, red = O. The distances in yellow, green and blue correspond to distances between amine-water, water-water and amine-amine.

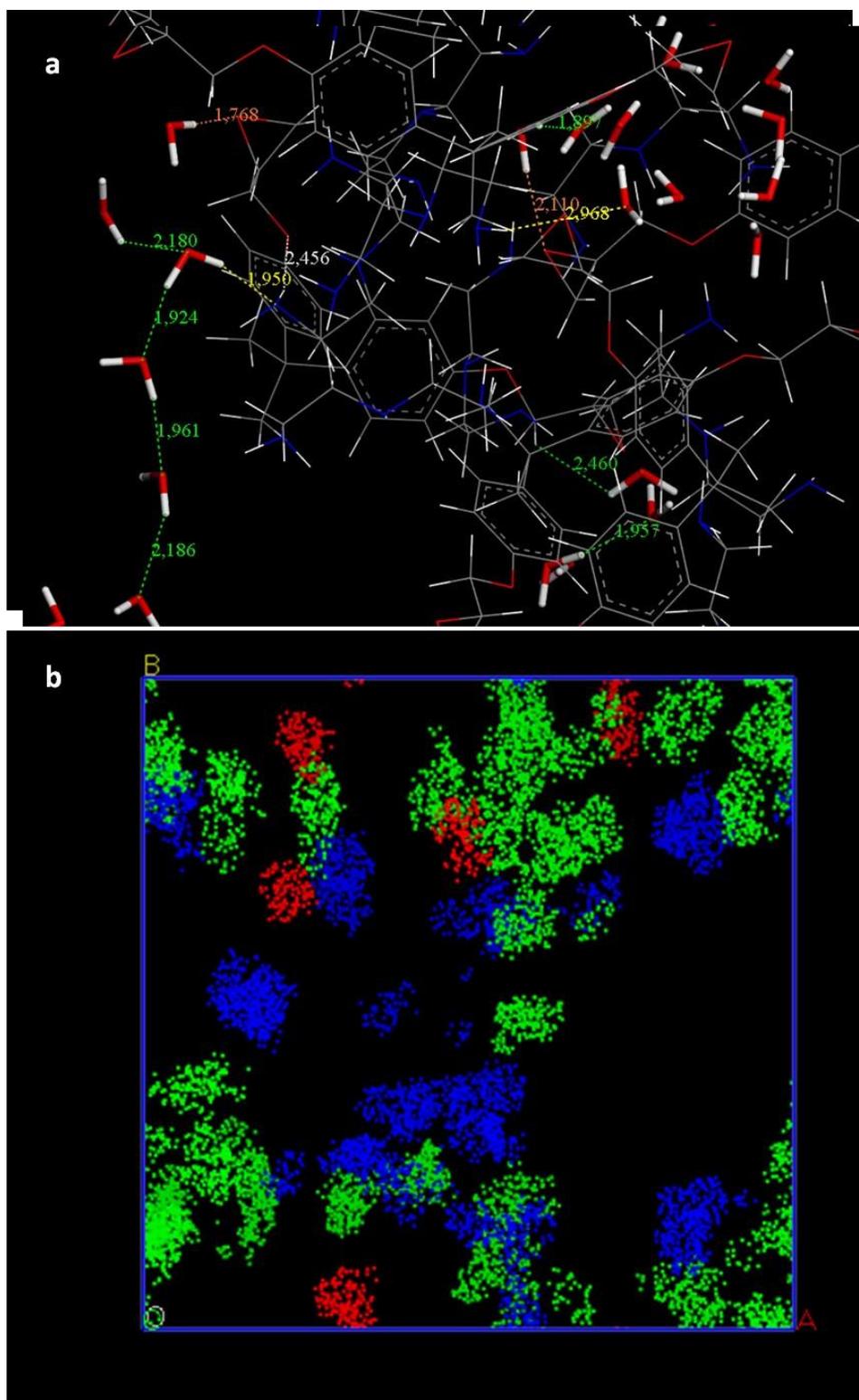


Figure 7: Configurations extracted from Monte Carlo simulations for {DETA-H₂O-DGEBA} systems (a) and density of presence (b). The atoms are represented in color: white = H, blue = N,

grey = C, red = O. The distances in yellow, green, orange and white correspond to distances between DETA-water, water-water and DGEBA-water and DGEBA-DETA. In figure b, the green, red and blue zones correspond to the density of presence for water, DGEBA and DETA respectively.

