

6. Spatio-temporal BRILLOUIN microscopic investigations of unstable liquid-liquid interfaces

Widespread research topics in natural and physical sciences deal with the structure and properties of liquid-liquid interfaces (e.g. JONES 2002). Current research problems in the field are the stability of dispersions in dependence of surfactants, the optimization of chemical reactions occurring at liquid-liquid interfaces, the modelling of biological membranes by means of liquid-liquid interfaces, etc. From the thermodynamic viewpoint stable, metastable and unstable interfaces between liquids need to be discriminated. Note that in general a system containing an unstable interface equilibrates until the chemical affinity, but not necessarily the concentration of molecular species, is identical throughout the whole system (JONES 2002).

In immiscible liquids or in miscible liquids which are under the given external conditions within their miscibility gap, stable liquid-liquid interfaces are created during the spatial equalization of the chemical affinity. For miscible liquids, the careful pouring of one liquid on top of the other leads to diffusive mixing processes through the interface. Instabilities of the interface can in addition give rise to convective transport processes (SAFFMAN & TAYLOR 1958, PODGORSKI *et al.* 2007). In the case of reactive liquid components, special attention must be paid to the specific molecular interactions and the long-lived or transient character of the created molecular structures. As the elastic properties vary in a highly sensitive way upon changes of molecular interactions and density, the spatial resolution of elastic properties at interfaces appears especially adequate.

The interfacial processes discussed in section 6.2 for water and diethylene triamine, which form transient molecular structures, makes one sense how complex the way to a homogenization of the whole system can be (PHILIPP *et al.* 2009). As exemplarily shown in section 6.1, in case of covalent bond formation of reactive liquids the aspect of competing processes becomes especially relevant: the global equalisation of the chemical affinity by transport mechanisms competes with its local equalisation by molecular structure formation (SANCTUARY *et al.* 2009,

SANCTUARY *et al.* 2010, PHILIPP *et al.* 2011). Highly heterogeneous metastable structures usually result from such competitions.

The current section deals with the question what molecular acoustics can tell us about the physicochemical processes occurring at liquid-liquid interfaces. From the experimental point of view the investigation of interphases is really delicate since the interphases are often extremely sensitive to perturbations imposed by the experimental probe. As SBM measures under linear response conditions, it is really suited to probe the linear mechanical properties with a sufficient spatial resolution at the immediate interface, but also in a sufficiently large zone adjacent to it. In addition, SBM is able to resolve the temporal evolution of the related molecular acoustic changes if the latter occur on timescales of minutes until weeks.

6.1. Interplay between matter transport processes and structure formation of selected covalent bond-forming systems

At the planar interface between the resin and hardener of an epoxy the hardly accessible competition between different matter transport processes and polymerisation was studied with a special version of scanning BRILLOUIN microscopy, SBM^{180-2D} (SANCTUARY *et al.* 2009, 2010, PHILIPP *et al.* 2011). As discussed in section 3.2, compared to SBM^{0A} and SBM¹⁸⁰, this technique allows for a comparably high temporal resolution of the transient processes happening in the vicinity of liquid-liquid interfaces while keeping a high spatial resolution in two dimensions.

The same epoxy components as discussed for the epoxy-silicone rubber in section 5.3, DGEBA and DETA, were utilized. The poor miscibility of both educts (ELLIS 1993), together with the significantly higher mass density and viscosity of the resin DGEBA compared to DETA enabled us to carefully stack the hardener DETA on top of the resin. Furthermore both constituents exhibit similar surface tensions so that the interface between both liquids is almost perfectly flat. The flatness of the optical meniscus is of great importance since otherwise the incident and the scattered light beams are bent at the meniscus. If this happens, the clear definition of

the scattering volume is impeded. In favour of time-resolved SBM investigations at planar DGEBA/DETA interfaces is the fact that at room temperature the epoxy-amine reaction rate is such that significant hypersonic changes occur on the time scale of hours. The following questions are subsequently addressed: (i) How does the reaction progress at the interface? (ii) What kind of network structures are realized in the presumably formed interphase? (iii) Which matter transport processes do occur? (iv) How does the interphase develop?

