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(Article begins on next page)

Wax Segregation in Oils: A Multiscale Problem.

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Preface

It is for me a great honour to be invited to deliver the Alan Tayler memorial lecture during this conference.

I had the fortune of sharing a long friendship with Alan, started more than forty years ago. But Beyond the sincere friendship, we shared a common way of looking at applied mathematics and its relations with industry.

Well before the nowadays popular slogans on “knowledge based economy”, Alan was deeply conscious that mathematics could (and should) be a fundamental driving force in promoting innovation in industry and more generally in the society.

Alan put on this goal all his enthusiasm and all his effective action as a leader and as an organizer.

His contribution to the foundation of ECMI, to its first activities, in obtaining the first ECMI-contract from the E.U. it is well known to the ECMI “old guard”. But it is up to us to act so that also our younger colleagues could thank Alan Tayler for the momentum he gave to the development of industrial mathematics in Europe.

This lecture is conceived in his spirit and not just in his memory.

1 Introduction

In the last few years our group was involved in a long-term research program partially supported by the societies of the ENI group (Enitecnologie and Agip), that is the main Italian holding in oil industry.

The program aims at understanding the behaviour of waxy crude oils subject to temperatures gradients. Indeed, this class of oils is characterized by the fact that they contain a relatively large amount of heavy hydrocarbons (paraffines, asphalthenes etc.) that - as we shall discuss in detail in the sequel

- may crystallize and eventually form gel-like structures thus influencing the motion of the oil in the pipeline.

The experimental evidence is that when these oils are pumped in pipelines crossing zones at relatively low temperature (as e.g. in the submarine pipelines) a deposit is formed at the walls that grows and hinders the flow, so that periodic “cleaning” operations are to be scheduled to keep a high efficiency of the transportation and to avoid a possible total clogging of the line. The research on the possible mechanisms responsible for the phenomenon and on their mathematical modelling is very active (see e.g. some general papers and reviews like [4], [23], [55], [68], [69]). The research program includes both an experimental part and a section aimed at modellization and simulation. The former is implemented in three laboratories: Eni Milano, the Istituto Donegani in Novara and the Department of Chemistry of the University of Florence. The latter is mainly done by our group: Antonio Fasano, Lorenzo Fusi and myself together with Loredana Faienza and Alessandro Monti and some others co-workers (Alberto Mancini, Fabio Rosso) who joined the team from time to time. A helpful contribution also came from John Ockendon.

It has to be noted that the cooperation among the teams is very intense, and this is witnessed by a number of papers in which experimental results are discussed in the framework of the mathematical models presented (see e.g. [13], [14], [15]).

To deal with a relatively simple situation, we will refer to an “ideal mixture” that mimics the behaviour of a real oil. It is a mixture of a given standard “wax” and a “solvent” (decane). The wax we chose has been characterized by its spectrum obtained by gas chromatography.

2 Segregation/dissolution of wax

For any waxy crude oil, and in particular for our “ideal mixture” with a given wax concentration c , a temperature T_{CL} can be defined such that, for $T > T_{CL}$ all wax is dissolved in the solvent while for $T < T_{CL}$ part of the wax segregates. Temperature T_{CL} is called **cloud temperature** or W.A.T. (wax appearance temperature). We are supposing that the system is always at thermodynamic equilibrium, a fact that is by no means granted.

Cloud temperature is usually determined by differential scanned calorimetry (DSC), and the measure can be made by raising or lowering the temperature of the sample: in the first case the temperature at which the peak in the heat exchanged occurs is sometimes called WDT (wax disappearance temperature) while the term WAT is used for the result obtained when the measure is performed with decreasing temperature.

Moreover, the determination of WAT and of WDT is influenced by the rate at which the temperature is varied. Here, we report the data of a typical experiment ([30], [36], [64]):

WDT $10^\circ C/min$	$T_1 = 29.3^\circ C$
WDT $1^\circ C/min$	$T_2 = 26.5^\circ C$
WAT $1^\circ C/min$	$T_3 = 21.3^\circ C$
WAT $10^\circ C/min$	$T_4 = 20.2^\circ C$

Table 1.

A few comments on these results are in order (for general theoretical discussion see e.g. [16], [17], [37], [39], [43], [48], [53], [65], [66], [67], [70]):

- (i) The differences between T_1 and T_2 and between T_3 and T_4 show that the process of dissolution (crystallization) is not instantaneous but that the system takes some time to reach the thermodynamical equilibrium;
- (ii) The difference between WAT and WDT shows that undercooling occurs practically always, as it is rather usual in phase-change processes;
- (iii) A difference of about $5^\circ C$ between T_2 and T_3 is commonly found in different situations of concentration.

We note that in the literature the term “cloud temperature” or “cloud point” is sometimes related to an optical determination. Of course the accuracy of this measurement is strongly dependent on the method used ([18], [19]), since it is difficult to measure the variation of optical properties when only micro-crystals are present (a possible colloidal transition state has been also supposed to exist). Moreover, the method is applicable to our “ideal mixture” that is optically transparent but practically useless when commercial oils are concerned. Let us come back to the definition of T_{CL} and assume we can associate a value T_{CL} to each value of the concentration c of wax in the mixture. As it can easily be expected, it turns out that T_{CL} is a monotonically increasing function of c . For our purposes, it will be useful to consider the inverse function of $T_{CL}(c)$ and to define $c_{SAT}(T)$ as the maximum amount of wax that can be added to a unit volume the solvent kept at temperature T without producing any crystallization. It can be seen as the *solubility* of wax in the solvent as a function of the temperature.

To model the phenomenon, we will use the following functions:

- (i) $c(\mathbf{x}, t)$: total wax concentration at point \mathbf{x} at time t ;
- (ii) $C(\mathbf{x}, t)$: concentration of dissolved wax;
- (iii) $G(\mathbf{x}, t)$: concentration of segregated (crystallized) wax.

Of course it is:

$$c(\mathbf{x}, t) = C(\mathbf{x}, t) + G(\mathbf{x}, t). \quad (1)$$

2.1 Case of thermodynamical equilibrium

As we will see, the phenomenon we are studying is a typical multiscale phenomenon, so that it is quite possible that in the time scale of the experiment the process of dissolution/segregation can be considered to be instantaneous. In this case we have

$$C(\mathbf{x}, t) = \min(c(\mathbf{x}, t), c_{SAT}(T(\mathbf{x}, t))) \quad (2)$$

$$G(\mathbf{x}, t) = \max(0, c(\mathbf{x}, t) - c_{SAT}(T(\mathbf{x}, t))) \quad (3)$$

so that (1) is automatically satisfied.

2.2 A case of macroscopic kinetics

Consider the case in which the thermodynamical equilibrium is reached in finite time with a characteristic time constant. If we still remain in the framework of a macroscopic description, we should postulate the existence of a sort of chemical potential acting as the driving force of the phenomenon.

The simplest assumption we can postulate is that the rate of segregation/dissolution is proportional to the deviation from the thermodynamical equilibrium i.e.

$$\frac{\partial G}{\partial t} = \theta \beta (C(\mathbf{x}, t) - c_{SAT}(\mathbf{x}, t)) \quad (4)$$

where $\beta > 0$ is the inverse of the characteristic time and θ is a factor that ensures that G_t vanishes if both $(C - c_{SAT})^+$ and G are zero. Thus

$$\theta = H(G + (C - c_{SAT})^+), \quad (5)$$

where H is the Heaviside jump function

$$H(z) = \begin{cases} 0, & \text{if } z \leq 0 \\ 1, & \text{if } z > 0. \end{cases} \quad (6)$$

A simple generalization consists in assuming different values of β for $(C - c_{SAT})$ positive and negative and/or to include the possible dependence of β on the temperature.

