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Alkane Coiling in Perfluoroalkane Solutions: A New Primitive Solvophobic Effect

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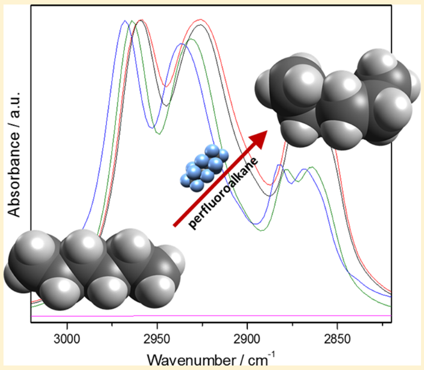
Supporting Information

ABSTRACT: In this work, we demonstrate that *n*-alkanes coil when mixed with perfluoroalkanes, changing their conformational equilibria to more globular states, with a higher number of *gauche* conformations. The new coiling effect is here observed in fluids governed exclusively by dispersion interactions, contrary to other examples in which hydrogen bonding and polarity play important roles. FTIR spectra of liquid mixtures of *n*-hexane and perfluorohexane unambiguously reveal that the population of *n*-hexane molecules in all-*trans* conformation reduces from 32% in the pure *n*-alkane to practically zero. The spectra of perfluorohexane remain unchanged, suggesting nanosegregation of the hydrogenated and fluorinated chains. Molecular dynamics simulations support this analysis. The new solvophobic effect is prone to have a major impact on the structure, organization, and therefore thermodynamic properties and phase equilibria of fluids involving mixed hydrogenated and fluorinated chains.



1. INTRODUCTION

The peculiar properties of mixtures of alkanes and perfluoroalkanes have been intriguing the liquids/fluids community since the pioneering work of Scott.[1] Given the similarity of the two components in terms of molecular structure and intermolecular forces, mixtures of alkanes and perfluoroalkanes could be expected to be the ultimate example of an ideal mixture. On the contrary, they show an enhanced tendency to phase separate, exhibiting extensive regions of liquid−liquid immiscibility, large positive deviations from Raoult's law, and large positive excess enthalpy and volume.

The changes in volume that occur when hydrogenated and fluorinated substances are mixed are impressive: the excess volume of the equimolar mixture of *n*-hexane and perfluorohexane is 5 cm^3 mol^{-1}; when perfluorohexane is immersed in *n*-octane at infinite dilution, its molar volume increases by 13%.[2,3] The effect is even more pronounced when *n*-alkanes are dissolved in perfluoroalkanes: their molar volumes increase by 20%![4] Literally, thin layers of empty space are created around each molecule.

This unusual behavior extends to transport and surface properties. We have recently shown that the viscosity of (hexane + perfluorohexane) mixtures is 17% lower than expected.[5] As for interfacial behavior, (*n*-hexane + perfluorohexane) mixtures display a minimum on the surface tension vs composition curve, a rare phenomenon called aneotropy.[6,7]

The atypical properties of mixtures of alkanes and perfluoroalkanes are far from being a mere scientific curiosity. The thermophysical and mechanical properties of fluorinated compounds, in particular fluorinated surfactants, indicate that they may be used in numerous applications in chemical engineering and material sciences. Thus, the presence of fluorinated materials in everyday life is pervasive. However, owing to their inertness and biocompatibility, it is in biomedical R&D that fluorinated substances find their most exciting applications as components in blood substitute formulations, emulsions for drug delivery in liquid ventilation, and components of microbubbles for drug delivery and oxygen transport.[8−11]

Additionally, the simultaneous presence of the mutually phobic hydrogenated and perfluorinated segments can dramatically influence the structure of the fluid/material, inducing new forms of organization. Semifluorinated alkanes, for example, which are diblock compounds of covalently bonded alkyl and perfluoroalkyl segments, display amphiphilic character, forming different types of supramolecular structures.[12−17] Given the lack of polarity or groups able to make

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hydrogen bonds, these compounds have been often called primitive surfactants. It should be emphasized that, in this case, amphiphilicity is the result of a subtle balance between weak dispersion forces. We have recently accomplished a systematic study of the thermophysical properties of liquid semifluorinated alkanes, either pure or in mixtures, which are crucial to characterizing and modeling systems with fluorinated chains in general.[18−21]