The experimental investigations at the DGEBA/DETA interface lasting for about 50 h clearly reveal that these initial questions are far from sufficient to grasp the full complexity of the processes occurring at this specific liquid-liquid interface. A planar phase boundary between both liquids was created by first pouring DGEBA in a glass cuvette and by carefully layering the less viscous and less dense DETA on top of it (SANCTUARY *et al.* 2010). In figure 6.1 the hypersonic velocities and hypersonic attenuations initially expected for the resulting layered system are indicated as red lines. Due to the time necessary to prepare the sample, to position the sample in the spectrometer setup and to start the experiment this initial state cannot be experimentally accessed. For the sake of clarity, only a few spatial profiles will be discussed in the following; these are representative for the 24 datasets recorded for the DGEBA/DETA system. Further details are elucidated in (SANCTUARY *et al.* 2010).

For the layered DGEBA/DETA system, the hypersonic velocity and attenuation profiles recorded after 2.7 h show an interphase region within the hardener compartment with a width of about 2 mm, whereas the resin compartment does not seem to be altered. Hence, the trans-interfacial chemical reaction is slow in comparison to that in a well-mixed stoichiometric bulk system, for which it is finished after about 6 h (MÜLLER *et al.* 2010). This slow reaction rate at the hardener-resin interface is a first indicator for the small reaction tendency of the epoxy components at the interface, or in other words for the pronounced demixing tendency of both reactants (ELLIS 1993). We surmise that the release of resin molecules into the hardener compartment is provoked by the ‘attack’ of thermally excited hardener molecules in terms of collisions. In the hardener compartment as

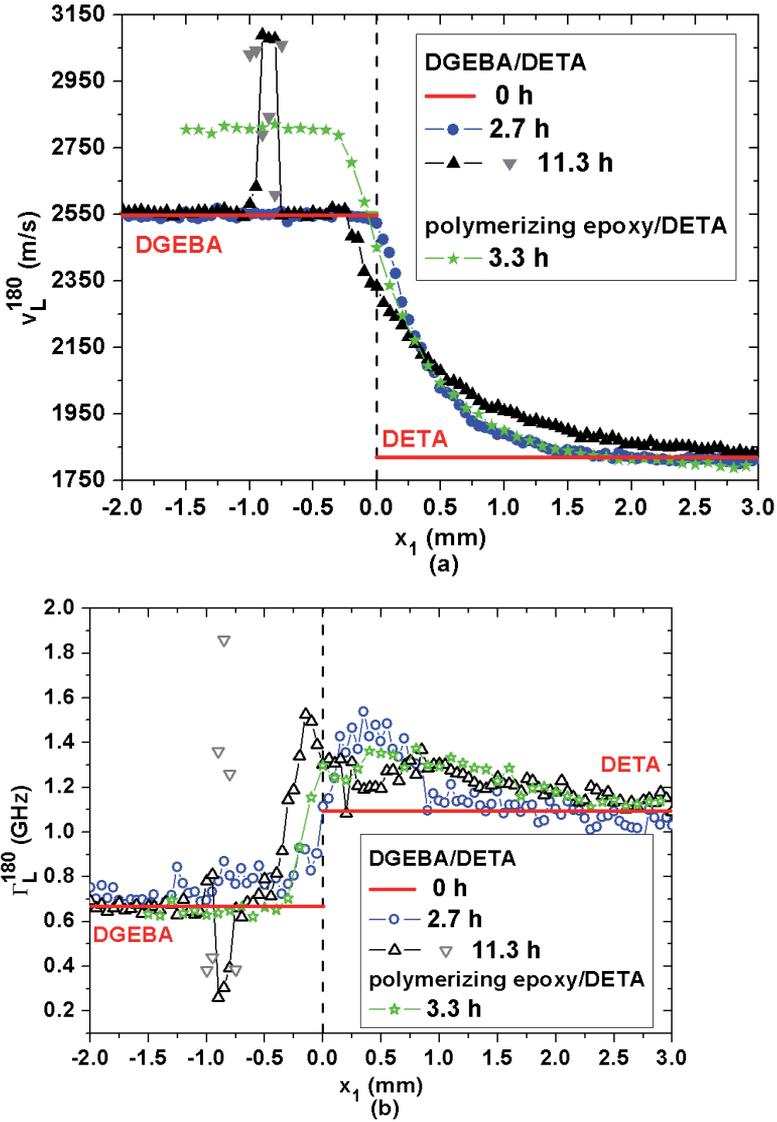


Fig. 6.1. Spatio-temporal evolution of (a) the sound velocity and (b) the hypersonic attenuation in the vicinity of liquid-liquid interfaces of the epoxy reactants DGEBA and DETA, respectively a freshly prepared polymerizing epoxy and DETA. Initial interface located at $x_1 = 0$ mm. For the profile recorded at 11.3 h two symbols are indicated as two phonon doublets are observed for several scattering volumes.

