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Supramolecular x-ray signature of susceptibility amplification in hydrogen-bonded liquids

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Mixing two nonconducting hydrogen-bonded liquids, each exhibiting a low dielectric relaxation strength, can result in a highly electrically absorbing fluid. This susceptibility amplification effect is demonstrated for mixtures of monohydroxy alcohols. Whereas in the pure liquids a tendency to form ringlike low-dipole moment clusters prevails, in the mixtures such supramolecular structures are disfavored leading to an up to tenfold enhancement of the dielectric loss. The compositional evolution of density and mean cluster-cluster separation is traced using x-ray scattering and indicates deviations from ideal mixing with decreased C-C but simultaneously increased O-O correlation lengths. Thus, the variation in the supramolecular absorption strength could be tracked using a static scattering technique. These observations are in harmony with volume exclusion and ring open effects that predict an optimized susceptibility amplification for mixtures in which the two components occupy equal volume fractions as experimentally observed.

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Hydrogen-bonded fluids play a fundamental role in nature: The structure of peptides and proteins which governs biofunctionality is stabilized by hydrogen bonds, and many of the water anomalies owe their existence to the hydrogen-bond mediated formation of supramolecular structures. Between high-molecular weight proteins and the small-molecule liquid water, at an intermediate complexity level, e.g., monohydroxy alcohols [1] (MAs) and model peptides [2] are being studied as model systems for hydrogen-bonded fluids in general. Currently, the microscopic mechanism leading to their strong electrical absorption, the so-called Debye relaxation, for water every day exploited in the microwave oven, is not fully understood, and in view of its utmost technological and scientific importance it attracts tremendous attention. The defining property of the Debye process is that it corresponds to a single-exponential relaxation proceeding slower and typically with a larger susceptibility than the liquid's structural relaxation [3].The Debye process is exhibited not only by water [4], secondary amides [5], and MAs [3], but also by certain pharmaceuticals [6], ionic liquids [7], and supramolecular polymers [8] as well. This absorption process was long believed to be accessible experimentally only via techniques, such as dielectric spectroscopy that are sensitive to electric dipole moment fluctuations [9]. Although recent nuclear magnetic resonance [10], mechanical spectroscopy [11], and dynamic light scattering [7] experiments were shown to probe the *dynamics* of the Debye relaxation as well, up to now [12] the *structural* basis of this phenomenon (e.g., in terms of supramolecular chains [10] or rings [13]) had to rely on more or less plausible assignments. By exploiting the prepeak in the structure factor of MAs [14,15], in the present article we will demonstrate that as a *static* probe even x-ray scattering allows one to track changes in the supramolecular structure of the MAs that are directly connected to changes in the relaxation strength of the Debye process and to obtain direct insights into the corresponding reorganization of the hydrogen-bond association in these fluids.

The current observation of the local rearrangement of supramolecular moieties has become possible by the discovery reported herein that MA mixing can amplify their dominant absorption process almost *ten*fold. This is remarkable because the intensity of this process is almost always *reduced* when perturbing the H-bond network, e.g., by admixture of ions that scissor it [16] or by solvent addition that dilutes it. Furthermore, confining environments can provide interactions competing with the intermolecular ones, sometimes suppressing the Debye process completely. Only a few recent studies report on its much more interesting fortification: Via application of strong electrical fields that drive a supramolecular ring-to-chain transformation a high-field dielectric study amplified its relaxation strength by about 4.5% [13]. Consequently, the effective dipole moment of the supramolecular structures changes from small as is appropriate for rings to larger when the moments add up in a chainlike fashion. By mixing isomeric MAs Gong *et al.* observed a Debye intensity increase by a factor of 1.5 [17]. Such an enhancement, completely unfamiliar from non-Debye liquids, was loosely ascribed to the formation of molecular structures with higher effective dipole moments [17].