While a definitive explanation for this intriguing behavior is still awaited, it is generally interpreted as an indication of weaker than expected dispersion interactions between hydrocarbons and fluorocarbons.[22−24] Most of the evidence comes from theoretical modeling, in which matching the experimental results implies the use of parameters that lower the intermolecular dispersion energy,[25−27] Structural factors, such as the rigidity of fluorinated chains, as opposed to the characteristic flexibility of hydrogenated chains, may also contribute to the observed behavior.[28] Additionally, it has been found that, in molecular dynamics simulations, a reduction of ~10% of the total dispersive interactions has almost no effect on the simulated excess volumes.[24,29,30] This uncovered that, contrary to what is usually assumed, the volume increase in these mixtures is not entirely related to weak dispersive interactions and should be associated with the repulsive part of the intermolecular potential.

One of the main differences between hydrogenated and fluorinated chains is conformational. *n*-Alkanes and perfluoroalkanes may exist in different conformers, whose diversity increases with chain length. In the case of *n*-hexane, these range from all-*trans* to three bonds with *gauche* rotations. In the solid state, *n*-hexane is entirely all-*trans*, while in the liquid state the populations of other conformers are significant.[31,32] It has been estimated that the conformer with a terminal *gauche* rotation (TTG) corresponds to ~35%, the all-*trans* corresponds to ~32%, and the TGT corresponds to ~18%.[33,34] At room temperature, conformers with two and three *gauche* rotations are estimated to be less than 15% and less than 1%, respectively. On their turn, *n*-perfluoroalkanes are known to exist in a helical conformation with C−C−C−C dihedral angles of ~13°.[35−39] In the solid phase, the more abundant population of conformers of *n*-perfluoroalkanes is in the spiral conformation.[35,36] Thus, a real TTT conformer is not predicted for these molecules.[37] This twisted spatial arrangement was initially attributed to repulsive van der Waals and electrostatic interactions between fluorine atoms, but more recent studies point to hyperconjugation as the cause of helicity.[38,39]

Valuable information on the conformational equilibria, both in pure components and binary mixtures, may be retrieved from vibrational spectra, as changes in chain conformations induced by a second component may be assessed by spectral analysis. For example, for *n*-hexane, the vibrational modes observable in the infrared spectrum depend on the conformational equilibrium. For the most abundant conformer, TTG (C_1 point group), and for TGT (C_2 point group), all 54 fundamental modes are infrared-active, whereas for the TTT conformer (C_{2h} point group) only 27 normal modes are observable.[40] The spectral regions corresponding to νCH, νCC, and/or δCH modes have been widely used to obtain direct information about the conformations of *n*-hexane.[41−44]

In a recent paper, we observed the coiling of alkyl chains in mixtures of hydrogenated and fluorinated alcohols.[45] However, in the case of alcohols, coiling could also be due to the presence of the strong hydrogen bonds and polar interactions. The present work was designed to eliminate that possibility. We found that mixing with fluorocarbons induces conformational changes in *n*-alkanes, from all-*trans* to more globular arrangements involving *gauche* conformations. This result was obtained from the quantitative analysis of the infrared spectra of (*n*-hexane + perfluorohexane) mixtures, and to the best of our knowledge, it is the first time that such a coiling effect has been observed and reported in fluids governed exclusively by dispersion interactions. In terms of liquid structure, the interpretation of the results is further supported by molecular dynamics simulations.

2. EXPERIMENTAL SECTION

All of the compounds used, *n*-hexane, *n*-octane, and perfluorohexane, were supplied by Sigma-Aldrich with stated purities better than 99%, and no further purification was attempted. The *n*-hexane + perfluorohexane mixtures were prepared by weight in screw-cap vials. For the *n*-octane + perfluorohexane system, appropriate amounts of both components were mixed in a screw-cap vial in order to obtain approximately equal volumes of the two immiscible phases. The vial was then stirred and left to decant at room temperature, and samples of the coexisting phases were collected with a hypodermic syringe.

The IR spectra of the pure components and binary mixtures were obtained in transmission mode, using a Mattson Research Series 1 FTIR spectrometer with a wide-band MCT detector (400−4000 cm^{-1}), with resolution 2 cm^{-1}. The samples were analyzed by placing 2 drops between polished KBr disks. Each spectrum is the result of ratioing 50 coadded scans for the sample to the same number of background scans (clean KBr disks). The spectra are presented in absorbance units without baseline correction.

