# ASPHALTENE
# OR
# HOW AND WHY I BECAME A FAN OF THE REGULAR SOLUTIONS THEORY

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**ABSTRACT**

Petroleum is a mixture of tens of thousands of organic compounds, with molecular weights spanning in a very large range. It was generated underground from the degradation of organic material accumulated over millions of years, and it stays at great depths within porous rocks, at high temperature and pressure. The crude oil is produced by means of long pipes, which allow the extraction of the oil to the surface, where it is then subject to processes of separation into different fractions.

Along the extraction process and the pipeline transport, the operating conditions change; this fact can induce phase separations. A first separation may occur when, due to the depressurization along the production string, the boiling pressure of the mixture is reached: a liquid-vapor separation happens, and the overall system becomes biphasic. In some oilfields and in some wells, however, the separation of a third phase is also observed. This solid or gel-like phase is mainly constituted by a specific class of compounds: the asphaltenes. The asphaltenes are "the bottom of the bottom of the barrel". Asphaltene is a fraction of the oil that contains the heavier and aromatic compounds.

At the beginning, the nature of this separation seemed mysterious, due to the fact that the oil industry has not observed such a phenomenon before. Different physical models and empirical studies have been proposed to explain the phenomenon, and each author has defended his own model. For this reason, at first, a thorough analysis of the various models has been carried out in our company, looking for a particular behavior and a possible "experimentum crucis" to evaluate the physical consistency of the models. We ended up focusing on a particular behavior observed by different researchers and linked to the beginning of phase separation. It is possible, in fact, to induce the asphaltene separation by adding a n-paraffin to the crude. For this reason the titration of the oil has been and is very employed to study the phenomenon; in this way a lot of data has been accumulated in the literature. In particular, there was a general agreement in the literature on an empirical observation that concerns the onset of phase separation. After checking that the oils of our interest had this behavior, we focused on finding a physical model consistent with the observations. We were able to reconcile the observations with the Flory-Huggins theory. In particular, an experimental linear trend is attributable to the regular solutions theory, in the limit of infinite dilution.

This presentation outlines a history of this logical path.

## INTRODUCTION

One of the distinguishing characteristics of the mankind is the conscious use of energy sources for its own purposes. For a very long time the only available energy was that of animals (or even that of other human beings); occasionally the energy of the wind and rivers was employed. But it was only with the extensive use of the fossil fuels that the industrial revolution became possible. The widespread availability of energy (ability to work) created the world in which we live.

The first industrial revolution was based on coal, and started in coal countries (Germany, France, England). The main energy source thus became then the oil, and we still live in the world of oil and gas. Our current way of life is based on the exploitation of fossil energy sources.

Fossil fuels (oil and gas) are formed due to the accumulation, in millions of years of organic material. This material over the millennia has been covered by the ground and has been subject to a burial process. In this way, in anaerobic conditions and at high temperatures and pressures, hydrocarbons were generated and accumulated in the underground porous rocks.

The first step to be able to produce hydrocarbons is to locate possible deposits; for this purpose seismic technologies have been developed. After the identification of a target reservoir, an oil field development plan is prepared and implemented. Hydrocarbons are produced through wells that are drilled from the ground surface to the reservoir. If the reader believes this whole process is too simple, we can add that, due to the increasing energy request, oil production has increasingly shifted to offshore fields. This greatly increases the difficulty of exploration, development and production: the overall production system can easily be something as complex as shown in Figure 1.

## THE OIL

What is commonly called petroleum (from latin "petrae oleum", meaning "oil from rock") turns out to be a mixture of many hydrocarbon components, twenty thousand compounds approximately. The composition is strongly dependent on the origin and the formation conditions of the oil reservoir: the overall properties may span from very dark, almost solid, bitumen-like materials to light, clear yellow liquid, to end up with light gas such as methane. The properties and the physical status of aggregation result to depend on the operating conditions, and separation of different physical phases is possible.

Along the producing pipe (tubing), from reservoir to the surface, the mixture is subject to variations in operating conditions. In particular, along the tube production, there is a pressure draw-down. If the pressure drops below the so-called bubble pressure of the mixture, a second phase separate: the overall system becomes a liquid-vapor biphasic one.

**Figure 1: Overall oil production system**

Due to this vapour-liquid separation, in the higher part of the tubing a bi-phase flux is realized.



**Figure 2: Asphaltene deposits**

In the surface facilities, the fluid stream reaches ambient conditions. Due to this change in conditions, various streams are separated. The main ones are: associated gas (gaseous mixture of hydrocarbon compounds), stock tank oil and produced water. Often the stock-tank oil is also referred to as "dead oil", as opposed to "live oil", that is the reservoir oil. Indeed, in the reservoir the gas, due to the high pressure, is completely dissolved in the liquid: in the reservoir hydrocarbons constitute in a single phase liquid

## THE ASPHALTENE PROBLEM

A production problem was noticed from the beginning of the twentieth century in some fields: it was observed a gradual decrease in the production, linked to the formation of deposits into the tubing. The deposition occurred especially in the area around the bubble point condition, and deposits were called "asphaltene", i.e. "asphalt-like" compounds. Properties and structure of asphaltene are still being studied, as it is a difficult and tricky topic [1,2]. The asphaltene deposition problem is in often encountered in field characterized by relatively "light" oil, with very low asphaltene content.

eni encountered this problem for the first time in the eighties, in relation to the production of one oil field located in the Po Valley. Various research projects were addressed at better understand and afford this problem.

