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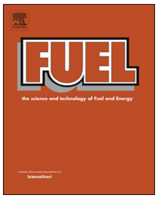

Full Length Article

Solubility and crystallisability of the ternary system: Hexadecane and octadecane representative in fuel solvents

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ABSTRACT

The solubility and crystallisability of a range of binary mixtures of n-hexadecane ($C_{16}H_{34}$) and n-octadecane ($C_{18}H_{38}$), as the predominant alkanes present in hydrotreated vegetable oil (HVO), from three representative fuel solutions (dodecane, toluene and kerosene) is presented. The dissolution (saturation) and crystallisation (supersaturation) points of the solutions are measured using poly-thermal methods utilising turbidometric detection over four concentrations from (192 g/l to 400 g/l). The data reveals the existence of more soluble, less stable crystal structures that form from the alkane mixtures, when compared to the stable triclinic crystal structures formed from the single solute component solutions. An increased carbon chain length results in lower solubility for all three solvents and the solvent type is not found to have any significant effect on the solid forms produced from the mixtures. van't Hoff analysis reveals the solvent type to influence the solute solubility with the closest to ideal behaviour being dodecane followed by kerosene and toluene, respectively. This finding is further supported by the calculated dissolution enthalpies and activity coefficients, which are the lowest in dodecane followed by kerosene and toluene. Larger values of activity coefficients are observed for compositions with molar fraction (y) = 0.1, 0.5–0.7 $C_{18}H_{38}$ which reflect the complex multi-phase formation in the solutions when compared with the more simple binary melt crystallisation system.

1. Introduction

A global concern towards greenhouse gas emissions and their impact on the environment has led to an ever-increasing use of sustainable, bio-derived feedstocks in fuel oils. By 2020, 10% of biofuel will be shared in transport as a blend component with the traditional fossil oil according to the target set by the European Union (EU) [1]. This second generation of biofuel has been intensively investigated by the EU due to its advantages regarding its compatibility with diesel fuel and its very high cetane number which can boost the fuel properties [2]. This biofuel can be produced by one- or more-step catalytic hydrotreating of different triglyceride containing vegetable oils (HVO) with typical production of a mixture of paraffins, namely $C_{15}H_{32}$, $C_{16}H_{34}$, $C_{17}H_{36}$ and $C_{18}H_{38}$ [3].

Technologically, the cold flow properties (notably its cloud and pour points) of hydrocarbon fuels, such as diesel and HVO are undesirable due to the high crystallisation temperatures of the long-chain alkanes within the fuel. The high molecular weight alkanes become supersaturated during cooling, which results in the precipitation of less soluble flat plate-like wax crystals, which can aggregate together to form an impermeable mass that can melt together and block a vehicle's fuel filter, causing low operability of vehicles in cold climate regions. Conventional additives can inhibit nucleation and partly destabilise the fast-growing faces of these wax crystals and produce more compact habits in which the crystals are usually tabular in shape and reduced in size, respectively. However, the consequence of variance distribution of carbon number blending with 10% HVO^3 into the traditional diesel [4] (Fig. 1) effects the carbon number chain distribution of the fuel fraction leading, in turn, to changes in the crystallisation behaviour and, potentially, the solid form that results. This outcome provides the incentive to obtain an improved fundamental knowledge of the crystallisation behaviour of blended HVO/diesel fuels in order to understand and mitigate any negative impact of HVO addition on the resulting cold flow properties of the fuel.

Since the studies of Müller [5–8], there has been much research into the crystalline structures of a wide range of alkanes (C_nH_{2n+2}). Full

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Abbreviations: EU, European Union; HVO, Hydrotreated vegetable oil; KBHR, Kashchiev–Borissova–Hammond–Roberts; MSZW, Metastable zone width; PXRD, Powder X-ray diffraction; STD, Standard deviation; XRD, X-ray diffraction

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List of symbols

C_nH_{2n+2}	alkane
$C_{16}H_{34}$	N-hexadecane
$C_{18}H_{38}$	N-octadecane
C_p	Heat capacity
M011	Monoclinic structure, space group ($P2_1/a$)
M_{dci}	Monoclinic structure with conformational defects, space group (Aa)
n	Number
O_{dci}	Orthorhombic structure with conformation defects, space group (Pnam)
O_i	Orthorhombic structure, space group (Pcam)
O_p	Orthorombic structure, space group ($Pca2_1$)
q	Cooling rate (°C/min)
R	Ideal gas constant (J/K.mol)
R_I	Rotator phase with orthorombic structure, space group (Fmmm)
R_{II}	Rotator phase with orthorombic structure, space group ($R\bar{3}m$)
R_{III}	Rotator phase with triclinic structure
R_{IV}	Rotator phase with monoclinic structure
R_V	Rotator phase with monoclinic structure
T	Solution temperature (°C)
T_c	Crystallisation temperature (°C)
$T_{c,l}$	Crystallisation temperature at the kinetic limit/equilibrium crystallisation temperature (°C)
T_{diss}	Dissolution temperature (°C)
T_e	Equilibrium saturation temperature (°C)
T_p	Triclinic structure, space group ($P\bar{1}$)
x	Molar solubility
x_ideal	Molar solubility in ideal state
y	Mol fraction $C_{18}H_{38}$ in $C_{16}H_{34}$
a	Activity of the solid phase
a_s	Activity of the solute in solution
T_m	Melting point (°C)
ΔH_f	Enthalpy of fusion (kJ/mol)
ΔH_{diss}	Molar enthalpy of dissolution (kJ/mol)
ΔS_{diss}	Molar enthalpy of dissolution (kJ/K.mol)
ΔS_f	Entropy of fusion (kJ/K.mol)
γ	Activity coefficient