3. RESULTS AND DISCUSSION

The infrared spectra of pure *n*-hexane and perfluorohexane (PFH) are shown in Figure 1. In the 3100−2700 and 1500−1400 cm^{-1} spectral regions, only *n*-hexane absorbs; the 1400−1150 cm^{-1} region corresponds almost exclusively to PFH bands, and in the 1000−500 cm^{-1} region, the two components' bands overlap. The complete band assignment is summarized in Table S1 of the Supporting Information.[35,46−48]

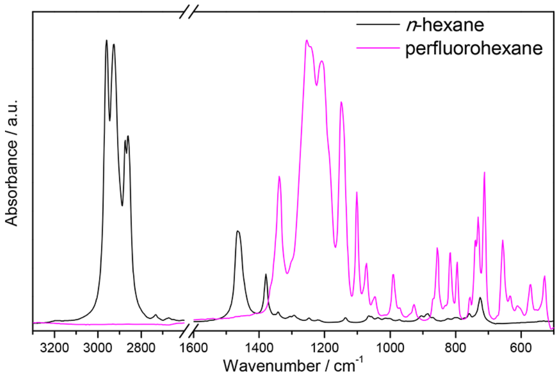

Figure 1. Transmission infrared spectra of *n*-hexane and perfluorohexane, normalized to the maximum absorption.

For a detailed analysis, these three spectral regions are presented separately for the pure components and binary mixtures in Figure 2. In the low-frequency region (Figure 2C), the bands assigned to PFH are stronger and more numerous. The spectra of mixtures richer in one component, $x(n\text{-hexane}) = 0.8$ and $x(\text{PFH}) = 0.8$, are very similar to those of pure *n*-hexane and PFH, respectively. The main changes caused by

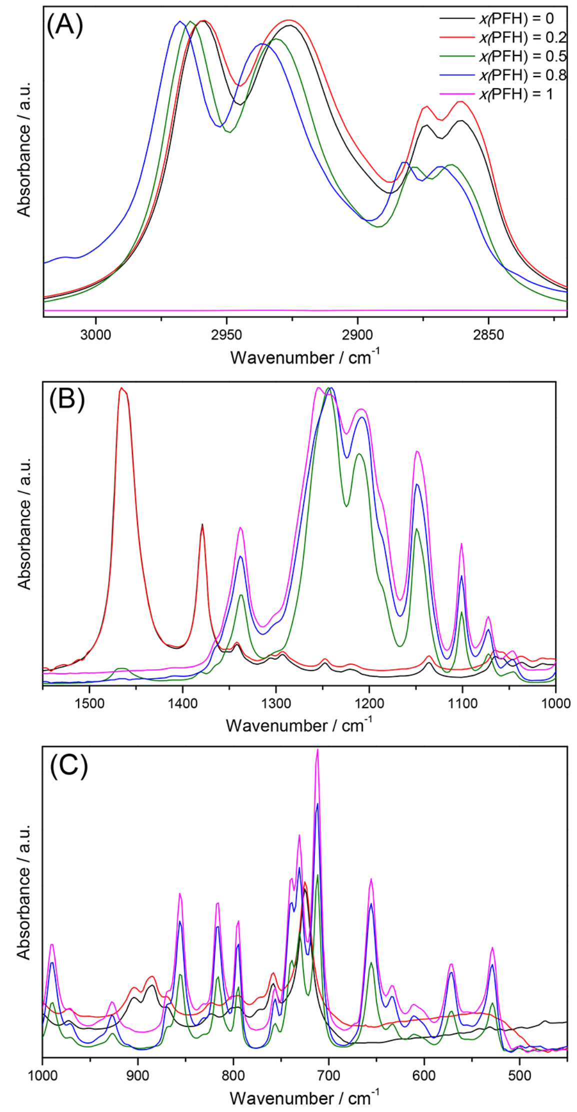

Figure 2. Three regions of the IR spectra of *n*-hexane, perfluorohexane (PFH), and their binary mixtures, normalized to the maximum absorption in the (A) 3100−2700 cm^{-1} region and (B and C) 1500−1200 cm^{-1} region, with (C) multiplied by 2.

mixing are observed in the C−H (Figure 2A) and C−F (Figure 2B) stretching regions.

