n-Hexanol association in cyclohexane studied by NMR and NIR spectroscopies

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ABSTRACT

In this work we present a study on the association of n-hexanol in cyclohexane using NMR and NIR spectroscopies. Abrupt changes on spectroscopic responses have been observed at low molar fractions of n-hexanol, which are related to hydrogen bond network formation that includes trace water. Molecular interactions are found to be dominated by dispersion forces, hydrogen bonding, and dipolar interactions, to different extents at different n-hexanol composition ranges. 1D, DOSY, and T_1 and T_2 relaxation time analyses by ^{1}H-NMR allow understanding the dynamics of the mixtures. NIR allows verifying the formation of n-hexanol polymeric species. In addition, an n-hexanol/cyclohexane mixture with an alcohol molar fraction of 0.177 has been titrated with water, revealing the formation of a microemulsion containing water droplets that evolves to a bicontinuous microemulsion with increasing water content. Stable boundary water is detected at the microemulsion interface.

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1. Introduction

Long chain alcohol molecules are considered as weak amphiphiles in ternary mixtures of alcohol, water, and oil, due to the presence of a polar hydroxyl moiety and an apolar alkyl chain [1]. They present low solubility in water, and tend to be partitioned between aqueous and oily domains [2]. They are normally used as co-surfactants in reverse micellar systems [2–5]. In these systems, they increase the water solubility and modify the phase diagrams of surfactant/water/oil ternary mixtures [6]. They can also influence the number of water molecules present in the surfactant hydration sphere before formation of reverse micelles [7]. Besides, water/alcohol/alkane mixtures may behave similarly to water-in-oil microemulsions containing surfactants, forming the so-called detergentless microemulsions [8–12]. These microemulsions have been efficiently used to isolate reaction products upon enzymatic transformations as well as for interesting analytical purposes [10,13,14].

Alcohol molecules in non-polar solvents tend to associate in polymolecular structures mainly driven by intermolecular hydrogen bonding and dipole–dipole interactions. The hydrogen-bonding process is cooperative, i.e., is influenced by the previously formed hydrogen bonds between molecules [15]. Hydrogen bonds are relatively weak and temperature produces reversible rupture and reformation [16].

The association phenomena of alcohols depend on several factors such as molecular structure, temperature, nature of the solvent, and others [17]. A large number of models have been suggested for the association process, describing the formation of cyclic and linear polymers. In pure alcohol solutions, n-alcohols assemble into linear polymers, whilst branched alcohols tend to associate into cyclic polymers [18,19]. Alcohol association may disrupt the ordered state of the non-polar solvent: high molar fractions of n-hexanol in cyclohexane present positive values of entropy of activation for viscous flow, generating a more disordered media [20,21].

The presence of water in mixtures containing associated species of alcohol influences the dynamics of alcohol association, since water molecules are able to form complexes with alcohol molecules [22–24]. Tetrahedral complexes consisting of water molecules coordinated to four molecules of n-pentanol have been reported [25]. Aggregates formed by alcohol molecules in non-polar solvents are able to disperse droplets of water, generating optically transparent and thermodynamically stable mixtures, dissolving and structuring water molecules inside hydrophilic cavities [10,11].

Association phenomena of n-alcohols in non-polar solvents have been studied using different volumetric [20,23] and spectroscopic techniques such as IR spectroscopy [24,26–28] and NMR [29–32]. Thermodynamic methods provide indirect information about conformation and association [26]. Spectroscopic experiments are used to characterize the association of alcohols, because free or monomeric alcohol

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chains present different spectroscopic responses compared to aggregated alcohol molecules. NIR has been used to characterize bound and free hydroxyl moieties, related to the absence or presence of hydrogen bonds [19,24,26]. NMR parameters such as ^{1}H chemical shifts, relaxation times, and diffusion coefficients are broadly used to characterize the association of low molecular-weight species [33–35], such as surfactants [36,37]. A drawback of the NMR technique for the study of several systems is the high concentration of the analyte needed to obtain the spectroscopic signals, which takes minimum values of around 10^{-4} M.

Therefore, direct observation of molecules that are part of self-assembled structures by spectroscopic techniques can provide information about packing and preferential interactions between them. In this paper, molecular association of n-hexanol in cyclohexane as a function of n-hexanol concentration will be shown. The influence of added water to the molecular assemblies will be also studied. ^{1}H-NMR experiments are used to study the molecular association by analyzing chemical shifts, relaxation times, and diffusion coefficients. NIR is used to characterize free and bound n-hexanol molecules, related to hydrogen bonding. Water-in-oil microemulsion formation is followed as a function of the water content.

2. Experimental

2.1. Reagents

Commercially available deuterated and non deuterated cyclohexane (Sigma Aldrich) and n-hexanol (TCI) (Fig. 1) were used without further purification. Anhydrous n-hexanol (water content < 0.005%, Sigma Aldrich) was used for specific experiments requiring anhydrous samples. Deionized water was used for titration experiments of n-hexanol/cyclohexane mixtures.

2.2. Equipment

1D and 2D ^{1}H-NMR measurements were made at 25 °C on an AVANCE 600 spectrometer (Bruker). FT-NIR measurements were made at 25 °C on a Nicolet 6700 spectrometer (Thermo Scientific).

