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Control of n-alkanes crystallization by ethylene–vinyl acetate copolymers

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Abstract

The crystallization of paraffins from their solution at low temperature was investigated in the presence of ethylene–vinyl acetate (EVA) copolymers that allow the control of the size of the crystals. Depending on the type of solvent and distribution of the paraffin lengths, the mechanisms of crystal formation and growth are different. Precipitation of the EVA prior to the paraffins leads to the nucleation of a large number of crystals, whereas the adsorption of EVA on the surface of the growing crystals slows down the crystal growth. EVA can act either as a nucleating agent or as a growth inhibitor. These two mechanisms were identified from the analysis of the temperature of crystallization (cloud point), the chemical composition of the crystals, and the observations of the crystal habit. The EVA was able to co-crystallize with the paraffins in crystals of an orthorhombic structure and the melting enthalpies of the crystalline paraffin did not depend significantly on their neighborhood. The energies of interaction between the different paraffinlike components are close to each other, so that minor changes of the experimental conditions may lead to dramatic effects. This is the basic rationale for the large behavioral diversity observed in these systems.

Keywords: Alkane; Paraffin; Ethylene–vinyl acetate copolymer; Crystallization; Crystal growth; Crystal habit

1. Introduction

The control of crystallization processes is a problem of quite general relevance, which appears in many practical fields. "Crystal design or engineering" enables, in principle, a direct handling of the structure, size, and shape of crystals entering into the elaboration of materials [1,2]. This appears as a complex issue where several different mechanisms are involved in the control of the final crystal properties [3,4]. Classical means of controling size, morphology, and polymorphic expression of crystals make use of parameters such as temperature, pH, supersaturation, and solvent quality [5]. Crystallization additives are also efficient for that purpose [6] but their mechanisms of action are several and difficult to assess. Additives may act as nucleation promoters, their action being considered as templated crystallization. In quite a different way, additives may control the crystal growth by adsorption at the surface of the growing crystals, specifically blocking some crystallographic faces [7,8]. Additives may also co-crystallize, at least at the beginning of the crystallization course. There are many illustrative examples of crystal design by means of amphiphilic biopolymers acting as templates in life processes [9,10]; surfactant monolayers [11] or block copolymers [12] are often used as templates.

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The crystallization of paraffins from solutions is of practical relevance in the petroleum industry: paraffinic crude oils, asphalt, and diesel oil [13–16]. Thus, linear n-alkanes have a limited solubility in the complex aromatic/aliphatic matrix and separate out from solutions either as long needles or as thin rhombic plates. The formation of crystals of large size by uncontrolled crystallization of paraffins leads to plugging phenomena in pipes, pumps, and filters or to gel formation [13,14]. Though energetically desirable, these long-chain alkanes cause recurrent problems to the oil industry and user alike in storage, transport, and use of petroleum distillates at low temperatures [13,14].

Depending on their length and evenness, pure paraffins crystallize as monoclinic (even n-alkanes with $n > 26$), triclinic (even n-alkanes with $n < 26$), or orthorhombic (odd n-alkanes) structure [17]. Paraffin mixtures crystallize as orthorhombic or hexagonal phases [18–21]. The thermodynamic behavior of paraffin mixture solutions resembles eutectic solidification [22]. Crystals are needle-shaped when the cooling rate is fast, whereas plates form when it is slow [23]. They often exhibit spiral growth on their faces but crystals most often grow faster on lateral faces, leading to plate formation [24,25].

Among the various additives that have been developed for the control of paraffin crystallization in order to improve the behavior of petroleum distillates at low temperatures [26,27], ethylene–vinyl acetate copolymers (EVA) show good efficiency in diesel oil [13,14,28]. The crystals formed in the presence of EVA are much smaller and more numerous, and they exhibit a more compact habit [23].

However, the action mechanism of the EVA copolymer is still unclear in spite of several investigations performed by means of viscosity measurements of EVA solutions [29–31], DSC [32,33], and reaction calorimetry [34]. One obstacle to academic research in this field is the strong dependence of the properties on the composition of the paraffin mixture and the matrix. It is difficult to select a paraffin and matrix that would allow generalization to different systems. The relevance regarding the application is everywhere questionable. Alkanes such as heptane [17,35,36] or tetradecane [22] did not reproduce phenomena observed in the practical application. Although imperfectly, ethylbenzene [37,38] simulates the aromatic part of diesel oil, which seems to play an important role in paraffin crystallization [39]. Finally, kerosene [40] or dewaxed diesel oil [24,25] is more complex but closer to the actual practice. The EVA copolymers have their maximum activity for the control of paraffin crystallization when the solvent has significant aromatic parts and the distribution of paraffin lengths is broad [41,42].

The two mechanisms of heterogeneous nucleation and growth inhibition have been proposed but there is no totally convincing evidence in favor of one or the other [24,25,33]. EVA copolymer as a nucleating agent should crystallize from the solution above the crystallization temperature of n-paraffins. Thus, measurements of cloud points are often in agreement with this idea, which seems widely accepted. However, contradictory results are given in the literature where cloud point depression [17] as well as increase [32] has been measured. A growth inhibition mechanism has been put forward as a result of several experimental investigations and simulations on polymeric flow improvers having long alkyl lateral chains [16,43–45].

The present study is an investigation into the mechanism of action of EVA copolymers for the control of paraffin crystallization. The paraffin crystals precipitating at low temperature from paraffin solutions were analyzed in terms of size, crystal habit, and chemical composition for four different systems with either a narrow or a broad distribution of paraffins and either ethylbenzene or kerosene as a matrix. Last, the interactions between a pure paraffin and the EVA copolymer have been investigated in EVA–paraffin blends by means of differential scanning calorimetry (DSC) and IR spectroscopy and X-ray diffraction, which proved to be well-suited techniques in that case [46].

2. Materials and methods

2.1. Chemicals

The commercial kerosene was a petroleum distillate containing less than 4 wt% of low-molecular-weight paraffins. Its density was 0.795 kg/L and its cloud point was −64.9 °C.

The commercial ethylene–vinyl acetate copolymer (EVA) from ATOCHEM referenced as CP7018 was a random copolymer of low molar mass having 12 mol% (28 wt%) of vinyl acetate units. Since the distribution of the VA units was random because ethylene and vinyl acetate have similar reactivities in radical polymerization [47,48], the average length of the polyethylene segments was about 22 carbon atoms. The molar masses as given by size exclusion chromatography were $M_{\mathrm{N}} = 2400$ g/mol and $M_{\mathrm{W}} = 10{,}800$ g/mol. This copolymer was precipitated in methanol, filtered, and dried under vacuum prior to utilization.

The paraffin mixture was purchased from Acros and distilled under vacuum to eliminate the highest molar mass alkanes. Its final composition as measured by gas chromatography was centered on tetracosane (Fig. 1). This mixture is referred to as “the paraffin blend” in the following.

Eicosane, docosane, and tetracosane (>99% purity from Aldrich) were used as received. Perdeuterated n-tetracosane $C_{24}D_{50}$ (>98 mol% isotopic purity) was from Eurisotop. All other compounds were supplied by Aldrich and used as received.

2.2. Methods

Differential scanning calorimetry (DSC) of samples sealed in aluminum capsules were performed with a V4.0B Dupont apparatus (sample weight ≈ 10 mg, heating rate = 10 °C/min). IR absorption spectra were recorded with a