soon as the resin molecules are molecularly dispersed within DETA, they react with DETA according to the kinetics of the related well-mixed epoxy composition. The ensuing reaction products exhibit a good chemical compatibility with both epoxy reactants so that they can be dissolved and transported deep into the low viscous hardener phase (SANCTUARY *et al.* 2010). As mass conservation is of course valid, the DGEBA released at the interface must be missing in the bottom DGEBA-rich compartment. This conclusion cannot be directly drawn from the sound velocity profile as v_L^{180} remains constant within the bottom compartment. Actually, already a few DGEBA molecules can lead to an important sound velocity increase in the interphase zone placed within the DETA compartment, due to the dramatically changed dynamic acoustic behaviour. The sound attenuation data of figure 6.1b clearly reveal that the molecular acoustics have significantly changed within the interphase zone.

Figure 6.1 includes the spatial profile recorded after similar times for a layered system containing an almost stoichiometric polymerizing epoxy (100/10) in the bottom compartment and DETA in the upper one (for any details, see PHILIPP *et al.* 2011). The interphase zone in the upper compartment is similar to that of the DGEBA/DETA sample, but obviously reaches much deeper, about 0.3 mm, into the bottom compartment. Hence, the above stated poor miscibility of the epoxy reactants can indeed be improved by molecularly dispersing DETA molecules into the bottom, DGEBA-rich compartment.

After 11 h the interphase region of the DGEBA/DETA sample extends to about 3 mm into the hardener compartment. But most astonishingly, a region possessing sound velocities comparable to those of glassy epoxies ($v_L^{180} \approx 3100$ m/s, SANCTUARY *et al.* 2010) is observed within the resin compartment at a distance of about 0.7 mm below the initial interface. The second phonon doublet (see grey triangles in figure 6.1) observed for six positions of the scattering volume is indicative for the heterogeneity of this zone. The data are in fact representative of a chemically induced glassy epoxy embedded in gelatinous epoxy.

Really astonishing is that immediately above this heterogeneous epoxy fragment the hypersonic properties of the pure resin are still observed. The glassy

nature of the epoxy fragment embedded in gelatinous epoxy within a DGEBA-rich environment indicates that a sufficient amount of hardener had to be transported over a distance of about one millimetre through the DGEBA phase without chemically reacting during the transport. This observation is obviously incompatible with a mere diffusion through the whole initial interface. Most likely the hardener dug one or more channels into the resin layer providing a path for convective matter transport. According to literature so-called viscous fingering, provoked by gradients in the interfacial tension, could be responsible for the observations made (SAFFMAN & TAYLOR 1958, PODGORSKI *et al.* 2007).

As documented by the 18.3 h profile in figure 6.2 the glassy layer has disappeared at later stages from the scanning trace within the bottom compartment. As a matter of fact for $x_1 < -0.5$ mm the sound velocities of pristine DGEBA are measured again! This means that either the glassy epoxy fragment is afforded sufficient mobility by the embedding material to be displaced from the scanning trace or, as discussed in section 5.4, the epoxy glass is swollen and disrupted by DETA supplied via continuous convective channels and subsequently displaced from the original scattering volume. More than 20 h later, after 43 h, a new glassy epoxy fragment, located at $x_1 = -1.5$ mm, has been created in the resin compartment. An indenter test evidences that this glassy region laterally goes throughout the whole sample and that it is topped by a layer of heterogeneous, gelatinous epoxy covered by liquid material in the upper compartment. The gelatinous material consists of swollen percolated epoxy fragments. In summary, during the complex interplay between chemical affinity leading to covalent bond formation on one side and molecular transport on the other, the system has undergone chemically induced sol-gel transitions and glass transitions at various times and locations within the cuvette that lead to multipart sequences of transient polymeric morphologies.