For the present paper, we mix 4-methyl-3-heptanol (4M3H), an MA known to form ringlike structures [18], with members of a homologous series of branched alcohols [19]. Apart from 4M3H, with a mean alkyl branch length of $l_{\mathrm{eff}} = 7.18$ Å [20], we study 2-butyl-1-octanol [(2B1O), $l_{\mathrm{eff}} = 11.35$ Å], 2-hexyl-1-decanol [(2H1D), 13.85 Å], and 2-decyl-1-tetradecanol [(2D1T), 18.85 Å]. These MAs are structurally related to 2-ethyl-1-hexanol [(2E1H), 8.85 Å], an alcohol supposed to form chainlike structures [10]. All chemicals (from Sigma-Aldrich, stated purities: 4M3H, >99%; 2E1H, >99%; 2B1O, >95%; 2H1D, >97%; 2D1T, >97%) were used as received or mixed in various mole fractions. The complex dielectric constant $\varepsilon^*(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu)$, i.e., the in-phase component ε' and out-of-phase absorptive component ε'', was measured as a function of frequency ν using an Alpha analyzer from Novocontrol. X-ray diffraction, employed to study the microscopic structure of 2E1H as well as of 4M3H, 2H1D, and their mixtures, was performed at a temperature of 298 K utilizing 1.54 Å wavelength Cu $K\alpha$ radiation at

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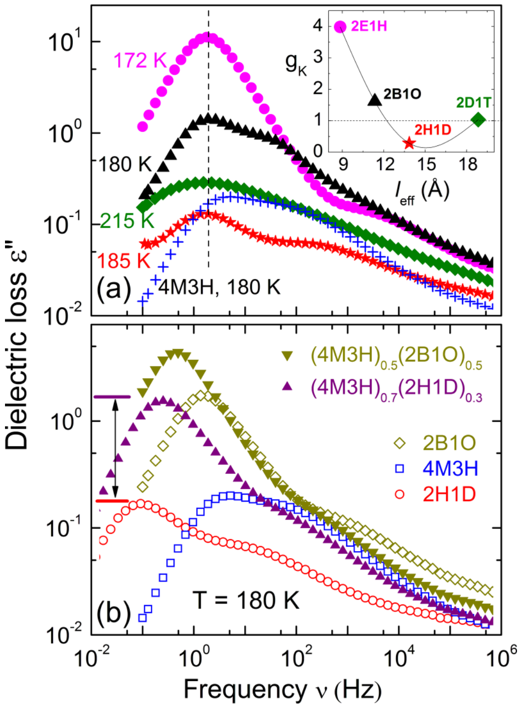

FIG. 1. (Color online) Dielectric loss spectra of a homologous series of branched MAs. Results are shown for 2E1H (circles), 2B1O (triangles), 2H1D (stars), and 2D1T (diamonds). The frequency position of the main peak is highlighted by the vertical line. For reference purposes, data on 4M3H are included as crosses. For the homologous series the inset shows g_K as a function of average alkyl branch length l_{eff}. The solid line is drawn to guide the eye, and the dashed line marks $g_K = 1$. (b) To demonstrate the enhancement effect, dielectric loss spectra of $(4M3H)_{0.7}(2H1D)_{0.3}$ and of $(4M3H)_{0.5}(2B1O)_{0.5}$ are compared to those of the pure MAs at 180 K. The arrow marks a susceptibility variation of one decade.

a laboratory x-ray source (Bruker AXS D8 Advance) with Montel optics. The macroscopic density of the liquids was measured at 295 K using commercial equipment (Anton-Paar DSA 5000 M).

In Fig. 1(a) the effect of a progressive chain length increase is demonstrated for the present series of similarly branched alcohols. When increasing l_{eff} from 8.85 Å (2E1H) to 13.85 Å (2H1D) the dominant loss peaks diminish by about two orders of magnitude, whereas the two-peak structure of the spectra is preserved. Here, the large peaks correspond to the Debye process, and the smaller ones correspond to the structural relaxation. For the longest member of the homologous series, 2D1T, only a single peak prevails, reminiscent of the dielectric loss of typical *non*-Debye liquids [21]. The finding for 2D1T demonstrates that the Debye process can be suppressed not only by diluting the hydrogen-bond network with *foreign* molecules, but also by just increasing the fraction of nonpolar molecular segments.

Even more remarkable is the nonmonotonic evolution of the total relaxation strength within this homologous MA series. This feature is readily explained by noting that the structural relaxation predominantly involves fluctuations in dipole moment components $\mu_\perp < \mu$ oriented perpendicular to the contour of the hydrogen-bonded supramolecular structures [10]. Here, the molecular dipole moment $\mu = 1.68\,\mathrm{D}$ is virtually independent of the molecular structure [18]. Hence, if sufficient intramolecular hydroxyl group dilution effectively suppresses supramolecular association and thus the Debye process, the simple liquid limit is obtained in which relaxation is governed by the full dipole moment as we find here for 2D1T.