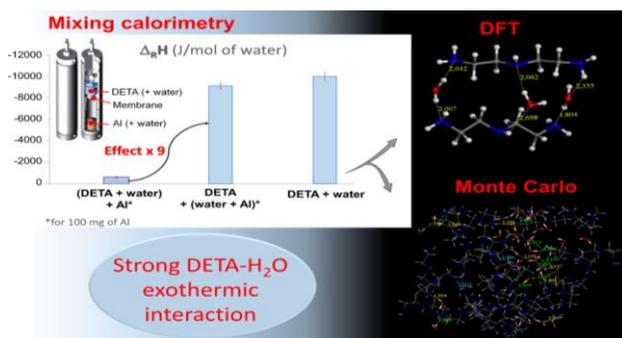
The above conclusions drawn both from IR spectral comparisons and from Monte Carlo assessments concur to show the relevance of taking into account the existence of initial molecular interactions among DETA molecules.

4. Conclusions

In this contribution on epoxy/amine-metal systems, we investigated for the first time the role of water as a potential 4th component produced in the suggested mechanism of interphase formation. The direct influence of the water content on the thermal properties of the obtained polymers was quantified by DSC, and could be related to previously reported results on the DETA-Al system. The *in situ* formation of DETA-Al interphase was scrutinized by mixing calorimetry in the presence of added amounts of water. Upon H₂O addition, a linear relationship was obtained between the enthalpy of interaction and the $n_{\text{water}}/n_{\text{DETA}}$ molar ratio. The {DETA-water} interaction was in particular found to be highly exothermic, and the underlying mechanism between these two molecular species was investigated through a first hypothesis of an acid-base reaction, which was ruled out in our experimental conditions, and a second hypothesis of DETA hydration, which was confirmed by DFT and Monte Carlo simulations. The comparison of experimental and computed IR spectra on DETA showed a very good agreement, confirming the validity of the simulation parameters used in this work. Consideration of a pre-existing network of H-bonds among adjacent

DETA molecules appeared particularly well suited to model all experimental data. This work demonstrates that water may indeed act as an additional component in epoxy-amine-based systems, and should probably also be considered in similar systems where H₂O could either be initially present or released upon formation of surface complexes on solid substrates.

Table of content graphic



Author contributions

Zineb Fritah: Experimental and DFT investigation, writing original draft

Christophe Drouet: Writing original draft, supervision, conceptualization

Fabrice Salles: DFT investigation, writing Monte Carlo results, supervision

Olivier Marsan: Infrared spectroscopy investigation

Maëlen Aufray: Writing original draft, conceptualization, supervision

Supporting Information (PDF file)

Figure S1: Chemical formula of the DGEBA and DETA monomers used in this study

Figure S2: Description of the three possible setups used in the *in situ* mixing calorimetry

Figure S3: Study of the Al-water enthalpy of interaction

Figure S4: Determination of the more stable charged structure of DETA by DFT calculations

Figure S5: DFT calculations: final configurations for DETA_xH₂O systems and resulting modes of interaction

Figure S6: Thermodynamic cycles for studying {DETA-water} system

Figure S7: Stability of DETA-water-DETA systems (DFT approach) with examples of thermodynamic cycles considered

Figure S8: DFT calculations: final configurations for DETA_xH₂O_DETA systems and resulting modes of interaction

Acknowledgements

This project was supported by the Chimie Balard CIRIMAT Carnot Institute through the ANR program N°16 CARN 0008-01.

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