



# Conformational mobility of small molecules in glass-forming solutions studied by FTIR spectroscopy

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## ABSTRACT

Small molecules with two or more stable conformations when embedded in a glass-forming liquid (matrix) serve the role of “conformational probes”, *i.e.*, their conformational transitions are used to follow local mobility in the matrix. In the present study, conformational probes were embedded in low-molecular-weight glass-forming liquids, and the molecular mobility was studied in a broad temperature range including the glass transition temperature ( $T_g$ ). Paraffin oil, dibutylphthalate, bis(2-ethylhexyl)phthalate and isopropylbenzene were used as glass-forming liquids while 1,2-dichloroethane, 1,2-diphenylethane, chlorocyclohexane and bromocyclohexane were used as conformational probes. For some of the matrix/probe systems, the conformational mobility was found to freeze-in at  $T_g$ , while for the others it froze-in at certain temperatures  $T_f < T_g$ . In the latter case, it was possible to evaluate the activation energies related to mobility of free volume entities in the glassy matrices. In addition, it was possible to estimate the volumes of sub-molecular groups of the matrix that freeze-in at  $T_f$ .

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## 1. Introduction

Physical and chemical properties of amorphous solids are strongly affected by the glass formation conditions and local molecular mobility in the glassy state. The molecular mobility of low- and high-molecular-weight glass forming liquids has been extensively studied by different physical methods, including those based on molecular probes (see [1] and references therein). In particular, it was proposed to use compounds with conformational flexibility as probes in glassy solids [2,3]. Any molecule having two or more stable conformations detectable by infrared spectra can be utilized as a probe (called hereafter “conformational probe”). The approach is based on imbedding a small amount of the probe into the studied glass forming liquid (called hereafter “matrix”) and following the temperature dependences of its conformationally sensitive bands in FTIR spectra. If at a certain condition the probe molecules can transform from one conformation (A) to another (B) within the observation time, *i.e.*, the conformers are in equilibrium, then the integrated intensities of the IR bands of the conformers,  $D_A$  and  $D_B$ , follow the relation [4]:

$$\ln \frac{D_A}{D_B} = \ln \frac{\alpha_A}{\alpha_B} + \frac{\Delta S_0}{R} - \frac{\Delta H_0}{RT}, \quad (1)$$

where  $\Delta S_0$  and  $\Delta H_0$  are the entropy and enthalpy differences of the conformers, respectively,  $\alpha_A$  and  $\alpha_B$  are the absorption coefficients of the conformer's bands under study,  $T$  is the temperature and  $R$  is the gas constant.

The conformational transitions in the probe molecules are possible only if the molecules of the surrounding matrix (or their fragments) exhibit sufficient mobility and if such mobility leads to creation of free volume entities large enough for the probe molecules to transform. Lowering the temperature may cause freezing-in of the molecular mobility of the matrix and this in turn may freeze-in the conformational transitions in the probe. Then below a certain temperature  $T_f$ , Eq. (1) transforms to:

$$\ln \frac{D_A}{D_B} = \ln \frac{\alpha_A}{\alpha_B} + \frac{\Delta S_0}{R} - \frac{\Delta H_0}{RT_f}, \quad (T < T_f), \quad (2)$$

where  $T_f$  is the temperature at which the conformational transitions in the probe “froze-in”.

The magnitude of  $T_f$  can be determined from the curvature of the dependence of  $\ln(D_A/D_B)$  upon  $T^{-1}$ . Then, knowing the “activation volume” (*i.e.*, the minimum volume required for conformational transitions to occur), one can estimate the size of the mobile units of the matrix which also froze-in at  $T_f$ .

The conformational probe must satisfy the following requirements. (i) The conformationally sensitive IR bands must be strong enough and do not overlap with the peaks of the studied matrix (*i.e.*, fall within the “transparency windows” of the matrix). (ii) The barrier hindering conformational transitions in the probe must be

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low enough, so that in the gas phase and/or liquid solutions the conformers are in equilibrium at  $T_f$  and somewhat below this temperature. (iii) The enthalpy difference of the conformers  $\Delta H_0$  must be such that FTIR bands of the conformers can be reliably detected in FTIR spectra in the whole temperature range under study. (iv) The probe must be soluble in the studied matrix and be chemically inert with respect to it.

Previously, the described approach was successfully used for analyzing local molecular mobility and free volume distribution in glassy polymers. For these systems, the conformational transitions in the probe froze-in significantly below the glass transition temperature of the matrix and were associated with secondary relaxation transitions. At that point, it helped in assigning relaxation transitions in polymers to certain types of mobility of the backbone and lateral groups of the polymers [1–3,5]. A quite different observation has been made when studying conformational mobility in low-molecular-weight glass forming liquids. It has been found that the conformational transitions in the probe freeze-in exactly at the glass transition ( $T_g$ ) of the studied matrices [6]. To our best knowledge, no observations of conformational transitions below the glass transition temperature were reported thus far for low-molecular-weight liquids.