For reference purposes, Fig. 1(a) contains a loss spectrum of 4M3H, which is not a member of the homologous series. Its susceptibility or relaxation strength $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ defined via the static dielectric constant ε_s and the high-frequency dielectric constant ε_∞, is very small for temperatures <250 K because the sterically screened OH group of 4M3H does not allow for efficient chain formation.

Dielectric relaxation strengths are often expressed in terms of the Kirkwood factor $g_K = 1 + z\,\langle\cos\,\theta\rangle$, which quantifies the orientational correlation of adjacent dipole moment vectors that enclose a mutual angle θ. Averaging over a coordination shell containing z molecules yields [13]

$$g_K = \frac{9\varepsilon_0 k_B T}{n\mu^2}\,\frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_s(\varepsilon_\infty + 2)^2}, \qquad (1)$$

where n denotes the number density ($\propto 1/l^3$). If *parallel* dipolar alignment prevails, then $g_K > 1$ is found, whereas for systems with overall antiparallel dipolar alignment, values smaller than unity emerge. For 4M3H g_K depends only weakly on temperature in the range $180\,\mathrm{K} \leqslant T \leqslant 215$ K and is very small $g_K \approx 0.2 \pm 0.01$. The slightly larger Kirkwood factor $g_K = 0.27 \pm 0.03$ of 2H1D behaves similarly. In Fig. 1(b), showing the unprecedented enhancement of the Debye process most impressively, the dielectric losses of $(4M3H)_{0.5}(2B1O)_{0.5}$ and of $(4M3H)_{0.7}(2H1D)_{0.3}$ are compared with that of the pure MAs. To determine the concentration of largest enhancement, the various 4M3H mixtures were studied as a function of the mole fraction x. Figure 2(a) shows that for $(4M3H)_{1-x}(2H1D)_x$ the maximum in $\Delta\varepsilon_D(x)$ is reached at 180 K for $x_{2H1D} \approx 0.35$. For $(4M3H)_{1-x}(2B1O)_x$ and 180 K the maximum appears at $x_{2B1O} \approx 0.45$ (not shown). The dramatic nonmonotonic evolution of $\Delta\varepsilon_D(x)$ evident from Fig. 2(a) presents a particularly striking example of nonideal mixing.

Such a behavior, entirely unknown for non-hydrogen-bonded liquids, calls for an explanation of its molecular origin. Let us start from the conjecture that pure 4M3H forms ringlike low-dipole-moment supramolecular structures [18] which "take a higher volume per molecule than the multimers with a high dipole moment" [22,23]. The similarly small g_K of 2H1D indicates that such low-entropy low-density structures also are prominent in this liquid. However, we will show that due to the rather different sizes of the 4M3H and 2H1D molecules formation of mixed rings containing both species is disfavored. To minimize their free energy these hypothetical higher-entropy lower-density objects are evidently avoided. Thus, mixing of two molecularly similar MAs, such as 4M3H and 3-methyl-3-heptanol, both exhibiting an almost negligible supramolecular relaxation [13], should not lead to an amplified Debye process as was confirmed experimentally (not shown). The observation of Kirkwood factors $g_K > 1$ in $(4M3H)_{1-x}(2H1D)_x$ reveals that chainlike