2.3 A microscopic description

A possible microscopic description of the process of segregation (crystallization) is based upon two mechanisms: **nucleation** and **growth**. One defines $\dot{\nu}$ to be the rate of birth of new crystals per unit volume of the solution and $\dot{\rho}$ as the radial growth of the crystals that are assumed approximately spherical.

We will neglect the radius of the newborn crystals and we will assume that $\dot{\nu}$ and $\dot{\rho}$ (both depending on C and T) are such that their ratio is constant. This is the so-called **isokinetic assumption** that can be written as:

$$\begin{cases} \dot{\rho} = \dot{\rho}_0 F(C, T), \\ \dot{\nu} = \dot{\nu}_0 F(C, T). \end{cases} \quad (7)$$

Under these assumptions (and normalizing the quantities so that the density is equal to one) we have:

$$\frac{\partial G}{\partial t} = 4\pi\dot{\rho}(t) \int_0^t \frac{\dot{\nu}_0}{\dot{\rho}_0} \dot{\rho}(\tau) \left[\int_\tau^t \dot{\rho}(s) ds \right]^2 d\tau, \quad (8)$$

and after some simple manipulations we get

$$\frac{\partial G}{\partial t} = 4 \left(\frac{\pi \dot{\nu}_0 \dot{\rho}_0^3}{3} \right)^{1/4} G^{3/4} F(C, T). \quad (9)$$

Consequently, we can obtain the number of crystallites per unit volume

$$N(t) = \left(\frac{3}{\pi} \right)^{1/4} \left(\frac{\dot{\nu}_0}{\dot{\rho}_0} \right)^{3/4} G^{1/4} \quad (10)$$

and the average radius

$$\bar{R}(t) = 4^{-1/3} \left(\frac{3}{\pi} \right)^{1/4} \left(\frac{\dot{\rho}_0}{\dot{\nu}_0} \right)^{1/4} G^{1/4}. \quad (11)$$

Of course, to complete the description of the process we have to specify the form of the function F in (7). We note that, in any case, this picture can only refer to the crystallization (of course it does not apply to dissolution) and hence F has to vanish if and only if thermodynamical equilibrium has been reached and thus if C reaches the value c_{SAT} . The simplest choice leads us to

$$\frac{\partial G}{\partial t} = K(\dot{\nu}_0 \dot{\rho}_0^3)^{1/4} [C(x, t) - c_{SAT}(T(x, t))] G^{3/4}, \quad (12)$$

or, more generally to

$$\frac{\partial G}{\partial t} = K(\dot{\nu}_0 \dot{\rho}_0^3)^{1/4} [C(x, t) - c_{SAT}(T(x, t))]^q G^{3/4} \quad (13)$$

for some q , in accordance with typical models for crystallization of polymer melts (see [1], [6]).

We note that this model is based on concepts similar to the ones used in [1], [2], [6], [44], [54], [61], with the difference that the phenomenon of “impingement” among growing crystals is much less relevant in the present case because concentration of wax in solvent is very low.

In the literature of waxy oils an approach similar to the one illustrated above has been adopted in [34], [35], [47], but just in spatially homogeneous

cases and when the cooling rate is constant. Under these assumptions the so-called “Avrami thumb rule” ([3]) is applied.

We conclude this section showing a comparison between the approaches illustrated under (2.1), (2.2) and (2.3) (see fig. 1).

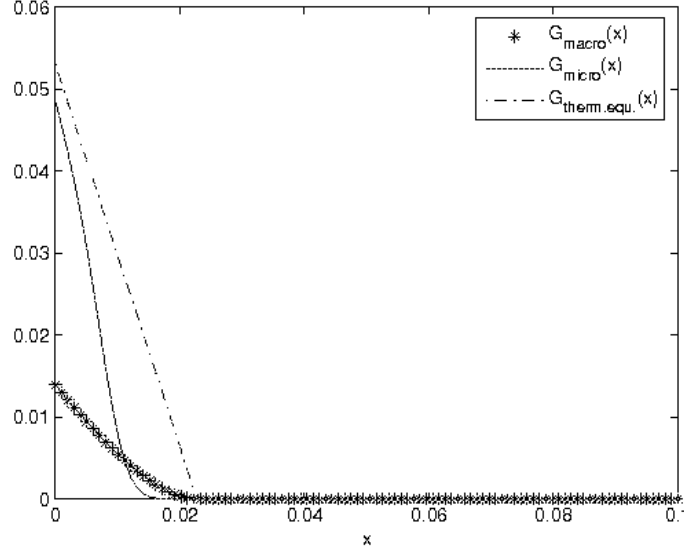


Fig. 1. Comparison of function G for the three approaches of macroscopic kinetics $G_{macro}(x)$, microscopic kinetics $G_{micro}(x)$ and thermal equilibrium $G_{therm.equ.}(x)$. The picture refers to a simulation of a stratum $0 < x < L$ where the boundary $x = L$ is at a constant temperature $T > \text{WAT}$ while the boundary $x = 0$ is being cooled at a temperature $T < \text{WAT}$; we assume that saturation is linear in x and that $G = 0$ initially.

3 Diffusion/convection of heat

Heat transfer turns out to be the driving force of the deposition of wax, since temperature is the key quantity in the process of change of state of wax¹. Conversely, one can ask how much the process of segregation/dissolution of wax influences the thermal field.

¹ Indeed, sedimentation by gravity is negligible, since wax and oil have almost the same density; indeed the deposit on the walls of pipelines has the same thickness at every point of a given cross section

Within the experimental uncertainty, one can claim that the state of aggregation of wax (and even its concentration in the mixture) does not have an important effect on the thermal diffusivity of oil (see [12], [32]).

Concerning the latent heat associated to the change of phase, it is around 10 J g^{-1} . Since concentration of wax is below 10% and the heat capacity of oil is about $5 \text{ J g}^{-1} \text{ K}^{-1}$ and the change of phase takes place across a few degrees, we can claim that the effect of latent on the determination of thermal field can be neglected². This means that the latter can be found without knowing C and G , as least as far as just conduction is considered. Of course this is no longer true in general when convection has to be taken into account, since the rheological properties of the mixture can be strongly influenced by the state of aggregation of wax and since the presence of deposit determines the motion.

4 Diffusion/convection of wax. Gelification

Let us turn our attention to the diffusion of segregated and dissolved wax in the solvent. We assume the validity of Fick's law and denote the diffusivity of segregated and dissolved wax by D_G and D respectively.

Of course, one expects that

$$D_G < D. \quad (14)$$

Moreover, the mobility of dissolved wax within the mixture is hindered by the presence of wax crystals, at least if G is "large enough". More precisely, one can see that when G exceeds a threshold value G^* , crystallites tend to aggregate and to entrap liquid (i.e. oil+dissolved wax) and form a gel. Process of gelification is not instantaneous but follows a kinetics that we can model by introducing a quantity $g(x, t)$ characterizing the **degree of gelification** whose evolution is governed by the following law

$$\frac{\partial g}{\partial t} = \Phi(G - G^*) \quad (15)$$

where Φ is a nondecreasing function of its argument, $\Phi(0) = 0$. In general, Φ will also depend on temperature (and will be monotonically decreasing). Of course (15) only refers to mixtures at rest since motion can strongly influence in contrasting gelification.

Consistently with the description above, we will assume that D (and also D_G whenever it will be taken into consideration) is a given decreasing function of $K = G(1 + g)$, vanishing when K exceeds some critical value K^* .

The degree of gelification is also relevant to the phenomenon of adhesion of wax aggregates to the pipe walls (deposition). In principle, in order to model

² On the other hand, the mathematical problem to be solved if one takes this coupling into account is far from being trivial (see [33]).

this phenomenon, one should also include the nature of the wall, its rugosity and so on. For simplicity, we can assume that when G reaches the value G^* at the wall, then the deposit begins to form and grow; in other words we identify the deposit with the region where $g > 0$.

