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Hydrogen bonds between methanol and the light liquid olefins 1-pentene and 1-hexene: from application to fundamental science†

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We have recently developed a new extraction process for significantly reducing the olefin content in commercial FCC gasoline. To gain insights into the origins of this process, we have investigated the dissolution of the light liquid olefins 1-pentene and 1-hexene in methanol through computer modelling together with NMR spectroscopy. We find two important hydrogen bonding modes for methanol olefin interactions – namely, O−H···π and C−H···O.

Fluid catalytic cracking (FCC) is one of the principal oil refining processes which converts heavy fractions crude oil into transportation fuels. Unfortunately, as-produced FCC gasoline contains high levels of olefins (in some cases up to 59% v/v) and appreciable levels of thiophenic sulphur impurities and aromatics,[1–4] all of which require further treatment to attain acceptable environmental levels set by the World Fuel Charter Standard.[5] The olefin and sulphur content is conventionally reduced by hydrogenation and hydrodesulphurization but inevitable olefin saturation leads to fuel octane loss and excessive consumption of hydrogen (produced of course by the carbon-footprint-intensive steam-reforming of methane).[2,6]

We have recently developed[7] a new "Extractive Refining" (ER) process which uses methanol as a highly effective solvent to extract olefins and other products such as organic sulphur compounds (OSCs) from FCC gasoline (Fig. 1: see ESI† for experiment details). For example, after just one methanol extraction cycle, the level of total olefin in FCC gasoline, which consists of C_4–C_8 olefins,[8,9] were significantly reduced by some 31.6% (Fig. 1). The resultant mixture of the olefin containing

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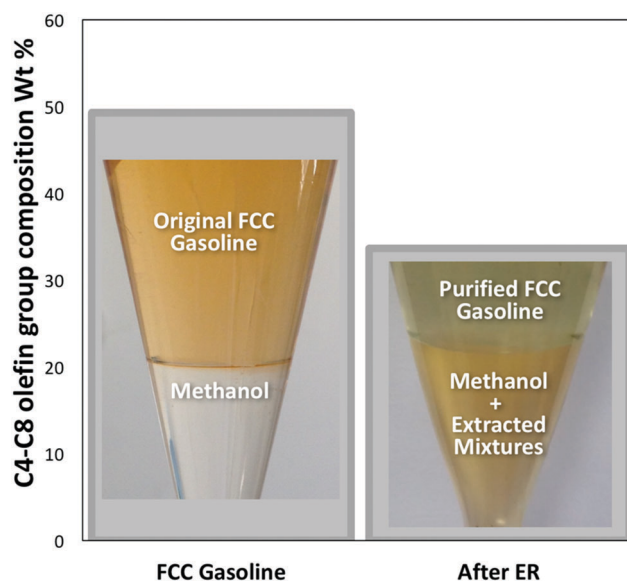
Fig. 1 Commercial FCC gasoline (SINOPEC) composition of C_4−C_8 olefins both before and after one cycle of the Extractive Refining process.

methanol can also be catalytically converted into high quality gasoline and other products.

We targeted methanol as a selective solvent for extraction since it is a high-volume, inexpensive commodity chemical, readily produced from a range of carbonaceous feedstocks, including biomass and of course CO_2, itself.[10,11]

To enhance the efficiency of the new ER process and with that the maximization of the environmental gain, it is necessary to have a fundamental understanding of the interaction, for example, between the extracting solvent, methanol and the constituent solute olefins.

It has been shown that C_4–C_8 olefins in exhaust emissions from vehicles are mainly unburnt components,[8,9] while C_6 olefins are the major olefinic constituent in FCC gasoline fraction.[12,13] We therefore targeted both the C_5 and C_6 homologous members for this study. Importantly, we find that both these light liquid

olefins, 1-pentene and 1-hexene are completely soluble in methanol at room temperature and room pressure.

It was previously reported that 1-heptene is mutually soluble in methanol above the Upper Critical Solution Temperature of 285 K and 271.6 K, respectively.[14–16] However, these studies did not interrogate the nature of the light liquid olefin–methanol interaction. Recently Heger *et al.* investigated the hydrogen bond between methanol and ethene molecules in the gas phase,[17] Oku *et al.* proposed a structure for the methanol–2-butene complex and structures based on their quantum chemical calculation of optimised interaction energies, but no direct experimental evidence was presented.[18] Medel *et al.* also investigated the molecular docking *via* olefinic O–H···π interactions,[19] but these studies did not encompass possible hydrogen bond interactions between methanol and liquid olefins, and the effect of these interactions on the solubility of olefins in methanol. Zwier extensively reviewed the complexation of methanol and the π-system of molecular benzene in detail, but did not extend the study to interactions between liquid methanol and olefin, the present system of interest here.[20]