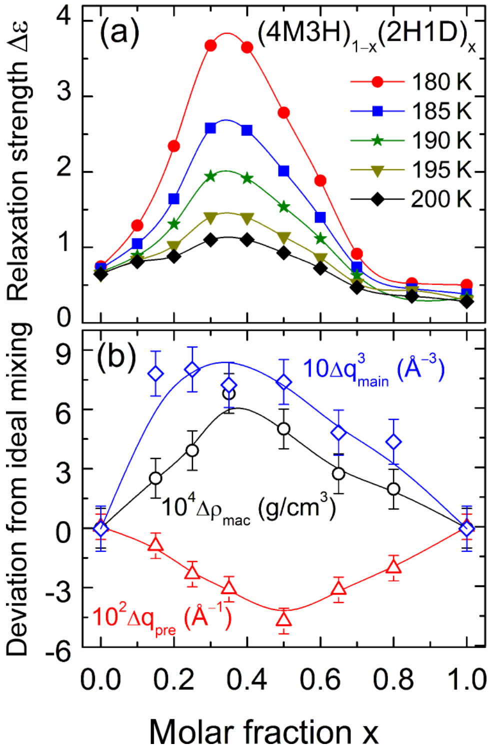

FIG. 2. (Color online) (a) Concentration dependent dielectric relaxation strength $\Delta\varepsilon_D\,(x)$ of (4M3H)$_{1-x}$(2H1D)$_x$ for various temperatures. Maxima in $\Delta\varepsilon_D\,(x)$ show up near $x_{\mathrm{2H1D}} = 0.35$. The lines are drawn to guide the eye. (b) Deviation in the measured density ρ_{mac} (circles), position of the prepeak q_{pre} (triangles), and microscopic density ($\rho_{\mathrm{mic}} \propto q^3_{\mathrm{main}}$) from linear x variations [25].

supramolecular aggregates can occur. In neat systems *pressure*-induced compaction of low-density MA structures can result in significantly enhanced Kirkwood factors as well [22,23,24].

Whether higher densities indeed occur in the present high-$\Delta\varepsilon_D$ samples was checked on microscopic and on macroscopic length scales by x-ray diffraction and by direct density measurements, respectively. The measured diffraction patterns $I(q)$ of the neat alcohols and of the mixtures are presented in Fig. 3(c). The main peak of $I(q)$ at wave vector transfers of $q \approx 1.35$ Å^{-1} is dominated by correlations among the carbon atoms and thus related to the macroscopic density. In contrast, the first sharp diffraction peak at $q_{\mathrm{pre}} \approx 0.55$ Å^{-1}, referred to as a prepeak, is due to oxygen-oxygen (O-O) correlations and gives a handle on supramolecular arrangements in MAs. This assignment of the prepeak as well as of the main peak is well established by combining x-ray data for a large number of MAs with various numerical simulation techniques [26–28].

Figure 2(b) reveals that with increasing the 2H1D mole fraction the position of the prepeak shifts to smaller momentum transfers whereas the main peak position q_{main} shifts to larger ones. Thus, the microscopic density $\rho_{\mathrm{mic}} \propto q^3_{\mathrm{main}}$ of the mixtures or the deviations thereof $\Delta q^3_{\mathrm{main}}$ vary nonlinearly with x. Figure 2(b) indicates that in the concentration range around $x_{\mathrm{2H1D}} \approx 0.35$ the deviations from ideal mixture behavior of ρ_{mic} are largest, an observation that is in line with the variation found for the measured macroscopic densities ρ_{mac}. The most remarkable observation from Fig. 2(b) is that the x dependence of the prepeak position is *opposite* to that of the main peak. Interestingly, q_{pre} deviates strongest from a linear variation in the range in which the strongest density and dielectric constant changes also are observed. For the mixtures the q_{pre} variation can be traced back to an increase in characteristic intermolecular O-O distances via the correlation length $d_{\mathrm{OO}} = 2\pi/q_{\mathrm{pre}}$, which essentially is a metric of the cluster-cluster separation.

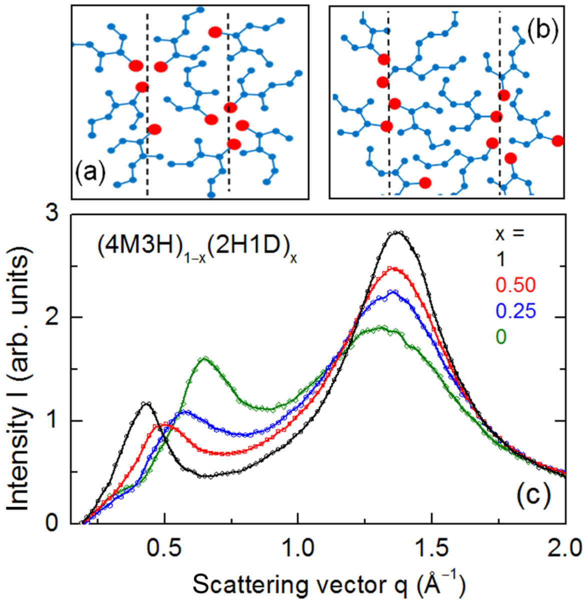

FIG. 3. (Color online) Schematic of (a) ringlike and (b) chainlike cluster-cluster arrangements with the dashed lines symbolizing typical cluster separation lengths. In (a) the O-O distances are shorter than in (b), yet for the chainlike scenario in (b) the alkyl chains are more densely packed. (c) x-ray diffraction patterns of (4M3H)$_{1-x}$(2H1D)$_x$ recorded at 298 K for different 2H1D mole fractions are shown as connected dots. The intensity patterns are background corrected and in the range from 0.2 to 2 Å^{-1} scaled to constant area.