The four bands of pure *n*-hexane in Figure 2A are assigned to stretching modes of methyl and methylene groups: antisymmetric $\nu_{as}CH_3$ (2959 cm^{-1}) and $\nu_{as}CH_2$ (2926 cm^{-1}) and symmetric ν_sCH_3 (2874 cm^{-1}) and ν_sCH_2 (2861 cm^{-1}). These bands are sensitive to conformations,[42] but not in a quantitative way, due to the possibility of combination bands and Fermi resonance with overtones of deformation modes ($2 \times \delta_{sc}CH_2$ or $2 \times \delta CH_3$). Nevertheless, it is commonly accepted that a shift of these bands to higher wavenumbers is associated with an increased population of conformers with *gauche* rotations.[41,42] The changes observed in Figure 2A with increasing PFH molar ratio suggest the alteration of the conformation equilibrium toward *gauche* conformers.

The methyl and methylene deformations (Figure 2B) can also contribute to the analysis of *n*-hexane conformers, in particular, the relative intensity of the methylene scissors mode of the TTT conformer.[34,44] Since the $\delta_{as}CH_3$ and $\delta_{sc}CH_2$ bands overlap, the spectral analysis in this region is not straightforward.

In an attempt to quantify the effects of mixing with PFH on the spectrum of *n*-hexane, a band deconvolution was performed in two spectral regions (3020−2820 and 1510−1420 cm^{-1}) by a nonlinear least-squares fitting method using a sum of Voigt components. For pure *n*-hexane, it was possible to retrieve two components of the symmetric and antisymmetric methylene stretching modes, to lift the degeneracy of the methyl antisymmetric stretching (Figure 3A) and to isolate the methylene scissors mode of TTT conformers, at 1445 cm^{-1} (Figure 3B). The deconvolution results obtained for the binary mixtures are summarized in Figures S1 and S2 and in Table 1.

As a general trend, the CH stretching components of *n*-hexane shift to higher wavenumbers with increasing PFH content, and the intensity ratio between the antisymmetric and symmetric components of the CH_2 stretching modes $[A_{Total}(\nu_{as}CH_2)/A_{Total}(\nu_sCH_2)]$ increases, confirming the tendency toward conformers with *gauche* rotations.

Assuming that the component at 1445 cm^{-1} ($\delta_{sc}CH_2$) is related exclusively to the all-*trans* conformer and the one at 1460 cm^{-1} ($\delta_{as}CH_3$ and $\delta_{sc}CH_2$) is related exclusively to all-*trans* and *gauche* conformers (TTT, TTG and TGT), the evolution of the all-*trans* conformer proportion with composition may be evaluated by the ratio $[A_{1445}/(A_{1445} + A_{1460})]$. The spectrum of the mixture with x(PFH) = 0.8 was not analyzed due to its very low intensity in this region. The results (last two rows in Table 1) confirm those obtained for the stretching region: the proportion of all-*trans* conformers falls from 32% in pure *n*-hexane to values well below 17%. Moreover, the sharp increase in the $[A_T(\nu_{as}CH_2)/A_T(\nu_sCH_2)]$ ratio above x(PFH) = 0.6 is a good indication of a very low

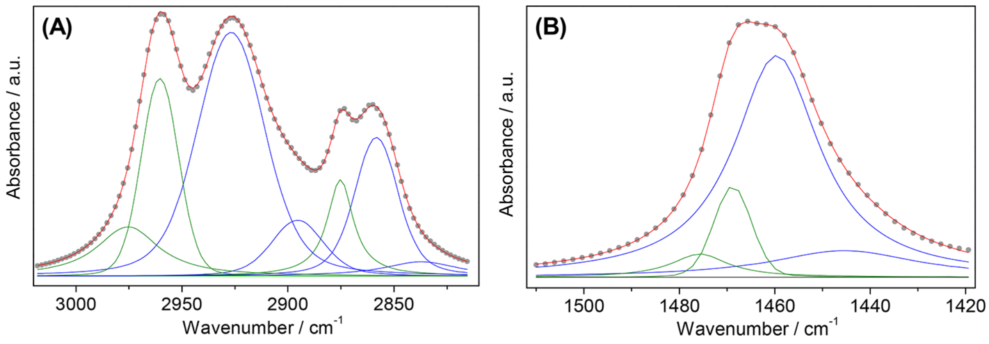

Figure 3. Deconvolution of the infrared spectrum of pure *n*-hexane in a sum of Voigt components for (A) the CH stretching region and (B) the CH deformation region. Blue lines, methylene components; green lines, methyl components.