Another phenomenon that is observed is the so-called **ageing** of the gel. In our model, this fact is explained both by the diffusion of liquid wax within the gel (although with lower diffusivity) and by the consequent additional segregation that takes place whenever

$$G(x, t) < C(x, t) - C_{SAT}(T(x, t)). \quad (16)$$

When a mixture is brought at $T_1 \gg T_{CL}$ and then put in a vessel whose walls are kept at $T_2 < T_{CL}$ the following facts are observed (see [31], [32] and also [49], [50]):

- (i) a deposit is formed at the walls and its final thickness is reached in a short time;
- (ii) the concentration of wax in the deposit continues to increase;
- (iii) in the deposited layer concentration of wax decreases when approaching the walls.

An additional information we got from experiment and from literature is that the mechanism of gelification - and hence its influence on diffusivity - is strongly dependent on the nature of wax since the geometry of crystallites plays an important role ([64]).

A multiscale problem

Summing up we have briefly discussed five processes that are relevant to the phenomenon to be studied, and each of them has a corresponding time scale:

- (i) thermal diffusion (t_1),
- (ii) segregation of wax (t_2),
- (iii) diffusion of dissolved wax (t_3),
- (iv) diffusion of segregated wax (t_4),
- (v) gelification (t_5).

Moreover, when the motion of the mixture is to be taken into account, we have also

- (vi) motion of the fluid (t_6).

Of course the model that can be used should take into account the practical cases to be studied. Since they span over a large variety of situations (depending on the type of oil and of thermal conditions) in the sequel we will consider different scenarios separately.

5 Thermodynamical and thermal equilibrium

A first scenario is studied in ([27]) where it is assumed that

$$t_1, t_2 \ll t_3, t_4 \ll t_5, t_6, \quad (17)$$

corresponding to a situation in which the fluid is at rest, the thermal field attains its asymptotic (stationary) profile in a very short time interval and phase equilibrium is instantaneously reached.

Under these assumptions, we will consider a one-dimensional geometry having in mind the interpretation of experiments done on commercial oils with a laboratory device called “cold finger” where a steady thermal gradient is applied between two co-axial cylinders kept at constant temperatures T_1 and T_2 and the gap between the two cylinders is filled by oil with given wax concentration c^* . Of course at least one of the two thermostats is maintained at a temperature below $T_{CL}(c^*)$ ([14], [15]).

Just to simplify notation, we refer here to plane (rather than cylindrical) symmetry, and for the same reason we will assume that T_{CL} depends linearly on concentration in the range of interest, so that

$$\frac{dc_{SAT}}{dT} = \gamma, \quad \gamma > 0 \text{ constant.} \quad (18)$$

Since we have assumed that temperature reaches its stationary (linear) profile, we have

$$c_{SAT}(x) = A + Bx, \quad x \in [0, l] \quad (19)$$

where $A = c_{SAT}(T_1)$ and B are positive constants assuming that T_2 (i.e. the temperature at the boundary $x = l$) is higher than the temperature T_1 of the wall $x = 0$ ($B = \gamma \frac{T_2 - T_1}{l}$).

But assuming that

$$c^* > c_{SAT}(l) = A + Bl,$$

the assumption of instantaneous thermodynamical equilibrium implies that

$$C(x, 0) = c_{SAT}(x), \quad G(x, 0) = c^* - c_{SAT}(x). \quad (20)$$

As long as deposition is not taken into account, the boundary conditions are of course

$$DC_x(0, t) + D_G G_x(0, t) = DC_x(l, t) + D_G G_x(l, t) = 0, \quad t > 0. \quad (21)$$

At this point we have to consider two different cases: first we will see what happens if diffusion of segregated wax plays a role, then we will discuss the case in which the crystallites can be thought to be immobile. We will start assuming that diffusivities are given and constant.

5.1 The case $t_3 \sim t_4$ (non-negligible crystal diffusivity)

Starting from the initial situation (20) we can define \hat{t} as

$$\hat{t} = \sup\{t : G(x, t) > 0, \quad x \in [0, l]\}. \quad (22)$$

This means that in the time interval $[0, \hat{t})$ the mixture is always **saturated** (that means $c > c_{SAT}(x)$). Therefore

$$C(x, t) = A + Bx, \quad 0 < x < l, \quad 0 < t < \hat{t} \quad (23)$$

$$\begin{cases} G_t - D_G G_{xx} = 0, & 0 < x < l, \quad 0 < t < \hat{t} \\ G(x, 0) = c^* - A - Bx, & 0 < x < l, \\ G_x(0, t) = G_x(l, t) = -\frac{D}{D_G} B, & 0 < t < \hat{t}. \end{cases} \quad (24)$$

Of course, $\hat{t} < +\infty$, if we exclude the non-realistic (and trivial) case $\frac{D_G}{D} > \frac{c_2 - c_1}{2c^* - c_1 - c_2}$ where we wrote $c_i = c_{SAT}(T_i)$, $i = 1, 2$.

Since G_x is negative, by maximum principle, the definition of \hat{t} implies $G(l, \hat{t}) = 0$ and, for any $t > \hat{t}$ a free boundary $x = s(t)$, $s(\hat{t}) = l$ will exist separating the **saturated** region $(0, s(t))$ where $G > 0$, from the **unsaturated** region $(s(t), l)$ where $c(x, t) = C(x, t) < c_{SAT}(x)$.

More specifically,

$$C(x, t) = A + Bx, \quad 0 < x < s(t), \quad t > \hat{t}, \quad (25)$$

$$\begin{cases} G_t - D_G G_{xx} = 0, & 0 < x < s(t), \quad t > \hat{t} \\ G(x, \hat{t}) = \hat{G}(x), & 0 < x < s(\hat{t}) = l, \\ G_x(0, t) = -\frac{D}{D_G} B, & t > \hat{t}, \\ G(s(t), t) = 0, & t > \hat{t}, \end{cases} \quad (26)$$

where $\hat{G}(x)$ is found as $G(x, \hat{t})$ from the solution of (24)³.

On the other hand

$$\begin{cases} C_t - DC_x x = 0, & s(t) < x < l, \quad t > \hat{t} \\ C_x(l, t) = 0, & t > \hat{t} \\ C(s(t), t) = A + Bs(t), & t > \hat{t}, \end{cases} \quad (27)$$

and

$$G(x, t) = 0, \quad s(t) < x < l, \quad t > \hat{t}. \quad (28)$$

Mass conservation, i.e. flux continuity across $x = s(t)$ provides the free boundary condition that completes the problem

³ The latter exists and is unique within the class of bounded functions.

$$DB + D_G G_x(s(t)_-, t) = DC_x(s(t)_+, t). \quad (29)$$

Problem (25)-(29) is an implicit two-phase free boundary problem. In [9] it is proved that it can be immediately reduced to a form for which the results of [9] and [42] can be applied and thus prove that a classical solution exists globally.

The asymptotic profile $(C_\infty, G_\infty, s_\infty)$ of the solution is the following:

$$G_\infty(x) = \begin{cases} \frac{D}{D_G} B(s_\infty - x), & x \in [0, s_\infty], \\ 0, & x \in [s_\infty, l] \end{cases} \quad (30)$$

$$C_\infty(x) = \begin{cases} A + Bx, & x \in [0, s_\infty], \\ A + Bs_\infty, & x \in [s_\infty, l] \end{cases} \quad (31)$$

and s_∞ is found from the global mass balance as the unique positive solution of the algebraic equation

$$\frac{B}{2} \left(\frac{D - D_G}{D_G} \right) s_\infty^2 + Bs_\infty - (c^* - A)l = 0. \quad (32)$$

As we anticipated the model above does not include a specific mechanism for deposition (i.e. for adhesion to the cold wall $x = 0$) and assumes that D and D_G are constant. In the spirit of sec. 4 we can say that this implies that G is always below the critical value G^* , i.e. when $G_\infty(0) = \frac{D}{D_G} Bs_\infty < G^*$.