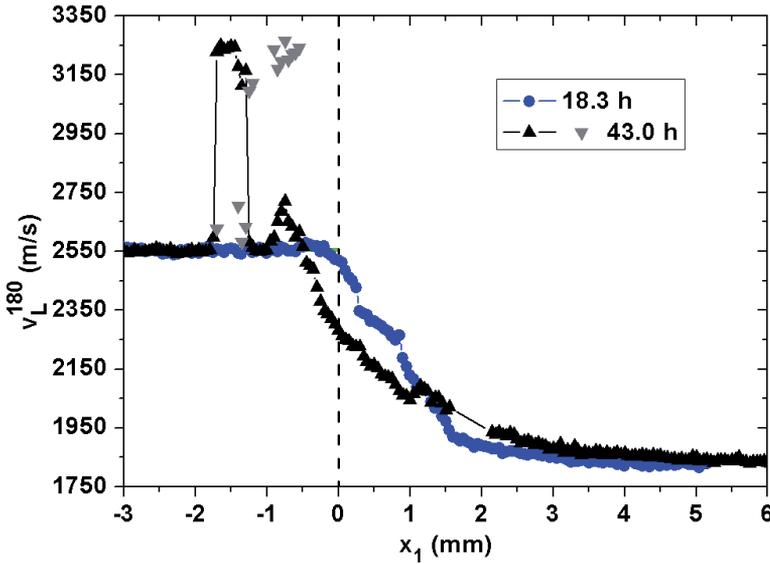


Fig. 6.2. Spatio-temporal evolution of the sound velocity in the vicinity of the initially layered DGEBA/DETA system. Grey triangles: for the profile recorded at 43.0 h a second phonon doublet was recorded for several scattering volumes.

A further question is addressed by studying planar interfaces between DGEBA loaded with alumina nanoparticles and pure DETA: how can additional interfaces, namely those created by adding nanoparticles into the resin, affect the previously observed processes in the vicinity of the planar DGEBA/DETA interface? The combination of SBM^{180-2D} and optical imaging allows discriminating between several effects, as described in detail in (SANCTUARY *et al.* 2010). We need to distinguish between effects related to the presence of the nanoparticles within the DGEBA resin (topological effects) and others related to the physicochemical surface properties of the alumina nanoparticles.

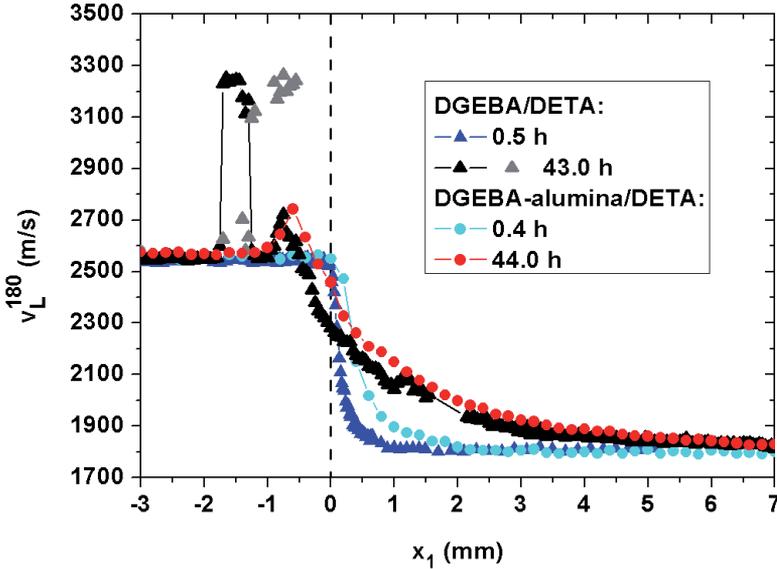


Fig. 6.3. Comparison between the spatio-temporal evolution of the sound velocity in the DGEBA/DETA and alumina loaded DGEBA/DETA systems. Dashed line: position of the initial phase boundary.

On short time scales, a faster mixing occurs for the alumina loaded system than for the pure resin/hardener system as evidenced in figure 6.3 by the significantly increased sound velocity in the upper compartment close to the initial phase boundary. After longer times, optical imaging clearly reveals that clusters of alumina nanoparticles are transported upwards over several millimetres into the hardener compartment (SANCTUARY *et al.* 2010). The unexpected transport of nanoparticle clusters having average cluster sizes around 100 nm against gravity is tentatively explained as follows: the driving force responsible for this transport likely relates to vertical gradients of interfacial tension along the surface of the particles. This gradient in interfacial tension is caused by a vertical gradient in the chemical potential due to the intermixing of resin and hardener close to the planar interface (SANCTUARY *et al.* 2010).