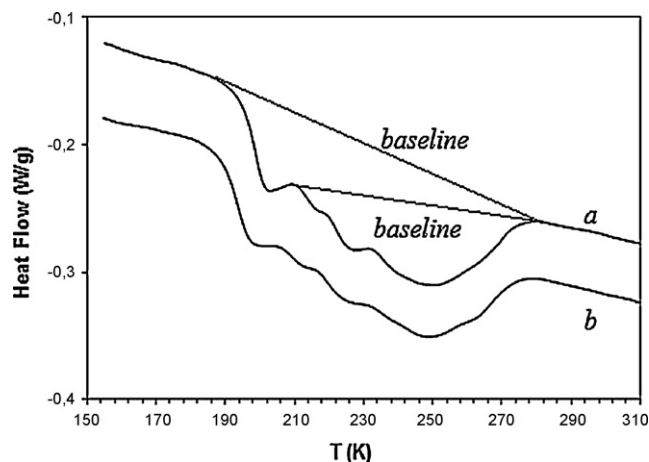
In the present work we performed a more extensive study of the conformational mobility of small molecules imbedded in glass-forming liquids (matrices). The following compounds were used as the matrices: paraffin oil (POil), dibutylphthalate (DBPh), bis(2-ethylhexyl)phthalate (more commonly referred to as dioctylphthalate, DOPh) and isopropylbenzene (more commonly referred to as cumene). Molecules of the studied liquids differ in their chemical structure, size, branching and conformational flexibility, which all might affect physical properties below  $T_g$ . Four different compounds were used as conformational probes: 1,2-dichloroethane (DCE), 1,2-diphenylethane (DPHE), chlorocyclohexane (ClCH) and bromocyclohexane (BrCH). Applying the described above approach we were able to evaluate the “activation energies” related to the mobility of the free volume entities in the glassy matrices. The glass transitions and possible crystallinity of the pure matrices and matrix/probe mixtures were also characterized by Differential Scanning Calorimetry (DSC).

## 2. Experimental

**Materials.** Paraffin oil (generic formula  $C_nH_{2n+2}$ ,  $n = 15–20$  was a product of Cumberland Swan (NDC 0869-0831-43, purity 99.9%, refractive index  $n_D = 1.478$ ). Dibutylphthalate (CAS 84-74-2, assay 99%), dioctylphthalate (CAS 117-81-7, assay 99%), isopropylbenzene (CAS 98-82-8, assay 98%), chlorocyclohexane (CAS 542-18-7, assay 99%), bromocyclohexane (CAS 108-85-0, assay 99%) and 1,2-dichloroethane (CAS 107-06-2, assay  $\geq 99\%$ ) were products of Sigma–Aldrich. 1,2-Diphenylethane (CAS 103-29-7, assay 99%) was a product of Acros. The above compounds were used as received without further purification.

**Sample preparation.** The volume fractions of the probes in the glass-forming liquids were in the range of 0.02–0.07 (*i.e.*, 2–7 vol.%). Pre-weighed amounts of a probe and a glass-forming liquid were placed in small closed containers and stirred 30 min on a hot plate using magnetic stir bars. The sample temperature during the stirring was maintained at 30–40 °C. Visual and spectroscopic observations of the created mixtures indicated that none of them was phase separated. This conclusion was also confirmed in the DSC experiments.

**FTIR measurements.** The infrared spectra were registered using a Bruker Tensor-27 spectrometer at a resolution of  $1\text{ cm}^{-1}$ . Each spectrum was an average of 32 consecutive scans. A droplet of the studied liquid was squeezed between two KBr plates and placed



**Fig. 1.** Thermograms obtained for pure POil (a) and a 2 vol.% solution of DCE in POil (b). The data were obtained at the heating rate of  $10\text{ K min}^{-1}$ . The plots are shown with arbitrary offsets. The meaning of the baselines is explained in the text.

into a cryostat. The sample cooling rate used in our experiments was  $0.5–1\text{ K min}^{-1}$ . The sample temperature was measured by a platinum thermometer with an accuracy of  $\pm 1\text{ K}$ .

For quantitative analysis, we subtracted spectra of the pure glass-forming liquids from the spectra of the probe solutions in those liquids, the involved spectra being registered at the same temperature. Then the areas under the bands belonging to the probe's conformers (*i.e.*, integrated intensities  $D_A$  and  $D_B$ ) were determined using the OPUS software supplied with the spectrometer.

**DSC measurements** were performed using a TA Instrument 2920 Differential Scanning Calorimeter. Standard aluminum pans were used for sampling. Typical sample weight was 12 mg. The sample chamber was purged by dry nitrogen during the whole study. Prior to each run, the chamber with a sample in it was cooled by liquid nitrogen at  $\sim 10\text{ K min}^{-1}$  down to  $\sim 133\text{ K}$ . Then the thermograms were registered at a constant heating rate of  $10\text{ K min}^{-1}$ . For each system, two measurements were performed. The data on the glass transition temperatures were reproducible within  $\pm 1\text{ K}$ .

## 3. Results and discussion

### 3.1. Characterization of the glass-forming liquids by DSC

Fig. 1(a) displays a DSC thermogram registered for pure POil. The curve shows a clear step transition between 188 and 203 K, which should be assigned to the glass transition of the sample. From the plot, the glass transition temperature was determined using TA Instrument software supplied with the calorimeter:  $T_g = 200\text{ K}$ . Dissolving 2 vol.% of DCE shifted the step transition to lower temperatures (Fig. 1(b)). For this system, the obtained value was found to be 194 K. Note that pure DCE is easily crystallizable, and its melting temperature is about 238 K. The absence of the melting peak of DCE in Fig. 1(b) confirms good compatibility of the components, *i.e.*, there are no features assignable to the phase separation.

A complex structure of the thermograms in the region between 205 and 270 K may be due to partial crystallization of POil. Upon heating above the glass transition, POil may experience a series of melting re-crystallization and relaxation events. Assuming that the area above the observed peaks is due to the melting of crystalline domains one can estimate the degree of crystallinity of the sample. Unfortunately, it is unknown whether the melting onset overlaps the glass transition, which somewhat complicates the problem. Fig. 1(a) shows two limiting positions for the baseline. The *baseline 1* assumes that the integration includes the glass transition

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