The deposit

A possible way of incorporating deposition in the model above is to assume that all the wax⁴ arriving at the cold wall sticks to its surface and does not take part in the diffusion process. This fact can be modelled introducing a second free boundary $x = \sigma(t)$ where $\sigma(t)$ represent the thickness of the deposit or assuming that such thickness is negligible and that the wax reaching $x = 0$ simply leaves the system; this corresponds to replacing the third condition in (26) by $G_x(0, t) = 0$. This approach (with or without the free boundary $\sigma(t)$) has been used to interpret the data of the cold finger experiment (see [14]); in [27] the difference of heat between the mixture and the deposit has been also taken into account.

A basic difficulty of this approach is to evaluate the wax concentration in the deposit i.e. the amount of oil (or, rather, of mixture) that is “entrapped” and, if not, to estimate how much the displacement of the liquid caused by the deposit is relevant to the process ([11], [26]).

A possible way of answering this question is to perform the experiment until the asymptotic situation is reached and to weigh the total mass M_D^∞ per unit surface of the deposit. Knowing the mass of wax initially present and

⁴ or a given fraction of it

the quantity that is still in the solution (at a concentration equal to $c_{SAT}(0)$), the mass of the deposited wax M_w^∞ can be calculated. Hence the mass of entrapped oil is given by $M_D^\infty - M_w^\infty$. Nevertheless, the experiment is delicate since it lasts for several hours and its results are still not conclusive ([14]). We add that, under the assumption of linear dependence of c_{SAT} on T , the gradient of solubility γ can be evaluated by means of two asymptotic measures M_D^∞ of the deposited mass corresponding to two values of T_2 (say \bar{T}_2 and $\bar{\bar{T}}_2$). Indeed

$$\gamma = \frac{|\bar{M}_D^\infty - \bar{\bar{M}}_D^\infty|}{l|\bar{T}_2 - \bar{\bar{T}}_2|}.$$

Hindered diffusion.

An alternative approach consists in prescribing the dependence of D (and of D_G) on G , as it was discussed in sec. 4, or even on $G(1+g)^5$.

Some preliminary simulations have been done (not taking into account g) and assuming that D is constant for $G < G^*$ and jumps to zero at G^* . Similar results were obtained imposing the threshold G^* not to G but to $G + C$.

In all these simulations the deposit was defined as the region where G (or $G + C$) exceeds G^* .

5.2 The case $t_3 \ll t_4$.

If we assume that, in the time scale of the experiment, the segregated wax is practically immobile the mathematical aspects of the model change totally, since letting D_G tend to zero is a singular perturbation of the problem.

Indeed, if we start from the same initial situation (20) with the natural boundary condition

$$C_x(0, t) = C_x(l, t) = 0, \quad (33)$$

The unsaturated region appears from the very beginning (i.e. $\hat{t} = 0$). Moreover, in order to make the model consistent it is necessary either to introduce a boundary layer close to $x = 0$ or to postulate a mechanism of deposition as we did above.

Let us confine ourselves to the approach used in 5. More specifically let us consider its simplest case in which the dissolved wax reaching $x = 0$ is assumed to be simply leaving the system.

Thus, we have the following problem

$$G(x, t) = \begin{cases} G_0(x) = c^* - c_{SAT}(x), & 0 < x < s(t), t > 0 \\ 0, & s(t) < x < l \quad t > 0 \end{cases} \quad (34)$$

⁵ In the latter case, we have to assume $t_6 \sim t_3, t_4$.

$$C(x, t) = A + Bx, 0 < x < s(t), t > 0 \quad (35)$$

while, in the unsaturated region we have

$$\begin{cases} C_t - DC_{xx} = 0, & s(t) < x < l, t > 0 \\ C_x(l, t) = 0, & t > 0, \\ C(s(t), t) = A + Bs(t), t > 0, \\ s(0) = l \end{cases} \quad (36)$$

with the free boundary condition

$$DB - DC_x(s(t), t) = -G_0(s(t))\dot{s}(t), t > 0. \quad (37)$$

This is a free boundary problem formally similar to a Stefan-type problem and its well-posedness in a classical sense is proved in [28].

6 Phase equilibrium in a transient thermal field. No gelification.

In this section we will assume that

$$t_2 < t_1, t_3, t_4 < t_5, t_6$$

so that the dissolution/segregation of wax can be considered as instantaneous while heat conduction and wax diffusion occur over the same time scale.

6.1 A general problem: weak solution.

Let $Q_{\tilde{t}} \equiv \Omega \times (0, \tilde{t})$ be a general smooth cylinder in $\mathbb{R}^3 \times \mathbb{R}$ and assume that initial and boundary conditions are given for temperature on $\Omega \times 0$ and $\partial\Omega \times (0, \tilde{t})$. In the assumptions of sec. 3 the function $T(\mathbf{x}, t)$ can be found and we can define Q^+ as the (so far unknown) subset of $Q_{\tilde{t}}$ where $c(\mathbf{x}, t) > c_{SAT}(\mathbf{x}, t)$, i.e. where $G(\mathbf{x}, t) > 0$ and $C(\mathbf{x}, t) = c_{SAT}(T(\mathbf{x}, t))$.

Assume that D and D_G are constant and define

$$\mathcal{L}_1 C = C_t - D\Delta C, \mathcal{L}_2 G = G_t - D_G\Delta C.$$

Mass conservation implies that

$$\mathcal{L}_1 C + \mathcal{L}_2 G = 0, \text{ in } Q^+. \quad (38)$$

But $C(\mathbf{x}, t) = c_{SAT}(T(\mathbf{x}, t))$ in Q^+ and hence $\mathcal{L}_1 C$ is a known quantity $q(\mathbf{x}, t)$

$$q(\mathbf{x}, t) = \frac{\partial}{\partial t} c_{SAT}(T(\mathbf{x}, t)) - D \Delta c_{SAT}(T(\mathbf{x}, t)). \quad (39)$$

Thus we have

$$\mathcal{L}_2 G = -q(\mathbf{x}, t), \text{ in } Q^+ \quad (40)$$

Now set $Q^- = Q_{\tilde{t}} \setminus Q^+$ so that

$$G(\mathbf{x}, t) = 0, \mathcal{L}_1 C = 0, \text{ in } Q^-. \quad (41)$$

If both Q^+ and Q^- are non-void and are separated by a smooth surface S , then we have

$$G = 0, c = C = c_{SAT}, \text{ on } S \quad (42)$$

$$\left[D_G \frac{\partial G}{\partial \mathbf{n}} + D \frac{\partial C}{\partial \mathbf{n}} \right]_{S^+} = \left[D \frac{\partial C}{\partial \mathbf{n}} \right]_{S^-} \quad (43)$$

where \mathbf{n} is the normal vector to $S \times \{t\}$ and \llbracket_{S^+} (resp. \llbracket_{S^-}) denote the limit of the quantity in brackets when $(\mathbf{x}, t) \in Q^+$ (resp. $\in Q^-$).

Defining

$$U(\mathbf{x}, t) = c(\mathbf{x}, t) - c_{SAT}(T(\mathbf{x}, t)) \quad (44)$$

the problem can be written formally as

$$U_t - \nabla \cdot \left(D \left[1 + \left(\frac{D_G}{D} - 1 \right) H(U) \right] \nabla U \right) \in -q(\mathbf{x}, t) \quad (45)$$

where H is the Heaviside graph.

Weak solutions $U \in H^{j,j/2}(Q_{\tilde{t}}) \cap W^{1,0}(Q_{\tilde{t}})$ for some $j \in (0, 1)$ and for any $\tilde{t} > 0$ has been proved to exist in [26].