On the other hand, the nanoparticles act as topological disturbances and partially provoke a slowdown of matter transport through the interface. This effect is especially relevant in the bottom compartment, where the nanoparticles seem to obstruct the formation of convective flow channels deep inside this compartment. The latter point is evidenced by the absence of glassy epoxy fragments within the resin compartment until the late stages of the experiment. Figure 6.3 demonstrates this exemplarily for spatial scans recorded after about 44 h as for the alumina loaded sample only gelatinous epoxy with sound velocities of maximal 2700 m/s has formed. Underlying reasons might be a significant increase of the resin's viscosity and topological boundaries caused by the nanoparticles within the bottom compartment.

As clearly exhibited by the above elucidations, SBM^{180-2D} is highly sensitive to the specific molecular interactions and the long-lived transient character of the created molecular structures formed in layered systems of epoxy reactants. The competing processes between the global equalisation of the chemical affinity ensured by transport mechanisms and its local equalisation resulting in covalent bond formation leads in all studied systems to highly heterogeneous metastable polymeric structures.

6.2. The different acoustic and visual perception of structure formation at the interface between two miscible liquids

As already mentioned in section 4.5, structure formation can couple in different ways to phenomenological material properties. Therefore for instance optical and elastic properties may give complementary perspectives on structure forming processes.

A very illustrative example concerns the molecular structures formed in mixtures of water and diethylene triamine (DETA). As DETA is a three-dentate ligand, the arising molecular structures are not induced by covalent interactions, but by hydrogen bonding and by chelate complex formation (SMITH & MARCH 2001,

PHILIPP *et al.* 2009). These interactions are expected to lead to chemically unstable structures, which are in constant transition between different states. Diverse average molecular structures result in dependence of the mixing ratio between both liquids.

Figure 6.4a shows the mass density $\rho(c_{\text{DETA}})$ and the refractive index $n(c_{\text{DETA}})$ versus the molar DETA concentration c_{DETA} of homogeneous DETA-water mixtures at ambient temperature. Both quantities vary qualitatively in different ways as a function of c_{DETA} and hence couple differently to the molecular structure formation of DETA-water systems. Whereas the refractive index increases strictly monotonously, the mass density possesses a pronounced maximum for $c_{\text{DETA}} = 18 \text{ mol}\%$. Consequently, the validity of the LORENZ-LORENTZ relationship (BÖTTCHER 1973) fails for these mixtures when applying as usually a linear mixing rule for the specific refractivity of water and DETA (PHILIPP 2009, MÜLLER *et al.* 2010). Figure 6.4b depicts the hypersonic velocity $v_L^{180}(c_{\text{DETA}})$ and the related attenuation $\Gamma_L^{180}(c_{\text{DETA}})$ for the same compositions.

Obviously the sound velocities of the homogeneous mixtures cannot be approximated by a simple linear mixing rule applied to the sound velocities of water and DETA, because for almost all concentrations the sound velocity is larger than the one of each component! Interestingly, the maximum of the hypersonic velocity curve is shifted by about 6 mol% to $c_{\text{DETA}} = 24 \text{ mol}\%$ in comparison to that of the mass density. The differently positioned maxima of the mass density and hypersonic velocity curves clearly indicate that molecular packing and elastic interactions between molecules are to a certain extent independent. The composition of the 24 mol% DETA-water mixture suggests that almost each of the three amine teeth of the DETA molecules forms a complex interaction with one water molecule (SMITH & MARCH 2001, PHILIPP *et al.* 2009). As the hypersonic attenuation is quite pronounced for most DETA-water concentrations, the typical structural relaxation times of these samples have to lie in the nanosecond regime at 295 K (PHILIPP *et al.* 2009).

In the following we study in how far the disparate evolution of optical and acoustic properties in dependence of the DETA concentration affects the different experimental perspectives on the mixing and structure formation processes

occurring when injecting water beneath the less dense DETA. Similar to the investigations described in section 6.1, it turns out that the competing physicochemical processes are more complex than intuitively expected. For instance, the rather facile mixing and homogenisation of water and DETA in all concentrations observed during the preparation of the aforementioned samples, raises the expectation that a continuous mixing front, thus a spatially extending interphase forms between both liquids after injecting water beneath DETA. However, the formation of a rather sharp optical boundary is provoked at room temperature, which persists for several hours (PHILIPP *et al.* 2009). In contrast, the molecular acoustics as probed by SBM^{180-2D} suggest the formation of a spatially expanded hypersonic interphase from the beginning of the experiment on!