To explore the possible origins of the interaction between the prototypical light olefins and liquid methanol we first carried out quantum chemical calculations of 1-pentene and 1-hexene (alpha-olefins are the main olefins in FCC gasoline) with a single methanol molecule (olefin···methanol) and found the stable structure of these olefins surrounded by 8 methanol molecules (olefin···8 methanol, see ESI† for full computational details). In the most stable equilibrium structures of the olefin···methanol associates, the hydroxyl hydrogen atom of methanol interacts with the π (C═C double) bond of the olefin with the OH···(C═C)$_{midpoint}$ distances of 2.36–2.41 Å (Table 1, Fig. 2 and Table S2, Fig. S1 in ESI†).

The methanol···1-hexene (O–H···π) binding energies computed at the M06-2X and CCSD(T) levels, both with and without basis set superposition error (BSSE) correction, are given in Table 1. Their values (−11.3 to −19.8 kJ mol^{-1}) are comparable for both levels, and the BSSE correction is rather insignificant (−2.4 kJ mol^{-1}). The topological analysis of the electron density
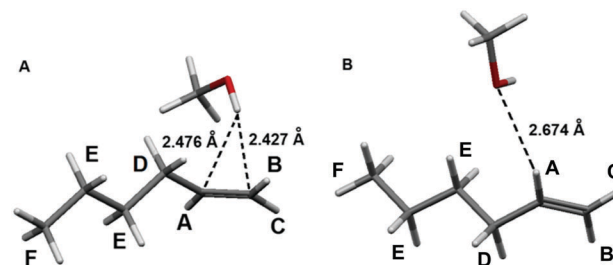

Fig. 2 Equilibrium structures of the 1-hexene···methanol associates exhibiting the O–H···(C═C) (A), the most stable structure and C–H···O (B) interactions.

distribution (the AIM method) revealed the existence of a bond critical point (BCP) corresponding to the interaction between the methanol hydroxyl hydrogen atom and the π bond in the 1-hexene···methanol associate. The electron density values (ρ) at this BCP do not exceed 0.10 e Å^{-3} (Table 1), the electron density Laplacian ($\nabla^2\rho$) is positive and the energy density values (H_b) are slightly positive. All these values are typical for the weak hydrogen bonding.[21–23] The natural bond orbital analysis demonstrates very small charge transfer (0.003 e) from 1-hexene to the methanol molecule in the associate 1-hexene···methanol which is associated with the π (C═C) → σ*(OH) transition with the $E(2)$ second order NBO energy of 10.5 kJ mol^{-1}. Both models, *i.e.* 1-hexene···methanol cluster with bulk solvent effects and 1-hexene···8 methanol cluster with explicit first solvation shell around olefin molecule, demonstrate very similar bonding features. Results obtained for the 1-pentene + methanol system are similar and given in ESI.†

These calculations indicate that the dissolution process could involve hydrogen bonds formed between the olefin and methanol, *via* O–H···π and C–H···O interactions as we will illustrate experimentally.[18,24]

To further probe the nature of the interaction of hydroxyl group in methanol with this light olefin, the mixtures were studied by high resolution ¹H-NMR spectroscopy using a Bruker Advance III HD Nanobay 400 MHz NMR spectrometer and utilising deuterated methanol and cyclohexane (to render these solvents "invisible" in the H spectra). Cyclohexane was chosen as the reference solvent in this analysis, and it is also mutually soluble with the olefin. Tetramethylsilane (TMS) was used as the internal standard, which is assigned the chemical shift zero (0 ppm).

We determined the precision and standard error of the chemical shifts by careful fitting of the NMR line positions from typically 10 separate runs for each sample and is ±0.005 ppm. The ¹H-NMR spectra of solutions of 1-pentene and 1-hexene in both of these solvents are shown in Fig. 3 and 4.

Here 1-pentene and 1-hexene are regarded as the solutes and methanol as the host solvent. The resulting chemical shifts are a direct consequence of electron redistribution around H atoms following H bond formation. In pioneering work, Buckingham *et al.* defined four interactions responsible for solvent effects in the NMR of solute species,[25] hydrogen bonding, anisotropy of the solute and solvent interactions and dipole–dipole and van der Waals interactions. The quantitative treatment of these

Table 1 The calculated parameters of the 1-hexene···methanol and 1-hexene···8 methanol associates