Remark 1. Note that U is positive in Q^+ and negative in Q^- and that the equation (45) could be interpreted as the model for the diffusion of two immiscible chemical substances (of concentration U in Q^+ and $-U$ in Q^-) that diffuse in a host medium and undergo, on the contact surface, a fast chemical reaction whose products precipitate. In this picture the term $-q(\mathbf{x}, t)$ would represent a volumetric source/sink.

6.2 One-dimensional classical solutions

In one-dimensional cases, more information can be obtained. Once again we refer for simplicity to planer symmetry $x \in (0, l)$.

Let us fix the temperature at $x = l$ at a value

$$T(l, t) = T_2, \quad t > 0, \quad (46)$$

and let

$$T(0, t) = T_2 - \phi(t), \quad t > 0 \quad (47)$$

with $\phi(t)$ monotonically increasing, $\phi(0) = 0$. To be specific we take $\phi(t) = \lambda t$.

Furthermore, we assume that

$$T(x, 0) = T_2, \quad 0 < x < l, \quad (48)$$

$$c(x, 0) = c^* < c_{SAT}(T_2), \quad 0 < x < l, \quad (49)$$

so that in the initial situation all wax is dissolved (i.e. the slab is completely unsaturated).

Of course, no segregation will take place till the time \bar{t} such that

$$c_{SAT}(T_2 - \lambda \bar{t}) = c^*. \quad (50)$$

Recall that, in our assumption, the thermal field can be found independently of the knowledge of $C(x, t)$ and $G(x, t)$.

For $t > \bar{t}$ a region $Q^+ \equiv \{(x, t) : 0 < x < s(t), t > \bar{t}\}$ will appear where $G > 0$ and $C(x, t) = c_{SAT}(T(x, t))$.

Within Q^+ we have

$$\frac{\partial G}{\partial t} - D_G \frac{\partial^2 G}{\partial x^2} = -\frac{\partial}{\partial t} c_{SAT}(T(x, t)) + D \frac{\partial^2}{\partial x^2} c_{SAT}(T(x, t)) \quad (51)$$

and on $x = 0$ the following condition has to be fulfilled for $t > \bar{t}$

$$\left[D_G \frac{\partial G}{\partial x} \right]_{x=0} + \left[D \frac{\partial}{\partial x} c_{SAT}(T(x, t)) \right]_{x=0} = 0. \quad (52)$$

On the other hand, the region $Q^- \equiv \{(x, t) : s(t) < x < l, t > \bar{t}\}$ is such that $G = 0$ and hence

$$\frac{\partial}{\partial t} C(x, t) - D \frac{\partial^2}{\partial x^2} C(x, t) = 0, \quad (x, t) \in Q^- \quad (53)$$

and

$$\left[\frac{\partial C}{\partial x} \right]_{x=l} = 0, \quad t > \bar{t}. \quad (54)$$

Finally, the free boundary is characterized by the conditions

$$C(s(t), t) = c_{SAT}(T(s(t), t)), \quad \text{i.e. } G(s(t), t) = 0, t > \bar{t}, \quad (55)$$

$$\left[D \frac{\partial}{\partial x} C(T(x, t)) \right]_{x=s(t)^+} = \left[D \frac{\partial}{\partial x} c_{SAT}(T(x, t)) + D_G \frac{\partial G}{\partial x} \right]_{x=s(t)^+}. \quad (56)$$

This free boundary problem is considered in [28] and its well-posedness in the classical sense is proved.

7 Phase equilibrium in a transient thermal field with gelification

Here, we consider cases in which gelification takes place, but its characteristic time t_5 (as well as t_2) is negligible with respect to t_1 , t_3 and t_4 so that the process can be thought as a change of phase, occurring at a given temperature depending on temperature.

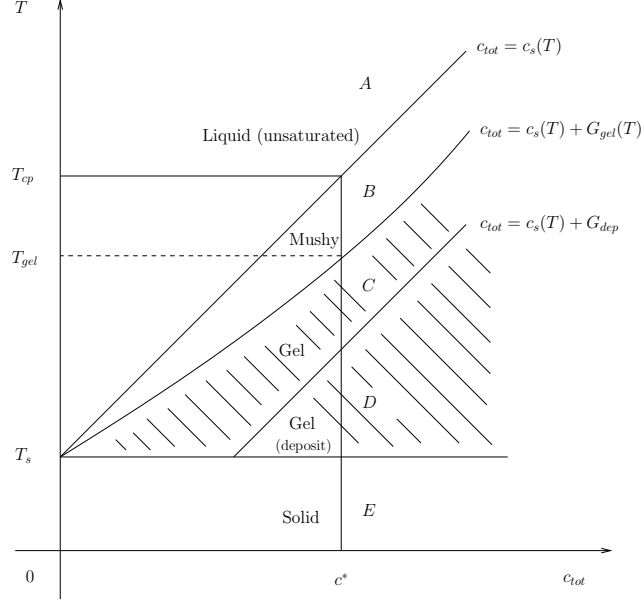


Fig. 2.

In this case a phase diagram for oil-wax mixtures can be drawn in the (c, T) plane in which (see Fig.2) zone A corresponds to dissolved wax ($T > T_{CL}(c)$, i.e. $c < c_{SAT}(T)$), in zone B we have coexistence of dissolved and segregated phases, while zones C and D correspond to gel and a $T_{GEL}(G)$ (or, equivalently, $G = G_{GEL}(T)$) can be defined. Zone D is separated from C by a line where $T = T_{DEP}(G)$ (or $G = G_{DEP}(T)$) and corresponds to a situation in which diffusivity of wax vanishes. Thus, zone C is called the gel zone and zone D is called the deposit.

In [25] a model problem in one space dimension is studied with initial and boundary conditions like in (46)-(49). Thermal field is computed such that $T_t < 0$, $T_x > 0$, $T_{xt} > 0$.

Since the case $D_G = 0$ is considered, the problem turns out to be a hyperbolic-parabolic free boundary problem. Indeed the evolution of G in the saturated zone and in the gel is governed by

$$\frac{\partial G}{\partial t} = \lambda \frac{\partial T}{\partial t} \quad (57)$$

if one assumes, for simplicity that c_{SAT} is a linear function of T .

The problem exhibits several free boundaries and its analysis is rather delicate; results on well-posedness in classical sense and on characterization of the free boundaries can be found in [25]. As expected (see fig. 3 where the qualitative behaviour of the solution is illustrated), the saturated region disappears in the long run and only an unsaturated region and the deposit are eventually present.

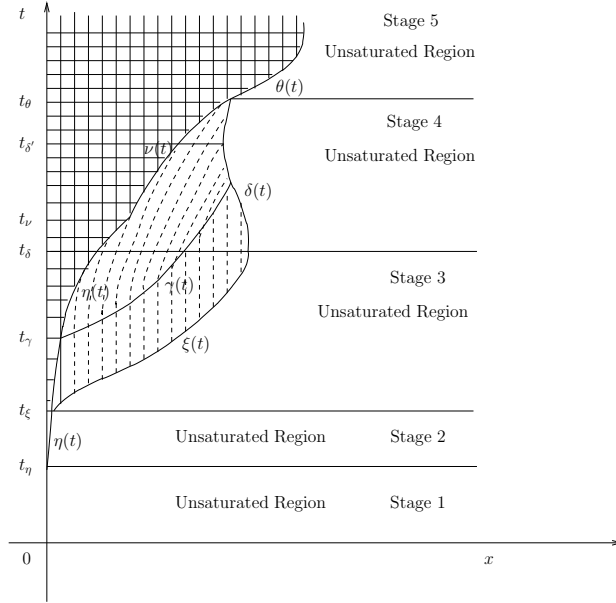


Fig. 3.