Essentially, the chemical affinity between DETA and water makes it impossible to achieve a layering of both liquids. The finally chosen preparation scenario consists in carefully injecting 1 cm³ of water underneath 2 cm³ of DETA, which leads to rapid but incomplete convective mixing, followed by gradual diffusive homogenisation. After less than one minute an optically visible phase boundary emerges, which persists for five hours.

The spatial shift of this meniscus versus time is indicated in figure 6.5. As no long-lived interface can be created between both liquids, the origin of the vertical position axis \bar{x}_1 is chosen at the bottom of the cuvette. The fact that the initial height of the bottom compartment is about 10.6 mm instead of 10.0 mm supports the argument that some DETA is incorporated in water during the initial turbulent flow. As the meniscus rises with time, DETA necessarily penetrates from the upper compartment into the bottom compartment. Therefore, at least during the first five hours, the DETA concentration within the bottom compartment must increase continuously. It is astonishing that during this period of time a sharp optical meniscus is visible between both compartments. This actually suggests that once DETA molecules cross the phase boundary they do not lead to a visible flattening of the concentration gradient at this interface. Apparently they dissolve and migrate rapidly into the bottom compartment and only increase the volume of the water-rich bottom compartment. After 26 h of the experiment the meniscus has totally blurred (PHILIPP *et al.* 2009).

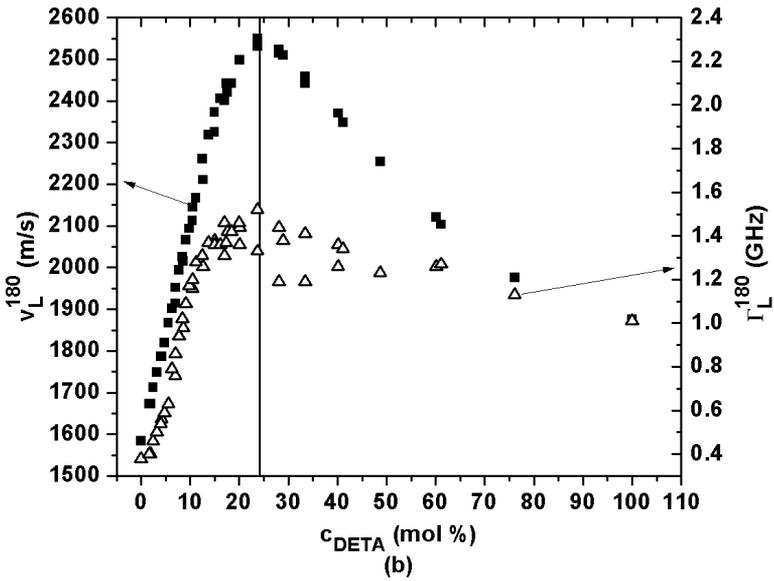
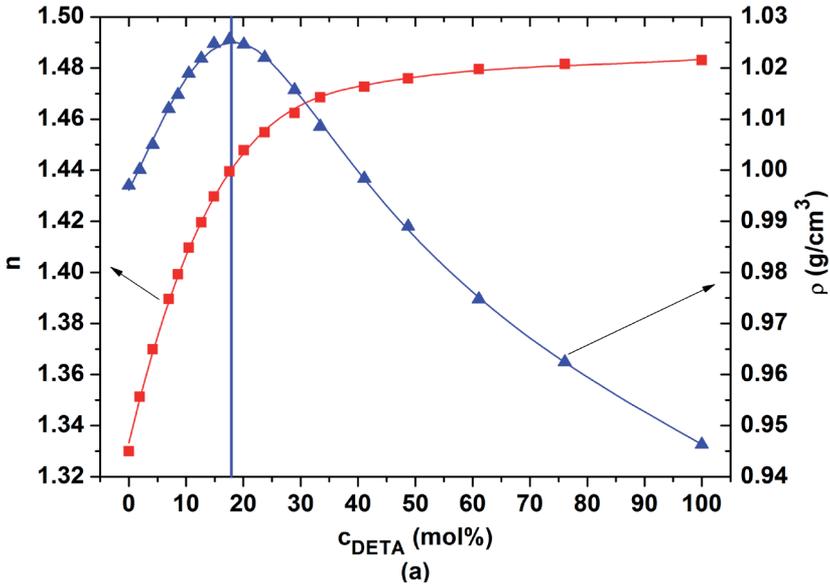