crystal-structure determination from single crystals of $C_{23}H_{48}$, $C_{36}H_{74}$ and $C_{18}H_{38}$, was carried out by Smith [9], Shearer [10], Nyburg and Luth [11], respectively. Further research relating towards lattice parameter measurements was performed by Retief [12,13], Nyburg and Potworowski [14], Luth [15] and Craig [16]. The latter confirmed the unit cell parameters as measured using high resolution synchrotron powder X-ray diffraction (PXRD), from $C_{13}H_{28}$ to $C_{60}H_{122}$ for even parity alkanes: triclinic ($P\bar{1}$) for [$12 \le CnH2n + 2 \le 26$] to monoclinic ($P2_1/a$) for [$28 \le C_nH_{2n+2} \le 36$] to orthorhombic ($Pca2_1$) for ($C_{36}H_{74}$, $C_{46}H_{94}$, $C_{50}H_{102}$ and $C_{60}H_{122}$). Odd parity alkanes were confirmed to have the Pbcm orthorhombic structure. It has also been found that disordered (rotator) phases are present between the liquid phase and the lower temperature ordered crystal phases, associated with rotational molecular positional disorder around the long molecular axis of the alkane molecules [17–20]. For even number alkanes, rotator phases were only observed in the longer chain systems with, $C_nH_{2n+2} \geqslant 20$, with their stability being highly dependent on chain length [17,20]. The most common rotator phase has been found to be R_I structure, space group (Fmmm), which occurs in odd alkanes, $C_{11}H_{24}$ through $C_{25}H_{52}$, and solid solution mixtures of even and odd alkanes within this range [18,19].

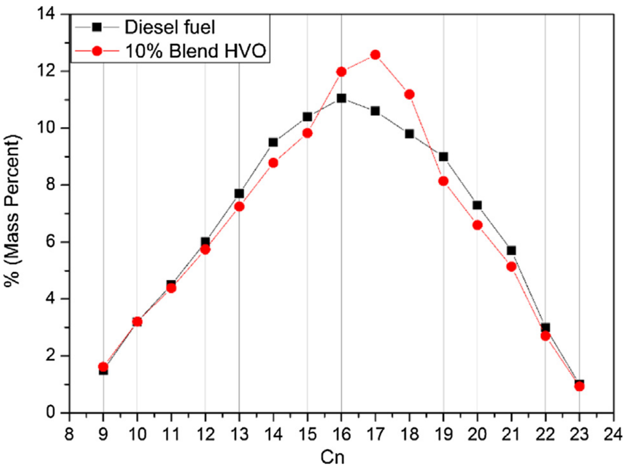

Fig. 1. Representative alkane distribution curves in traditional diesel fuel (■) and the blended fuel with 90% diesel + 10% HVO (●). This shows the variance distribution of carbon number blending with 10% HVO into the traditional diesel [3,4] highlighting an enhancement in the $C_{16}H_{34}$: $C_{18}H_{38}$ content.

The known phase behaviour for binary mixtures in the range of C_8H_{18}-$C_{28}H_{58}$ was summarised by D. Mondieig et al. [21] for systems with $\Delta n = 1$ and 2. This revealed a number of additional phases by mixing – R_I at high temperature and the ordered phases of Odci, Mdci, Mdcp, and Op forms at low temperature, shown in Table 1.

The solubility of alkanes has been widely studied, with a large amount of experimental data collected, regarding solutions containing either one or two solutes, which create pure crystals of the independent components [22–27]. However, studies of systems that form mixed crystals, i.e. solid solutions in a solvent environment, have been very limited, e.g. Gerson [28] and Flöter [29] who studied mixtures of $C_{20}H_{42}$:$C_{22}H_{46}$ in dodecane and n-heptane solutions, respectively. Both studies examined the saturation temperatures as a function of varying mixture composition, observing a clear pattern in saturation temperatures and the formation of different solid-solution phases. However, the phases of the solid solutions formed were not clearly defined in these studies. Early synchrotron diffraction work by Cunningham et al. [30] and Gerson et al. [31–33] suggested the existence of complex phase behaviour with triclinic, and up to three orthorhombic phases.

A recent PhD study [34] by one of the authors has provided some insight into phase behaviour understanding of $C_{16}H_{34}$:$C_{18}H_{38}$ binary mixtures and a subsequent ternary system in kerosene solutions. Examination of the binary $C_{16}H_{34}$:$C_{18}H_{38}$ equilibrium phase diagram

Table 1
Crystallographic characteristics of pure alkanes [21]. Subscripts 'dc', 'i' and 'p' represent conformational defects, even parity and odd parity, respectively. M011 is one of the M(hkl) phases; where (hkl) describes the plane formed by the methyl end groups in the referential of the orthorhombic subcell.

Phase	C_nH_{2n+2}/C_nH_{2n+2} Range	Crystal System	Space Group	Z
R_I	$9 \le n_{odd} \le 25$ and $n_{even} = 22{,}24$	Orthorhombic		4
R_{II}	$22 \le n \le 26$	Trigonal		3
R_{III}	28	Triclinic	–	–
R_{IV}	28	Monoclinic	–	–
R_V	23, 25	Monoclinic	–	–
T_p	$8 \le n_{even} \le 24$	Triclinic		1
M011	$n_{even} \ge 26$	Monoclinic		2
O_i	n_{odd}	Orthorhombic		4
O_{dci}	$n_{odd} \ge 23$	Orthorhombic		4
M_{dci}	$n_{odd} \ge 25$	Monoclinic		4
O_p	36	Orthorhombic		4