8 Thermal equilibrium with crystallization kinetics

In this section we will consider situations in which phase transition is not assumed to occur instantaneously, i.e. we allow t_2 to be of the same order of t_3 . Hence we assume

$$t_1 \ll t_2, t_3, t_4, t_5 \ll t_6 \quad (58)$$

and we consider both the macroscopic and the microscopic description of the crystallization kinetics.

8.1 A problem with uniform temperature

This situation is elementary from the point of view of its mathematical description, but provides a useful insight to interpret the experimental results.

Assume the mixture with wax concentration c^* is initially at a uniform temperature $T_0 > T_{CL}$. Assume that the boundary of the domain Ω occupied by the mixture has a prescribed time dependent temperature, e.g.

$$T(\mathbf{x}, t) = T_0 - \lambda t, \quad \mathbf{x} \in \partial\Omega, \quad t > 0, \quad (59)$$

for some $\lambda > 0$. Since we are assuming that t_1 is negligible w.r.t. the time scale of the experiment and we disregard the effect of latent heat of crystallization (see. sec 2), we have

$$T(\mathbf{x}, t) = T_0 - \lambda t, \quad \mathbf{x} \in \Omega, \quad t > 0. \quad (60)$$

Therefore, starting from the time t^* such that

$$T_0 - \lambda t^* = T_{CL}(c^*)$$

we will have that the segregation (and, eventually, gelification) starts and $G(\mathbf{x}, t)$ will become positive and increasing (and independent on t) for $t > t^*$.

Its time evolution can be described by (4) or (12) according to the point of view we want to assume. In both cases we have one parameter to fit the experimental data (or two if we take equation (13)).

The results of numerical simulations [22] and the comparison with experimental data, show that it is quite difficult to discriminate between the two models. Investigation in this sense is still going on.

8.2 A problem with constant thermal gradient

This problem has been studied in [21] and in [28]. In both papers the kinetics of crystallization is described by a macroscopic equation. We also note that in [28] gelification is not taken into account (and thus, in (58), we would have $t_5 \gg t_2, t_3, t_4$).

The temperature is stationary and, referring once more to planer symmetry we will write

$$T(x, t) = a + bx, \quad 0 < x < l, \quad t > 0. \quad (61)$$

We also assume that both $c_{SAT}(T)$ and $c_{GEL}(T)$ are linear. Therefore, they can be written as two linear function of x that we denote by $c_1(x)$ and $c_2(x)$ respectively:

$$c_1(x) = a_1 + b_1x, \quad 0 < x < l, \quad (62)$$

$$c_2(x) = a_2 + b_2x, \quad 0 < x < l, \quad (63)$$

and the positive constants a_i, b_i ($i = 1, 2$) are such that

$$c_1(x) < c_2(x), \quad 0 < x < l. \quad (64)$$

Recalling (4)-(6) and neglecting diffusion of the segregated phase, we have

$$\frac{\partial G}{\partial t} = H(G + (C - c_{SAT})^+) \beta[C(x, t) - c_1(x)], \quad 0 < x < l, \quad t > 0. \quad (65)$$

As we noted in Sec. 2, dependence of β on $T(x)$ could also be taken into account.

Now, let us turn our attention to $C(x, t)$. In [21] it is postulated that diffusivity of dissolved wax jumps to zero in the gelified part. Hence C will have to satisfy, in a suitable weak sense, the following equation

$$C_t - [DH(c_2 - c)C_{xx}] = -G_t, \quad 0 < x < l, \quad t > 0, \quad (66)$$

where

$$c(x, t) = C(x, t) + G(x, t), \quad 0 < x < l, \quad t > 0. \quad (67)$$

Moreover

$$C_x(0, t) = 0, \quad t > 0, \quad (68)$$

$$C_x(l, t) = 0 \quad t > 0, \quad (69)$$

$$C(x, 0) = c_1(x), \quad 0 < x < l, \quad (70)$$

$$G(x, 0) = c^* - c_1(x), \quad 0 < x < l, \quad (71)$$

assuming that, for $t = 0$, the mixture is everywhere saturated ($c^* > c_{SAT}(T(x, 0))$)

It can be proved, [21], that

- (A) there exist two Lipschitz continuous functions $s(t), \sigma(t)$ such that the half strip $K = (0, l) \times (0, +\infty)$ in the (x, t) plane is partitioned in three regions:
 - (i) the gel region $\mathcal{G} = \{(x, t) : 0 < x < s(t), \quad t > t_g, \quad s(t_g) = 0\}$
 - (ii) the undersaturated region $\mathcal{U} = \{(x, t) : \sigma(t) < x < l, \quad t > t_u, \quad \sigma(t_u) = l\}$
 - (iii) the saturated region $\mathcal{S} \equiv K \setminus (\mathcal{U} \cup \mathcal{G})$.
- (B) in region \mathcal{G} (no mass transfer)

$$c = c_2(x) \quad (72)$$

- (C) in region \mathcal{S} , c and $G \in C^{2,1}(\mathcal{S})$, and $C, C_x, G \in C(\bar{\mathcal{S}})$ and satisfy the differential equations (65) and (66) with initial conditions (70), (71), while boundary conditions (68) and (69) are fulfilled for $t < t_g$ and t_u respectively
- (D) in region \mathcal{U} , $G = 0$, $C \in C^{2,1}(\mathcal{U})$ and $u, u_x \in C(\bar{\mathcal{U}})$. Moreover

$$C_t - DC_{xx} = 0 \quad (x, t) \in \mathcal{U}, \quad (73)$$

- (E) on $x = \sigma(t)$ it is

$$G(\sigma(t), t) = 0, \quad t > t_u, \quad (74)$$

$$[C]_-^+ = [C_x]_-^+ = 0, \quad t > t_u, \quad (75)$$

where by $[\]_-^+$ we denoted the jump of the quantity in bracket across the curve $x = \sigma(t)$.

- (F) on $x = s(t)$ it is

$$C(s(t), t) + G(s(t), t) = c_2(s(t)), \quad t > t_g, \quad (76)$$

$$C_x(s(t), t) = 0, \quad t > t_g. \quad (77)$$

Assuming the microscopic description of the crystallization process simply consists in substituting (12) or (13) to (65). The results are quite similar as in the case of uniform temperature.

9 Variable thermal fields and crystallization kinetics: is diffusion relevant?

When the domain occupied by the mixture is not “thin” and the waxes that are contained in the oil are “heavy” enough, neither t_1 nor t_2 can be thought to be negligible with respect to the time scale of the experiment. On the other hand, some authors tend to disregard the influence of diffusion in the interpretation of experimental results.

In any case, we still retain the assumption that the thermal field can be determined independently of the knowledge of $C(x, t)$, $G(x, t)$.

Referring to the experimental situation, we consider a cylinder of radius R , containing a mass M of oil (per unit axial length) at concentration c^* . The initial temperature T_0 is larger than $T_{CL}(c^*)$ while the surface of the cylinder is maintained, for any $t > 0$ at a temperature T_{EXT} that is less than $T_{CL}(c^*)$.

The thermal field is the solution of the following parabolic problem

$$\begin{cases} \frac{\partial T}{\partial t} = D \left\{ \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right\}, & 0 < r < R, t > 0 \\ T(r, 0) = T_0, & 0 < r < R \\ \frac{\partial T}{\partial r}(0, t) = 0, & t > 0 \\ T(R, t) = T_{EXT}, & t > 0, \end{cases} \quad (78)$$

that can be expressed in series of Bessel functions (see e.g. [10] chap. VII).

Neglecting diffusion, we can compute $G(x, t)$ according to the macroscopic and microscopic crystallization kinetics (as well as to the assumption of phase equilibrium (3)). The corresponding simulations seem to show that a model that does not take diffusion (at least of the dissolved wax) into account cannot interpret the experimental results. Once again, it is difficult to discriminate between macroscopic and microscopic crystallization kinetics, unless we confine to the initial stage of the phenomenon.