Fig. 6.4. DETA molar concentration dependence c_{DETA} of (a) the refractive index n and the mass density ρ and (b) the hypersonic velocity v_L^{180} and attenuation Γ_L^{180} for homogeneous equilibrated DETA-water samples at 295 K.

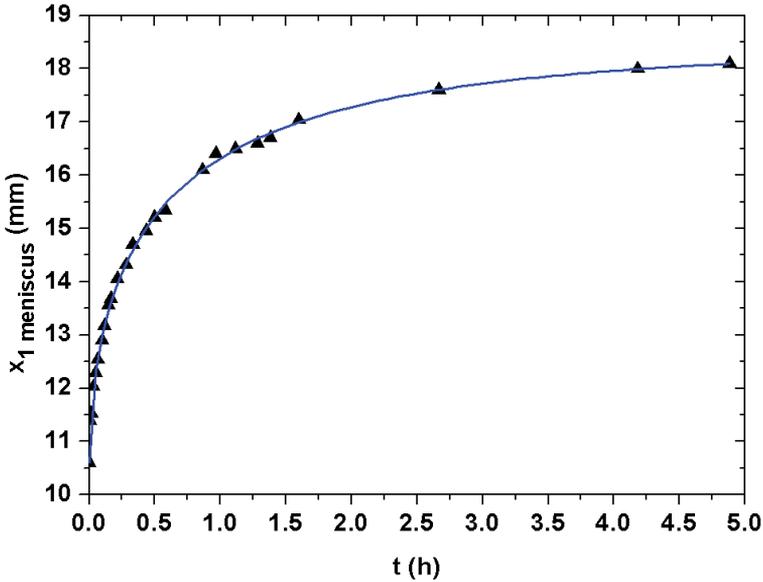


Fig. 6.5. Position of the optical meniscus versus time after injecting 1 cm^3 of water underneath 2 cm^3 of DETA in a glass cuvette having a base of $10 \times 10 \text{ mm}^2$ and a height of 40 mm.

At first sight the optical and acoustic perspectives of the DETA-water mixing process lead to completely disparate interpretations. According to figure 6.6, SBM^{180-2D} indicates the evolution of a more gradually evolving and longer-lived three phase structure than optical imaging. The first acoustic profile could be recorded only 0.2 h after injecting water underneath DETA. The position of its steepest descent coincides with that of the optical meniscus after 0.2 h and is designated as x_{10} . Given that the sound velocities determined in the lower compartment, i.e. below x_{10} , are considerably higher than those of pristine water (ca. 1570 m/s), DETA-water mixing and physicochemical interactions must indeed have taken place therein.