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Table 1. Summary of the Band Deconvolution Results in the CH Stretching and Deformation Regions for Pure *n*-Hexane and (*n*-Hexane + Perfluorohexane) Mixtures[a]

	x(PFH) = 0		x(PFH) = 0.2		x(PFH) = 0.5		x(PFH) = 0.8	
assignment[34,44]	$\tilde{\nu}$ (cm^{-1})	A (%)	$\tilde{\nu}$ (cm^{-1})	A (%)	$\tilde{\nu}$ (cm^{-1})	A (%)	$\tilde{\nu}$ (cm^{-1})	A (%)
ν_sCH_2	2837	2.7	2834	3.4	2836	1.6	2841	3.6
	2858	15.2	2858	14.5	2862	14.0	2866	10.8
ν_sCH_3	2875	8.4	2875	8.3	2880	8.7	2883	6.4
$\nu_{as}CH_2$	2895	7.3	2893	9.3	2900	6.0	2910	5.7
	2927	40.4	2927	39.1	2931	39.1	2937	55.2
$\nu_{as}CH_3$	2960	17.4	2961	18.3	2964	17.5	2966	7.0
	2975	8.7	2981	7.2	2977	13.1	2974	11.3
$A_T(\nu_{as}CH_2)/A_T(\nu_sCH_2)$	**2.67**		**2.71**		**2.89**		**4.22**	
					1412	11.9		
$\delta_{sc}CH_2$ (TTT)	1445	12.4	1443	9.7	1447	4.7		
$\delta_{as}CH_3$ (TTT + TTG) and $\delta_{sc}CH_2$ (TGT)	1460	72.1	1459	73.1	1461	56.7		
$\delta_{as}CH_3$	1469	10.2	1469	14.2	1471	22.0		
$\delta_{as}CH_3$	1476	5.3	1474	3.0	1474	4.7		
$100 \times [A_{1445}/(A_{1445} + A_{1460})]$[b]	14.6		11.7		7.7			
% TTT[c]	**32**		**26**		**17**			

[a] In the deformation region, the band assignment includes the associated rotational isomer. [b] Ratio between the fitted areas of the indicated components. [c] Scaled to the % of TTT referred to in refs 33 and 34 for liquid *n*-hexane.

proportion of the TTT conformer. Therefore, the infrared spectra unambiguously indicate that the addition of PFH induces coiling on the *n*-hexane chain, shifting the conformational equilibrium toward conformers with more *gauche* rotations.

Information on PFH may be retrieved from two spectral ranges: 1375−1025 cm^{-1}, the CF stretching region without a significant contribution from the *n*-hexane spectrum, and 1025−625 cm^{-1}, with strong/medium PFH bands partially overlapped with weak/very weak bands of *n*-hexane. There are several PFH bands that can be correlated with conformers,[47] in particular, the CF_3 deformations at 795 and 712 cm^{-1} (symmetric and antisymmetric of TTT conformer) and at 816 and 731 cm^{-1} (symmetric and antisymmetric of TTG conformer).[46] As previously stated, the PFH conformer referred to as TTT is not a truly all-*trans*, as the F atoms are not eclipsed. Apparently, mixing with *n*-hexane induced no systematic band shifts or changes in relative intensities (Figure 2C). The analysis was complemented with a band deconvolution in Voigt components (Figure S3 and Table S2), which showed that the relative intensity of the PFH band component at 795 cm^{-1} is not sensitive to the increasing content in *n*-hexane, suggesting that the population of TTT conformers remains stable. If *n*-hexane perturbs the structure of liquid PFH, then it is not sufficient to change the infrared bands sensitive to rotational conformations. This suggests the possibility of segregation between the two substances, which, given their tendency to phase separation, is not physically unreasonable.