How is it possible that the O-O distances increase while the overall density decreases? This can happen if the structural organization changes on a molecular level. As illustrated in Fig. 3(a) ringlike suprastructures with their outwards radiating alkyl spacers produce a more open hydrophobic shell around their polar hydroxyl cores than chainlike associates do. In chainlike arrangements, see Fig. 3(b), on the other hand, a more compact shell is evident with less interdigitation of the nonpolar spacers from adjacent clusters which consequently is accompanied by an increased d_{OO}. Hence, a transformation from supramolecular rings to chains implies that the average C-C distances decrease while simultaneously the average O-O distances increase.

Now, it remains to be examined why for (4M3H)$_{1-x}$(2H1D)$_x$ the maxima in $\Delta\varepsilon_D\,(x)$ and in the corresponding structural parameters appear at $x_{\mathrm{2H1D}} \approx 0.35$, which is the composition at which the two involved MAs occupy about equal volumes $x_{\mathrm{2H1D,iso}\text{-}V} \approx 0.35$ [29]. In other words, why are isovolume compositions so effective

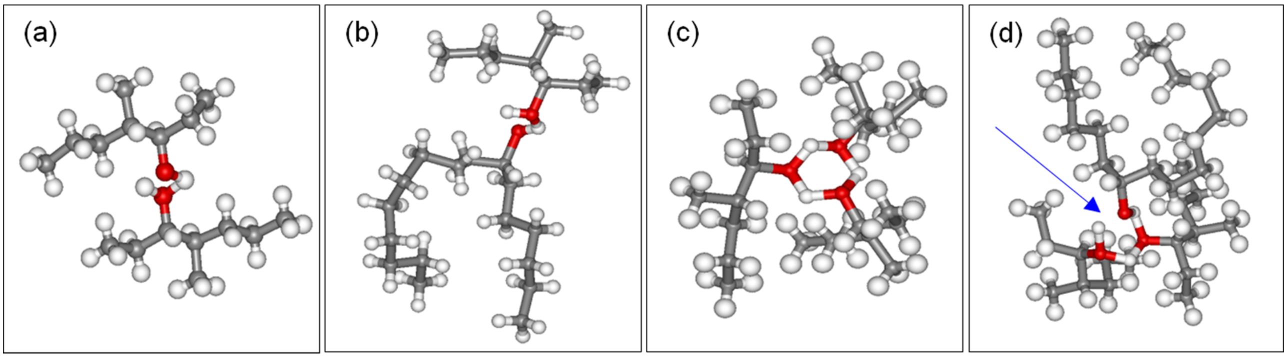

FIG. 4. (Color online) Sketch of local hydrogen-bonding patterns formed by several alcohol molecules. (a) An almost closed so-called ring dimer of 4M3H. (b) A heteromolecular 4M3H-2H1D ringlike structure. (c) A cyclic trimer structure of 4M3H. (d) A trimer structure corresponding to a $(4M3H)_{0.66}(2H1D)_{0.33}$ mixture. To avoid spatial overlap of the alkyl rests the ring structure is breaking up (see arrow) in contrast to the situation for the 4M3H trimer.

in breaking up ring structures? In an effort to answer this question let us follow arguments supposing that ring structures are present predominantly in the form of dimers [30], trimers [31], or tetramers [32].

Ring dimers, sketched in Fig. 4(a) for 4M3H, are envisioned to comprise two nearly antiparallel dipole moments that almost cancel. Figure 4(b) illustrates that it is easily possible to pack two different alkyl rests in a dimeric structure. However, if ring dimers would be the prevalent species in the mixtures, $g_K(x)$ should reflect the fraction of OH groups and hence exhibit a linear x dependence at variance with the experimental results.