10 Deposition in moving mixtures

As we said in Sec. 1, the final aim of the research is a descriptive and predictive model for wax deposition on the walls of pipelines. There exists a huge literature on this subject (see e.g. [5], [7], [20], [29], [38], [41], [45], [56], [60]) aimed at interpreting the results on experimental loops and field experiments.

At the present stage of our research program, we can claim that our model can actually be used in a quite large class of “field” conditions, i.e. in cases in which quantities like temperature, mean axial velocity, wax concentration can be thought to be independent of the radial coordinate r within a bulk core $0 < r < R - \delta$, δ being the thickness of a boundary layer.

This problem has been studied in [24]. the basic assumption is that the flow in the pipeline is turbulent and that molecular diffusion is a thin boundary layer is the only mechanism responsible for deposition.

The model includes the mechanism of ablation that has the effect of limiting the thickness of the deposit.

Just to give a rough idea of the model, the starting point is to write down the quasi-steady profile of the temperature in the boundary layer

$$T(r, z, t) = -a(z, t)(R - \delta) \ln \left(\frac{r}{R - \delta} \right) + T_c(z, t), \quad R - \delta < r < R, \quad z > 0, \quad t > 0 \quad (79)$$

In (79) $a(z, t)$ is a coefficient that has to be determined and T_c is the temperature of the bulk of the fluids; in general the analysis may take into account the variation of δ with z and t that will be ignored here to simplify the discussion.

Imposing thermal balance allows to find $a(z, t)$ that represent the thermal gradient in the boundary layer as a function of z and t . Since the model applies to oils for which the characteristic time of crystallization is negligible w.r.t. the time scale of the experiment, the thickness of the deposit can be found applying the techniques we used in sec. 5. As long as the “core” remains saturated, an explicit approximated formula for the thickness of the deposit can be found

$$\delta = \frac{Rt}{T_{CL}t_0} \frac{T_0 - T_l}{\mu} \exp \left[-\frac{2\pi D_T}{\mu Q} z \right] H(T_{CL} - T_W)^6 \quad (80)$$

where Q is the volumetric flow rate, T_l is the temperature of the surroundings and

$$\mu = \frac{k}{hR} \quad (81)$$

where k is the thermal conductivity of the mixture and h the heat transfer coefficient between the pipe and the surroundings.

Since $T_W(z)$ is the temperature of the wall and H is the Heaviside function, it is clear that the line will have a “deposit free zone” z_F that can be easily calculated.

For the case in which the core may desaturate, the analysis has some additional difficulties and we refer the reader to the original paper.

As a conclusion, we report that the model is consistent with field experiments made on two different pipelines, where the discrepancy between measured and calculated quantities is below 10%.

References

1. D. Andreucci, A. Fasano, M. Primicerio: *On a mathematical model for the crystallization of polymers*. in “Proceedings of ECMI 4” (H.J. Wacker et al. eds.), 3-16 Kluwer, Dordrecht (1991).
2. D. Andreucci, M. Primicerio, L. Borrelli, V. Capasso, P. Li: *Polymer crystallization kinetics: the effect of impingement*. Math. Engrg. Ind., **4**, 249-263 (1993).
3. M. Avrami: *Kinetics of Phase Change I: General Theory*. J. Chem. Phys. **7** (1939).
4. L.F.A. Azevedo, A.M. Teixeira: *A critical review of the modeling of wax deposition mechanism*. Petroleum Science and Technology, **21** (3&4), 393-408 (2003).
5. N. Bath, A.K. Mehrotra: *Modeling of deposition from “waxy” mixtures in a pipeline via moving boundary formulation*. Ind. Eng. Chem. Res., **44** (2005).
6. J. Berger, W. Schneider: *A zone model of rate controlled solidification*. Plastic and Rubber Processing and Applications, **6**, 127-133 (1986).
7. P.A. Bern, V.R. Winthers, J. Cairns: *Wax deposition in pipelines*. European Offshore Petroleum Conference & Exhibition, London, 21-24 (1980).
8. G.B. Borghi, S. Correria, M. Merlini, C. Carniani: *Prediction and scaleup of waxy oil restart behavior*. Soci. Petrol. Engi. SPE **80259**, 1-5 (2003).
9. J.R. Cannon, A. Fasano: *Boundary value multidimensional problems in fast chemical reactions* Arch. Rat. Mech. Anal., **53**, 1-13 (1973).
10. H.S. Carslaw, J.C. Jaeger: *Conduction of heat in solids* Oxford, at the Clarendon Press (1959).

⁶ In (80) we did not write the ablation term

11. E. Comparini, F. Talamucci: *A general model for wax diffusion in crude oils under thermal gradient* in Applied and Industrial Mathematics in Italy (V. Cutello et al. eds), World Scientific, 259-270 (2007).
12. S. Correra, M. Andrei, C. Carniani: *Wax Diffusivity: is it a physical property or a pivotal parameter?* Petroleum Science and Technology **21** (9), 1539-1554 (2003).
13. S. Correra, A. Fasano, L. Fusi, D. Merino-Garcia: *Calculating deposit formation in the pipelining of waxy crude oils*. Meccanica, **42**, 149-165 (2007).
14. S. Correra, A. Fasano, L. Fusi, M. Primicerio: *Modeling wax diffusion in crude oils: the cold finger device*. Appl. Math. Model., **31**, 2286-2298 (2006).
15. S. Correra, A. Fasano, L. Fusi, M. Primicerio, F. Rosso: *Wax Diffusivity under given thermal gradient: a mathematical model*. ZAMM, **87**, 24-36 (2007).
16. J.A.P. Coutinho, K. Knudsen, S.I. Andersen: *A local composition model for paraffinic solis solution*. Chem. Eng. Science, **51** (12), 3273-3282 (1996).
17. J.A.P. Coutinho: *Predictive UNIQUAC: a new model for the description of multiphase Solid-Liquid Equilibria in Complex Hydrocarbon Mixtures*. Ind. Eng. Chem. Res. **37**, 4870-4875 (1998).
18. J.A.P. Coutinho and J.-L. Daridon: *The Limitations of the Cloud Point Measurement Techniques and the Influence of the Oil Composition and its detection*. Petroleum Science and Technology, **23**, 1113-1128, (2005).
19. J.A.P. Coutinho, B. Edmonds, T. Moorwood, R. Szczepanski, X. Zhang: *Reliable wax predictions for flow assurance*. Energy & Fuels **20**, 1081-1088 (2006).
20. J.L. Creek, H.J. Lund, J.P. Brill, M. Volk: *Wax deposition in a single phase flow*. Fluid Phase Equilibria, **158** (1), 801-811 (1999).
21. L. Faienza, A. Fasano, M. Primicerio: *Gelification of hydrocarbons, a model problem*, in "Some Topics in Industrial Mathematics" (R. Jeltsch et al eds.), World Scientific, 120-133 (2007).
22. L. Faienza: *Numerical simulations for deposition in paraffine-decane mixtures*. Tech. Rep. Dept. U. Dini (2008).
23. L. Faienza, L. Fusi: *The literature on waxy crude oils*. Tech. Rep. Dept. U. Dini (2008).
24. A. Fasano, L. Fusi, S. Correra: *Mathematical models for waxy crude oils*. Meccanica, **39**, 441-483 (2004).
25. A. Fasano, L. Fusi, M. Primicerio, J. Ockendon: *Gelification and mass transport in static non-isothermal waxy solution*, to appear on ESAM
26. A. Fasano, M. Primicerio: *Heat and mass transfer in non-isothermal partially saturated solutions*. New Trends in Mathematical Physics, (P.Fergola et al. eds.) pp 34-44, World Scientific (2003).
27. A. Fasano, M. Primicerio: *Temperature driven mass transport in concentrated saturated solutions*. Progress in Nonlinear Differential Equations and Their Applications, **61**, 91-108 (2005).
28. A. Fasano, M. Primicerio: *Wax deposition in crude oils: a new approach*, Rend. Mat. Accad. Lincei, **9**, 251-263 (2005).
29. N. Fong, A.K. Mehrotra: *Deposition under turbulent flow of wax-solvent mixtures in a bench-scale flow-loop apparatus with heat transfer*. Energy & Fuels, **21** (3), 1263-1276 (2007).
30. D.M. Garcia: *Progress in cold flow I*. Enitecnologie Techincal Report (2004).
31. D.M. Garcia: *Wax Cold Flow: report II*. Enitecnologie Technical Report (2005).