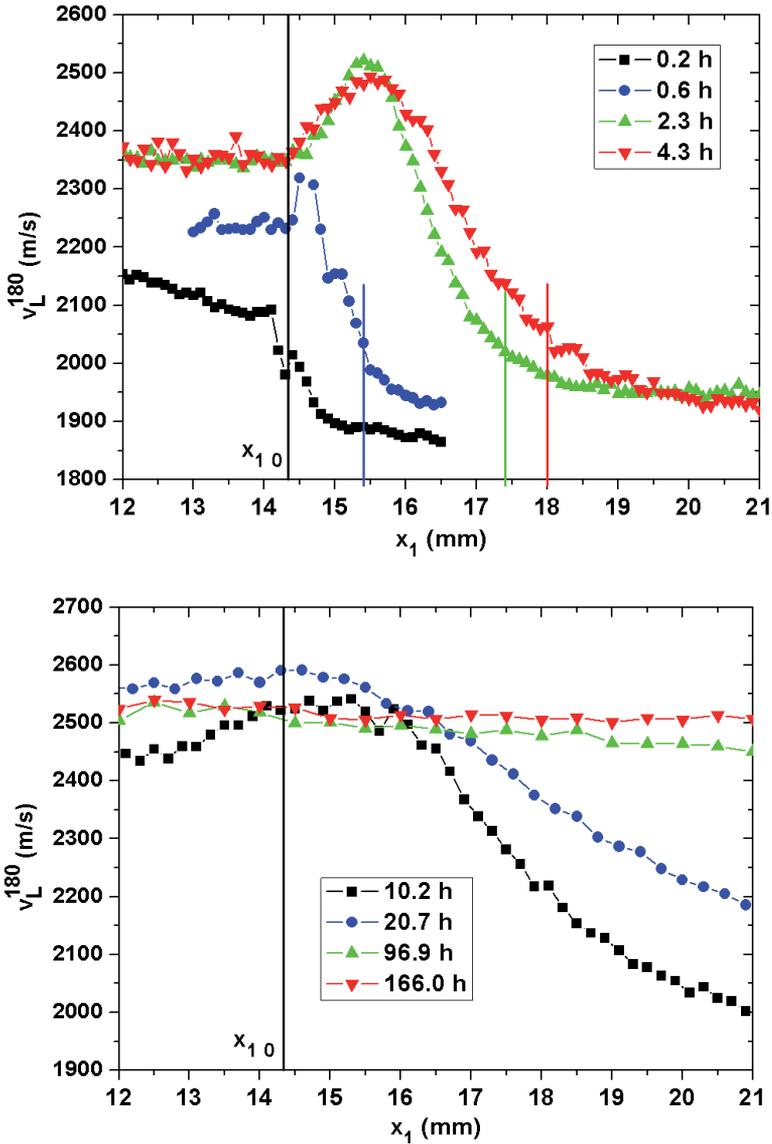


Fig. 6.6. Spatial evolution of the hypersonic velocity between (a) 0.2 h and 4.3 h, respectively (b) 10.2 h and 166.0 h. The vertical line at x_{10} indicates the position of the optical meniscus after 0.2 h. The other lines designate the position of the optical phase boundary after the corresponding times between 0.6 and 4.3 h.

Neglecting the non-equilibrium nature of the structures that form upon injection, the sound velocity versus concentration data of figure 6.4b suggest that a DETA concentration of about 11 mol% is present in the bottom compartment after 0.2 h. The drop of the sound velocity below that of pure DETA determined above x_{10} seems to be a transient phenomenon, possibly related to the only partially established complex or hydrogen bond network.

Subsequently, up to 4.3 h the sound velocity profiles develop a maximum and the acoustic interphase region located in between the DETA-water mixture (below x_{10}) and pristine DETA in the upper compartment of the cuvette broadens more and more. The vertical bars in figure 6.6a give the position of the optical meniscus after the indicated times. Interestingly, the optically perceptible phase boundary does no longer coincide with the steepest descent in the acoustic profile! The meniscus is actually located close to the top of the acoustic interphase at the transition towards pristine DETA. Accordingly there appears to be a significant mismatch between optical and acoustic properties within the interphase zone. As the optical interface resides at a location of almost constant sound velocity, we surmise that a particular structural characteristic, such as a percolation threshold for dipolar interactions within a liquid partially constrained by a network of DETA-water complexes, may cause a small jump in optical polarisability. The coupling of the sound velocity to this structural characteristic is apparently too small to be resolved acoustically. On the other hand continuous refractive index variations, which should accompany the large transient acoustic interphase, could not be resolved by our simple optical imaging technique.

While the optical meniscus considerably blurs after 4.3 h, the acoustic interphase remains for much longer times. Beyond 20.7 h the acoustic peak broadens significantly and slightly drops in magnitude. Until 166 h of the experiment especially the upper DETA-rich compartment undergoes changes until the same sound velocity is observed along the scanning trace. The sound velocity noticed in the equilibrated sample after 166 h is quite consistent with the ones recorded for similar concentrations in homogeneous samples (see figure 6.4b). Accordingly, the transport barriers in the acoustic interphase region seem to be sufficiently permeable

and transient in nature so that the homogeneous equilibrium state can be achieved after more than 160 h.

Both experimental studies delineated in chapter 6 exemplarily illustrate how SBM^{180-2D} can contribute to the elucidation of the manifold phenomena happening at unstable reactive liquid-liquid interfaces. As demonstrated in the latter section, especially the combination of SBM^{180-2D} with other experimental techniques has great potential.