Let us therefore assume that cyclic *trimers* with relatively linear, thus, stable OH$\cdots$O bonds and $g_K \approx 0$ dominate in pure 4M3H, see Fig. 4(c). Replacement of one out of the three 4M3H molecules by the much larger 2H1D will, however, destabilize the $g_K \approx 0$ suprastructure to avoid spatial overlap of adjacent alkyl branches. Thus, as highlighted by the arrow in Fig. 4(d), 2H1D acts as a ring opening agent so that short heteromolecular chains are favored. Adding more 2H1D will simply dilute these chains until again rings are formed that now contain only 2H1D molecules. In agreement with experiment, a maximum in the dielectric strength is therefore expected for a molar ratio of 2:1 corresponding to $(4M3H)_{2/3}(2H1D)_{1/3}$ or to a volume ratio of 1:1 [33].

This rationalization of the compositional trends is somewhat simplified because mixtures of (also larger) multimeric species may be present. However, the agreement of our prediction with the experimental observations suggests that the present mixtures contain only a small fraction of tetrameric 4M3H species. Furthermore, volume exclusion phenomena could enter in a subtle way via sterical screening effects as may be inferred from results on mixtures of the hexanols 2-ethyl-1-butanol (2E1B) and 4-methyl-2-pentanol (4M2P) for which a slight maximum in $\Delta\varepsilon$ occurs in $(4M2P)_{0.75}(2E1B)_{0.25}$ [17].

To summarize, we found that by increasing the size of the alkyl branches in a homologous series of MAs the formation of hydrogen-bonded networks can be suppressed entirely. More surprisingly, an up to tenfold enhancement of the dielectric relaxation was observed when mixing two MAs that in their pure states both tend to form ringlike associates. Volume exclusion effects applied to the bulky alkyl chains of some mixing partners are made responsible for the composition dependent transformation of rings to chains which is in line with experimental x-ray scattering observations of changes in both, the density and the characteristic intermolecular oxygen-oxygen distances. These arguments lead to a quantitatively correct prediction for the composition of maximum relaxation strength in $(4M3H)_{1-x}(2H1D)_x$. Our results demonstrate that simple mixing of suitable hydrogen bonded liquids allows one to tune the amplitude of the dominant electrical absorption, the Debye process, not just towards small values, as previously extensively documented, but also in the opposite direction. A clear correlation among static quantities from dielectric spectroscopy and from x-ray scattering was established, although the two methods probe the underlying structure of the investigated liquids in entirely different ways. Most importantly, we demonstrated that the strength of the Debye process is not just associated with densification effects, but that it reveals itself by nontrivial changes in the low-q range of the static structure factor which allowed us to track the supramolecular reorganization. Our approach to resolve the structural basis of a dynamic phenomenon should be useful to explore and understand the complexities of other associating fluids as well. In particular, it will offer a new perspective on the intricacies of solutions of water. This most common and apparently most complex of all liquids features a Debye-type process which provides many examples for nonideal mixing behavior.

ACKNOWLEDGEMENTS

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[25] For $x = 0$ we used $\rho_{\text{mac}} = 0.8332 g/\text{cm}^3$, $q_{\text{pre}} = 0.643\ \text{Å}^{-1}$, and $q_{\text{main}} = 1.299\ \text{Å}^{-1}$. For $x = 1$ we used $\rho_{\text{mac}} = 0.8370 g/\text{cm}^3$, $q_{\text{pre}} = 0.418\ \text{Å}^{-1}$, and $q_{\text{main}} = 1.364\ \text{Å}^{-1}$.

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[29] For a homogenous equivolumetric mixture of components A and B one has $x_{\text{A,iso-}V} = [1 + (\rho_{\text{B}} M_{\text{w,A}})/(\rho_{\text{A}} M_{\text{w,B}})]^{-1}$. Here M_{w} is the molecular weight and ρ is the macroscopic density, see Ref. [26] for numerical values. Using $M_{\text{w,2H1D}} = 242.44\ g/\text{mol}$ and $M_{\text{w,4M3H}} = 130.23\ g/\text{mol}$ yields $x_{\text{2H1D,iso-V}} \approx 0.35$. From our experiments on $(\text{4M3H})_{1-x}(\text{2B1O})_x$ the maximum in $\Delta\varepsilon_D(x)$ is found at $x_{\text{2B1O}} \approx 0.45$ (not shown), which compares favorably with $x_{\text{2B1O,iso-}V} \approx 0.41$ as estimated from $M_{\text{w,2B1O}} = 186.33\ g/\text{mol}$ and $\rho_{\text{2B1O}} = 0.83\ g/\text{cm}^3$.

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