32. D.M. Garcia, S. Corraera, M.Margarone: *Kinetics of waxy gel formation from batch experiments* 7th Conf. Petroleum Phase Behaviour and Fouling, Asheville (2006).
33. R. Gianni, A.G. Petrova: *One dimensional problem for heat and mass transport in oil-wax solution*. Rend. Mat. Accad. Lincei, **9** (16), 181-196 (2005).
34. A. Hammami, A.K. Mehrotra: *Non-isothermal crystallization kinetics of n-paraffins with chain lenght between thirty and fifty*. Thermochimica Acta, **211**, 137-153 (1992).
35. A. Hammami, A.K. Mehrotra: *Non-isothermal crystallization kinetics of even-numbered and odd-numbered normal alkanes*. Thermochimica Acta, **215**, 197-209 (1993).
36. A. Hammami, J. Ratulowski, J.A.P. Coutinho: *Cloud Points and can we measure or model them*. Petrol. Sci. Technol. **21** (3&4), 345-358 (2003).
37. J.H. Hansen, A. Fredenshund, K.S. Pedersen, H.P. Ronnigsen: *A Thermodynamic model for predicting wax formation in crude oils*. AIChE J., **34** (12), 1937-1942 (1988).
38. J.J.C. Hsu, M.M. Santamaria, J.P. Brubaker: *Wax deposition of waxy live crudes under turbulent flow conditions*. SPE 28480.
39. H.-Y. Ji, B. Tohidi, A. Told: *Wax Phase Equilibria: Developing a Thermodynamic Model using a Systematic Approach*. Fluid Phase Equilibria, **216** (2004).
40. W.M. Kays, M.E. Crawford: *Convective Heat and Mass Transfer*. McGraw-Hill, New York (1980).
41. M.V. Kok, O. Saracoglu: *Mathematical modelling of wax deposition in crude oil pipeline system*. SPE, 1-7 (2007).
42. O.A. Ladyszenskya, V.A. Solonnikov, N.N. Ural'ceva: *Linear and Quasi-linear Equations of Parabolic Type*. America Mathematical Society, Providence (1968).
43. C. Lira-Galeana, C. Firoozabadi, J.M. Prausnitz: *Thermodynamics of Wax Precipitation in Petroleum Mixtures*. AIChE J., **42** (1) (1996).
44. A.Ya. Malkin, V.P. Beghisev, I.A. Keapin, S.A. Bolgov: *General treatment of polymer crystallization kinetics I*. Polym. Eng. Sci. **24**, 1396-1401 (1984).
45. S.A.R. Nazar, B. Dabir, H. Vaziri, M.R. Islam: *Experimental and mathematical modeling of wax deposition and propagation in pipes transporting crude oil*. SPE 67328, 239-248 (2001).
46. D.V. Nichita, L. Goual, A. Firoozabadi: *Wax Precipitation in Gas Condensate Mixtures*. SPE Prod.Facil., 250-9 (2001).
47. T. Ozawa: *Kinetics of non-isothermal crystallization*. Polymer, **12**, 150-158 (1971).
48. H. Pan, A. Firoozabadi: *Pressure and composition effect on wax precipitation: experimental data and model results*. SPE Prod. Facil., 250-9 (1997).
49. K.G. Paso, H.S. Fogler: *Influence of n-paraffin composition on the aging of wax-oil gel deposits*. AIChE J., **49** (2003).
50. K.G. Paso, H.S. Fogler: *Bulk Stabilization in Wax Deposition Systems*. Energy Fuels, **18** (4), 1005-1013 (2004).
51. S.K. Pedersen, P. Skovborg, P.D. Hans: *Wax Precipitation from North Sea Crude Oils: Thermodynamic Modeling*. Energy & Fuels, **5**, 924-932 (1991).
52. R.H. Perry, D.W. Green, J.O. Maloney: *Perry's chemical engineers' handbook*. McGraw-Hill, New York (1999).
53. J.M. Prausnitz, R.N. Lichtenthaler, E.G. Azevedo: *Molecular Thermodynamics of Fluid Phase Equilibria*. Prentice-Hall (1986).

54. J. Rabesiaka, A.I. Kovacs: *Isothermal crystallization kinetics of polyethylene III*. J. Appl. Phys., **32**, 2314-2320 (1961).
55. J.C.M. Escobar-Remolina: *Characteristics of wax precipitation in synthetic mixtures and fluids of petroleum*. Fluid Phase Equilibria, **240**, 197-203 (2006).
56. P. Singh, H.S. Fogler, N. Nagorajan: *Prediction of wax content in a pipeline: an application of the controlled-stress rheometer*. J. Rheol. **43**(6), 1999.
57. P. Singh, R. Verkatesan, S. Fogler: *Formation and ageing of incipient thin film wax-oil gels*. AIChE J., **46** (5), 1059-1074 (2000).
58. P. Singh, R. Verkatesan, S. Fogler: *Morphological evolution of the tick wax deposits during aging*. AIChE J., **47**, 6-18 (2001).
59. P. Singh, A. Youyen, H.S. Fogler, AIChE J., **47** (9), 2111-2124 (2001).
60. J.A. Svendsen: *Mathematical modeling of wax deposition in oil pipeline system*. AIChE J. **39**(8), 1377-1388 (1993).
61. M. Tobin: *Theory of phase transition kinetics with growth site impingement I*. J. Polym. Sci., **14**, 399-406 (1974).
62. R. Venkatesan: *The deposit and rheology of organic gels*. Ph.D. Thesis, University of Michigan (2004).
63. R. Venkatesan, H.S. Fogler: *Comments on analogies for correlated heat and mass transfer in turbulent flow*. AIChE J., **50**, 1623-1626 (2004).
64. E. Vignati, R. Piazza, R.F.G. Visintin, R. Lapasin, P. D'Antona, T.P. Lockhart: *Wax crystallization and aggregation in a model crude oil*. Eni Technical Report (2006).
65. J.S. Weintgarten, J.A. Euncher: *Methods for predicting wax precipitation and deposition*. SPE Prod. Eng., 121-126 (1988).
66. K.W. Won: *Thermodynamics for Solid Solution-Liquid-Vapor-Equilibria: Wax Phase Formation from Heavy Hydrocarbon Mixtures*. Fluid Phase Equilibria, **30** (1986).
67. K.W. Won: *Thermodynamic Calculation of Cloud Point Temperatures and Wax Phase Composition of Refined Hydrocarbon Mixture*. Fluid Phase Equilibria, **53** (1989).
68. C.H. Wu, J.L. Creek, K.S. Wang, R.M. Carlson, S. Cheung, P.J. Shuler, Y. Tang: *Measurements of wax deposition in paraffin solutions*. AIChE Proceedings of the 4th International Symposium on wax Thermodynamics and Deposition (2002).
69. M.I. Zougary, T. Sopkow: *Introduction to Crude Oil Wax Crystallization Kinetics: Process Modeling*. Ind. Eng. Chem. Res., **46**, 1360-1368 (2007).
70. J.Y. Zuo, D.D. Zhang, H.J. Ng: *An Improved Thermodynamic Model for Precipitation from Petroleum Fluids*. Chem. Eng. J., **56** (2001).