The above conclusions on the mutual conformational influence of the two components according to the infrared analysis are graphically summarized in Figure 4.

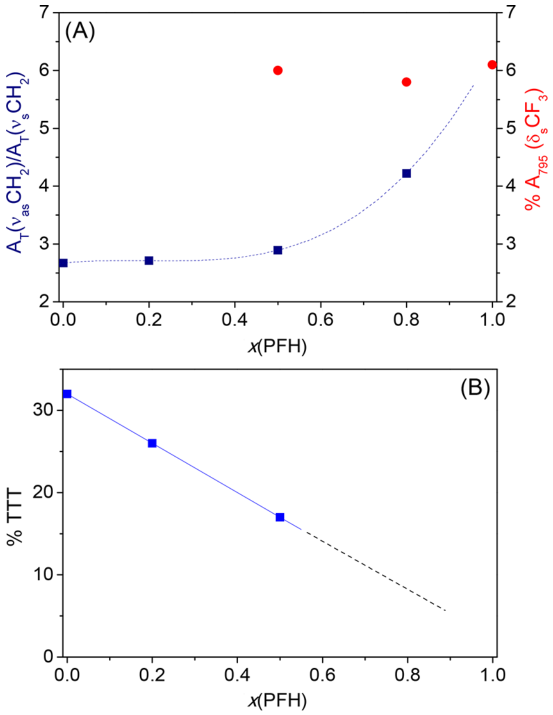

Figure 4. (A) Influence of the second component on the spectra of *n*-hexane (left) and PFH (right): the ratio $A_T(\nu_{as}CH_2)/A_T(\nu_sCH_2)$ is related to the population of *n*-hexane *gauche* conformers; $A_{795}(\delta_sCF_3)$ is related to the population of TTT conformers of PFH. (B) Influence of PFH content on the population of *n*-hexane TTT conformers.

In order to obtain further molecular-level support of the hypothesis of segregation, atomistic molecular dynamics (MD) simulations were performed. The OPLS-AA force-field was used,[49,50] with the dispersive cross-interaction parameters between alkyl hydrogen and perfluoroalkyl fluorine atoms adjusted to capture the properties of (alkane + perfluoroalkane) mixtures: the H−F cross-interaction energy was reduced by 20%, and the cross-interaction diameter was increased by 4% relative to the geometric mean rule. These adjustments were obtained in a previous work and reproduce the experimental excess enthalpy and volume.[4,51−54] MD runs in the *NpT* ensemble at 298.15 K and 1 bar, using the Nosé−Hoover thermostat and barostat, were done using the DL-POLY Classic package[55] for systems containing 256 molecules in cubic boxes with periodic boundary conditions. The simulations were run for 10 ns, with a time step of 2 fs, and the second half of the simulation was used for data collection. Bonds involving hydrogen atoms were treated as rigid using the SHAKE algorithm. A 14 Å cutoff was used, with standard analytical tail corrections for the dispersion terms and Ewald sum calculations for long-range electrostatics.

Carbon−carbon radial distribution functions (rdf) are shown in Figure 5 for (n-hexane + PFH) mixtures. As can be seen, peaks between hydrogenated chains increase significantly as the concentration of PFH increases and are always much larger than that of pure hexane. Similar behavior is found for peaks between fluorinated chains: they increase as the concentration of n-hexane increases, although with a weaker dependency on composition. This is a clear sign of segregation as, for both substances, the relative density of neighbors of the same species is larger in the mixtures than in the pure liquids. It is also seen that peaks between hydrogenated and fluorinated groups are much less intense (Figure 5B).

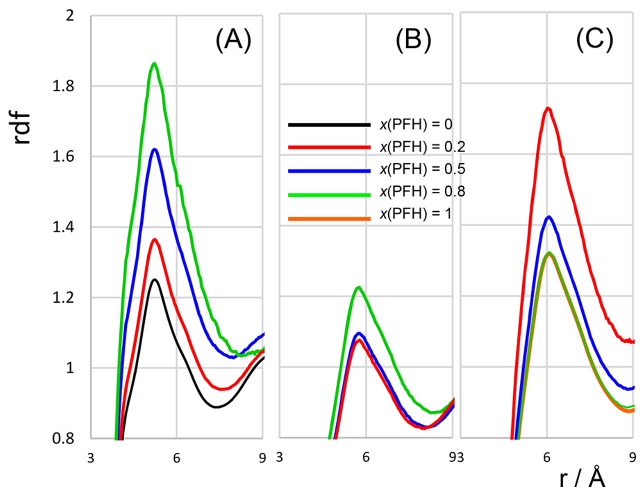

Figure 5. Intermolecular radial distribution functions between (A) CH_n groups, (B) CH_n-CF_n groups, and (C) CF_n groups for (n-hexane + PFH) mixtures at 298 K.