	1-Hexene···methanol			
	Gas phase^a	SMD (1-hexene as solvent)^b	SMD (methanol as solvent)^b	1-Hexene···8 methanol^{a,c}
$E_b{}^d$	−19.6 (−17.2)^e	−19.8	−13.6	
$E_b{}^f$	−15.8	−14.8	−11.3	
l(OH···π)^g	2.409	2.376	2.360	2.361
ρ^h	0.082	0.090	0.088	0.096
$\nabla^2\rho^i$	0.859	0.912	0.919	1.012
$H_b{}^j$	0.010	0.011	0.012	0.010

^{a} Isolated molecular associate without bulk solvent effects. ^{b} SMD solvation model. ^{c} Molecular associate with a 1-hexene molecule surrounded by 8 methanol molecules. ^{d} Binding energies (in kJ mol^{-1}) at the M06-2X/6-311+G** level. ^{e} BSSE corrected value. ^{f} Binding energies (in kJ mol^{-1}) at the CCSD(T)/6-311+G**//M06-2X/6-311+G** level. ^{g} Intermolecular OH···(C═C)$_{midpoint}$ distances (in Å). ^{h} Electron density (in e Å^{-3}) at the OH···(C═C) BCP. ^{i} Laplacian (in e Å^{-5}) at the OH···(C═C) BCP. ^{j} Energy density at the OH···(C═C) BCP (in Hartree Å^{-3}).
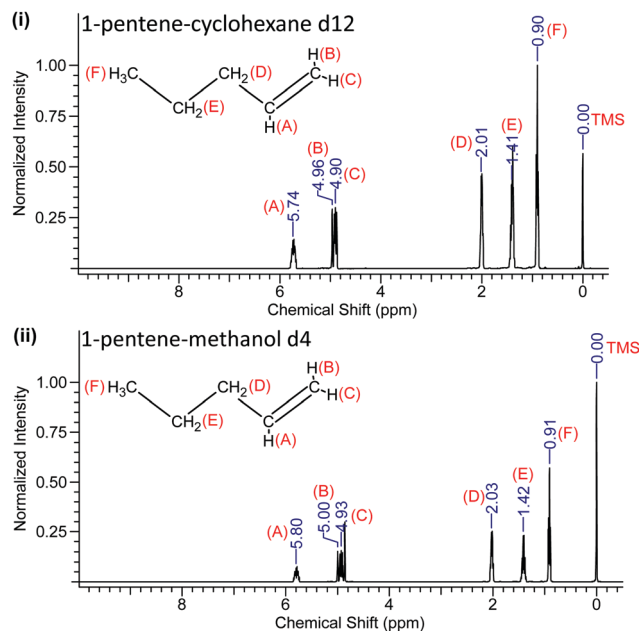
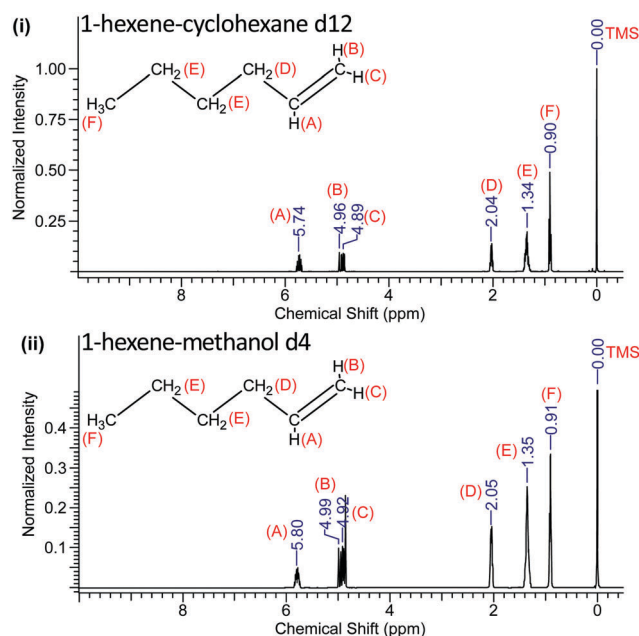**Fig. 3** ^{1}H-NMR spectra of 1-pentene in cyclohexane-d$_{12}$ (i) and in methanol-d$_4$ (ii).

Fig. 4 ^{1}H-NMR spectra of 1-hexene in cyclohexane-d$_{12}$ (i) and in methanol-d$_4$ (ii).

relative contributions to solvent shifts of solutes still remains a major challenge.[25,26]

The recorded values of the NMR chemical shifts of the various protons are indicated in Fig. 3 and 4 and the location (A–F) of the 1-pentene and 1-hexene's protons are also labelled.