2.3. Procedures

Conventional methods were used in NIR and NMR measurements. Particular experimental conditions are reported in the figure captions. NIR and NMR samples were prepared by successively adding the required amount of n-hexanol in cyclohexane (or cyclohexane-d$_{12}$) in order to obtain the desired concentrations. The samples were sonicated for 1 min in order to obtain a homogeneous mixture. Addition of water to an n-hexanol solution in cyclohexane at an n-hexanol molar fraction ($X_{hexanol}$) of 0.177 was carried out until turbidity and macroscopic phase separation were observed. NIR was done in a 1 cm path length quartz vessel, using cyclohexane as blank. NMR experiments were done at 25 °C in cyclohexane-d$_{12}$. T$_1$ relaxation times were obtained applying the standard inversion recovery pulse sequence [38]. In the applied sequence the delay between π and π/2 pulses is varied, programming 8 delay times in the range from 0.1 to 16 s. The repetition time was set to 20 s and the number of scans was 8 for each delay time. T$_2$ relaxation times were obtained applying the Carr–Purcell–Meiboom–Gill pulse sequence [38]. In this sequence, eight echo times ranging from 0.2 to 1.6 s
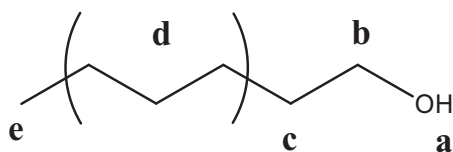
were programmed, the repetition time was set to 20 s, and the number of scans was 8 for each echo time. 2D diffusion-ordered spectroscopy (DOSY) experiments were made under a stimulated echo sequence using bipolar gradients and a longitudinal eddy current delay. Diffusion delays of 40 ms and a gradient pulse length of 3 ms were applied in order to obtain appropriate curves (25 points) for inverse Laplace transformation.

3. Results and discussion

3.1. n-Hexanol association in cyclohexane

A set of ^{1}H-NMR spectra has been measured as a function of $X_{hexanol}$ ranging between 0.002 and 0.904, which are shown in Fig. 2. The assignment of the corresponding peaks has been made based on intensity, multiplicity, and chemical shift analyses, and related to the molecular structure of n-hexanol shown in Fig. 1. Resonance peaks of Hb protons appear at 3.53 ppm as a triplet related to coupling with Hc protons, appearing at 1.50 ppm. Resonance peaks of Hd appear at 1.31 ppm as a multiplet and He protons appear at 0.90 ppm as a triplet. There is no dependence of the observed chemical shifts of these protons on $X_{hexanol}$. However, the position of the resonance peak of the hydroxyl proton (Ha) presents a dependence on $X_{hexanol}$, as can be seen in Fig. 2, and more precisely in Fig. 3. At low $X_{hexanol}$, *i.e.* 0.002, the chemical shift of the hydroxyl proton appears as low as 1.04 ppm. An increase on $X_{hexanol}$ produces a sharp downfield shift of the corresponding resonance peak, taking a value of around 4.8 ppm at $X_{hexanol}$ of 0.131. Further increase on $X_{hexanol}$ up to 0.904 generates a smooth downfield shift up to 5.24 ppm.

A 1.7–2.2% of trace water has been identified in the liquid n-hexanol used to prepare the samples, as seen by integration of ^{1}H-NMR signals. Water chemical shifts have been also plotted in Fig. 3. The corresponding chemical shifts follow the same tendency of n-hexanol hydroxyl protons when $X_{hexanol}$ increases, and the difference on the chemical shifts corresponding to water protons and alcohol hydroxyl protons tends to a constant value of almost 1 ppm as can be seen in Fig. 3, inset.

On the other hand, it is interesting to note that the multiplicity of the resonance peaks of Ha and Hb protons depends on $X_{hexanol}$. In Fig. 4 it can be seen that, when $X_{hexanol}$ remains in the range of 0.002 to 0.350, Ha appears as a singlet and Hb appears as a triplet, as a consequence of the coupling with Hc protons. For values of $X_{hexanol}$ between 0.350 and 0.659 broadening of both signals, showing higher complexity, is observed. Finally, above $X_{hexanol}$ of 0.659 Hb appears as a quartet, whereas Ha appears as a triplet, revealing coupling between Ha and Hb. A similar pattern has been observed when the ^{1}H-NMR spectra of pure alcohols is recorded [39,40].

DOSY experiments allow determining the diffusion coefficients of n-hexanol and water in the mixtures as a function of $X_{hexanol}$. The DOSY spectra show the signals from each hydrogen atom in the molecule.
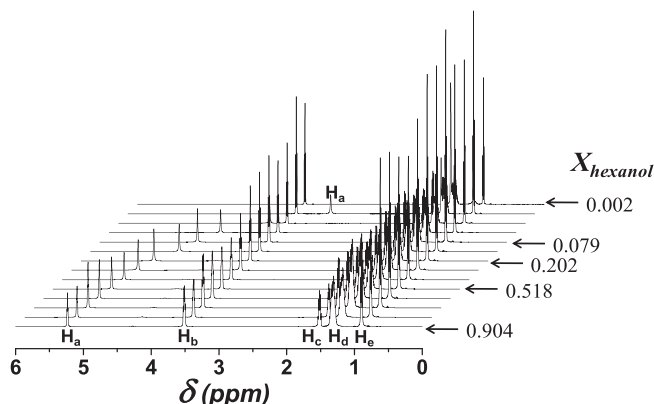

Fig. 1. Molecular structure of n-hexanol.

Fig. 2. Stacked ^{1}H-NMR spectra of n-hexanol in cyclohexane$_{d-12}$ at different $X_{hexanol}$.