The dihedral distribution and end-to-end distances of the hydrogenated chains were also obtained from the simulation trajectories. However, the simulation results do not show any conformational differences from pure hexane for hexane in perfluorohexane solutions, contrary to what is observed experimentally. We believe that this is an indication that the conformational model used in the simulations is either not adequate or insufficiently accurate to capture the new reported effect.

Extending the present study to other (alkane + perfluoroalkane) mixtures poses significant experimental difficulties due to liquid−liquid immiscibility in the case of mixtures involving longer components or too high a volatility if shorter compounds are used. Nevertheless, we obtained FTIR spectra of the coexisting phases of an (n-octane + PFH) mixture. The effect of PFH on the conformational equilibrium of n-octane is clearly seen in Figure 6, which shows shifts of the CH_2 stretching bands comparable to those observed for (n-hexane + PFH), denoting coiling of the n-octane molecules.

The potential coiling of n-alkanes in water and aqueous systems is a very important subject and has been addressed and discussed repeatedly in the literature.[58,59] It should be emphasized that, given the completely different nature of the solvents, the coiling of n-alkanes in perfluoroalkanes, now reported, and in water occurs through different mechanisms.

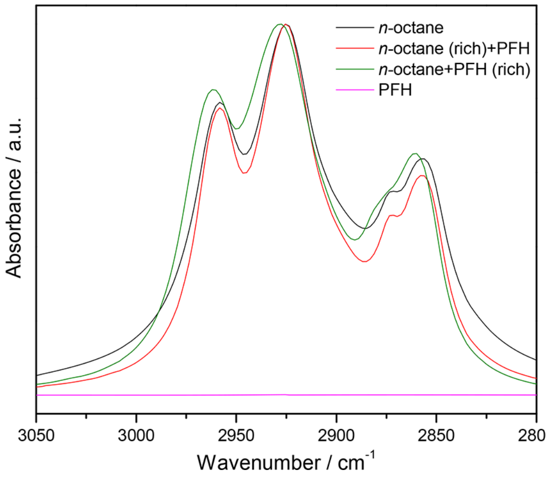

Figure 6. CH stretching region of the IR spectra of n-octane, PFH, and their coexisting liquid phases at ∼294 K.[56,57]

In the case of water, coiling, segregation, and ultimately phase separation should result from the maximization of the strong intermolecular forces between water molecules (hydrophobic effect); in the case of the (alkane + perfluoroalkane) mixtures studied in this work, only dispersion forces are present, and as previously discussed, those between alkanes and perfluoroalkanes are unexpectedly weak. In this case, we believe that coiling and segregation possibly result from trying to maximize alkane−alkane and perfluoroalkane−perfluoroalkane dispersive interactions. The fact that perfluoroalkanes do not show experimental evidence of coiling agrees with the known stiffness of fluorinated chains compared to the flexibility of hydrogenated chains.

4. CONCLUSIONS

It is demonstrated that n-alkanes change their conformational equilibria in the presence of perfluoroalkanes, favoring more globular states, with a higher number of *gauche* conformations. To the best of our knowledge, this is the first time that such a solvophobic coiling effect was observed in mixtures governed solely by dispersion interactions. Moreover, the origin of the observed effect lies on a subtle balance between weak and even weaker dispersion forces. The implications of the novel solvophobic effect with respect to the structure and properties of fluids involving mixed hydrogenated and fluorinated chains are apparent: coiling of hydrogenated chains will influence the organization of the fluid which in turn will impact the thermodynamic properties and phase equilibria. Additional evidence was found for molecular-level segregation in the (n-hexane + perfluorohexane) mixture above the upper critical solution temperature.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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IR band assignment and deconvolution analysis (PDF)

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Notes

The authors declare no competing financial interest.

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