The NMR data reveal that when 1-pentene and 1-hexene are dissolved in methanol, all the protons are de-shielded relative to those in cyclohexane solutions with chemical shifts moving downfield. The protons located at A, B and C become more

Table 2 ^{1}H-NMR results for the mixtures of 1-pentene (1-pen) and 1-hexene (1-hex) in methanol-d$_4$ (M-d$_4$) or cyclohexane-d$_{12}$ (C-d$_{12}$), and DFT calculated protons' (^{1}H) chemical shift for 1-hexene (1-hex) and 1-hexene···methanol (1-hex···MeOH)

Proton	^{1}H chemical shifts (experimental) δ^a				^{1}H chemical shifts (calculated) δ	
	1-pen in C-d$_{12}$	1-pen in M-d$_4$	1-hex in C-d$_{12}$	1-hex in M-d$_4$	1-hex	1-hex···MeOH
A	5.74	5.80	5.74	5.80	6.72	7.05
B	4.96	5.00	4.96	4.99	5.80	5.91
C	4.90	4.93	4.89	4.92	5.60	5.74
D	2.01	2.03	2.04	2.05	2.09^b	2.26^b
E	1.41	1.42	1.34	1.35	1.26^b	1.30^b
F	0.90	0.91	0.90	0.91	0.96^b	0.97^b

^{a} Chemical shift (in ppm), standard errors are ±0.005 ppm. ^{b} Average values for all protons of a given type.

de-shielded as compared to the other protons located at D, E and F (Fig. 3 and 4). The chemical shift changes for the 1-pentene's proton located at (A), (B) and (C) were 0.06 ppm, 0.04 ppm and 0.03 ppm, for the 1-hexene's proton located at (A), (B) and (C) were 0.06 ppm, 0.03 ppm and 0.03 ppm (Table 2). It is important to note that these shifts are outside of the experimental error estimates (±0.005 ppm) in carefully measured chemical shifts across ten recordings of each sample and the results reveal excellent reproducibility.[27] We note that these (A), (B) and (C) protons are located on the unsaturated carbon atom (Fig. 3 and 4).

The complete ^{1}H-NMR results for the mixtures of 1-pentene and 1-hexene in cyclohexane-d$_{12}$ or methanol-d$_4$ are listed in Table 2.

Bulk magnetic susceptibility differences between cyclohexane and methanol will make contributions to the magnetic shielding of all constituent protons; and these should be identical and independent of their position along the hydrocarbon chain. The fact that the observed chemical shifts for the H associated with all constituent carbon atoms are different in magnitude (Table 2) reflect site-specific interactions which contribute to the magnetic shielding of individual protons.

The combination of the spectroscopic and computational data enables us to conclude that these NMR chemical shifts originate from the two types of olefin–methanol interactions highlighted in our computational studies (Fig. 2).

The first is the O–H···π interaction,[17,18] sometimes referred to as the "pi hydrogen bond". When the O–H···π hydrogen bond is formed, the 1-pentene or 1-hexene acts as a π base (hydrogen bond acceptor) where the electron density from the olefin's π-electron system is donated to the proton (σ^* orbital) of the methanol's hydroxyl, and this reduces the electron density of the protons (A), (B) and (C) which are linked with the unsaturated carbon atom in the olefins.[22,23,28,29]

The second type is the C–H···O interaction,[24] where the oxygen atom on methanol acts as an hydrogen bond acceptor,[22,23] and due to an electrostatic interaction the electron density from the methanol's oxygen atom is donated to the protons located at (B) and (C) of 1-pentene or 1-hexene.[30–32] However, compared with the energy of O–H···π interactions, the C–H···O interaction between these olefins and the methanol molecule is weaker.[18]

Because of the formation of these hydrogen bonds, the electron density of the protons linked to the unsaturated carbon atom is thereby decreased. This leads to the reduction of the shielding effect on these protons. It is particularly noteworthy that the chemical shift of the protons (A) to (C) increases more than the remaining protons (D) to (F) (Table 2). In addition, proton chemical shift of 1-hexene and 1-hexene in methanol calculated from DFT shows the similar trend (Table 2).

Hence, through the analysis of these ^{1}H-NMR results and computational studies, we conclude that hydrogen bonds are formed (1) between methanol and olefins through the interaction of the π-electron cloud of 1-pentene or 1-hexene and the hydrogen atom of the methanol hydroxyl group,[18,33] together with the interaction of a proton of these olefins and the oxygen atom of the hydroxyl group on methanol.[31]

In conclusion, we have demonstrated that both 1-pentene and 1-hexene are completely miscible in methanol at room temperature. A combination of computational and high resolution NMR studies indicates that the interaction between these olefins and the host solvent methanol molecules is mainly due to the presence of O–H···π and C–H···O hydrogen bonds. Understanding the microscopic interactions of these prototypical light liquid olefins with methanol provides valuable insights into this new removal/separation process for olefin reduction from FCC gasoline in refineries world-wide.

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