## MODELING OF THE PHASE SEPARATION

Various possible physical models of asphaltene phase separation were proposed in literature, spanning from liquid-liquid equilibrium (LLE), solid-liquid equilibrium (SLE), colloidal and empirical models [3]. This variety of models was linked to the various physical picture proposed by researchers.

On the other hand, in order to have a strong physical basis, we looked for an unambiguous and reproducible behaviour,

that could allow an insight into the physics of the phenomenon. After a careful analysis of the literature, we identified the "onset of precipitation" test as a distinctive behaviour [4]. Our effort were the focused on these data.

The onset of asphaltene precipitation is detected by gradually adding to the oil (eventually pre-diluted with a solvent) a n-paraffin (often n-heptane or n-cetane). After some additions of paraffin, an asphaltene-rich phase precipitate out of the mixture. The onset is identified as the point at which this second phase start nucleating. If the following definitions are adopted:

$$X = \frac{(\text{solvent amount})}{(\text{oil amount})} \qquad (1)$$

$$Y = \frac{(\text{anti - solvent amount})}{(\text{oil amount})} \qquad (2)$$

then straight lines are obtained by plotting Y vs. X. These straight lines constituted the empirical set-up against which we tested our models.

On the basis of our knowledge of the physical system and of the analysis of the previous literature, we choose to try to describe our system by employing a pseudo-binary Flory-Huggins approach [5]. Indeed, the Flory-Huggins theory was developed to thermodynamically describe polymer-solvent solutions, i.e. mixtures in which there is a big amount of relatively small molecules "solvent" and a little amount of relatively big "solute" molecules. From what we knew about asphaltene, this description seemed to be right one. In order not to have a very complex model, with a lot of tunable parameters, we adopted a pseudo-binary approach: in the mathematical description, the overall mixture is constituted by two components, component (2) being the asphaltene and component (1) being the overall mixture constituted by others chemical species. The following equations are then to be considered:

$$\frac{\Delta\mu_1}{RT} = \ln\varphi_1 + \left(1 - \frac{1}{r}\right)\varphi_2 + \chi\varphi_2^2 \qquad (3)$$

$$\frac{\Delta\mu_2}{RT} = \ln\varphi_2 - (r-1)(1-\varphi_2) + r\chi(1-\varphi_2)^2 \quad (4)$$

$$\chi = \frac{v_1}{RT}(\delta_2 - \delta_1)^2 \qquad (5)$$

$$r = \frac{v_2}{v_1} \qquad (6)$$

Symbols are defined as follows:

| | |
|---|---|
| r | ratio of molar volumes |
| $v_i$ | molar volume of component i |
| R | gas constant |
| T | temperature |

| | |
|---|---|
| $\Delta\mu_i$ | chemical potential of component i |
| $\delta_i$ | solubility parameter of component i |
| $\varphi_i$ | volume fraction of component i |
| $\chi$ | interaction parameter |

A phase equilibrium between two phases (I and II) is considered, by imposing that the chemical potential of each component in both phases must be the same:

$$\Delta\mu_1^I = \Delta\mu_1^{II} \qquad (7)$$

$$\Delta\mu_2^I = \Delta\mu_2^{II} \qquad (8)$$

The properties of the pseudo-component 1 are to be evaluated -of course- by means of opportune mixing rules. In particular the molar volume can be evaluated as molar average of molar volumes:

$$v_1 = \sum_{\text{mixture}} x_i v_i \qquad (9)$$

Here $x_i$ is the molar fraction.

The solubility parameter has to be evaluated instead as a volumetric average:

$$\delta_1 = \sum_{\text{mixture}} \varphi_i \delta_i \qquad (10)$$

The overall model (i.e. Eq.s (3) ÷ (10) ), when applied, give rise to a miscibility gap as reported in Figure 3.
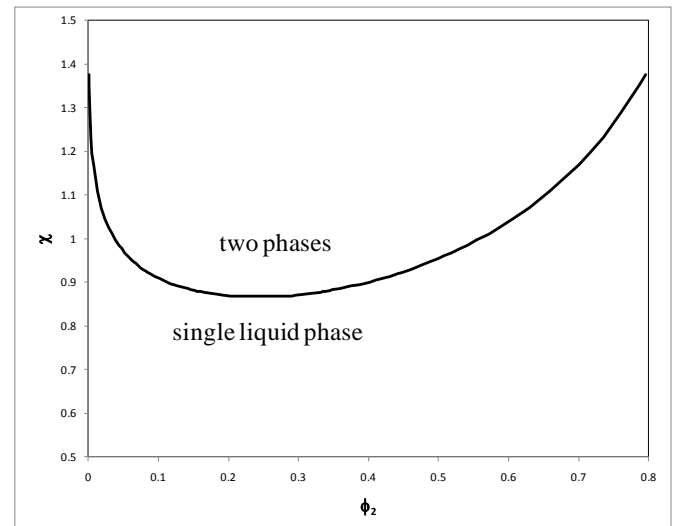


**Figure 3: Miscibility gap for r = 10**

The curve, of course, depends on the ratio of molar volumes r. In the plane (asphaltene volume fraction) vs. (interaction parameter) there is a two-phase zone, corresponding to the equilibrium between two solutions at different compositions.

**THE APORIA IN WHICH WE FOUND OURSELVES**

At this point, we found ourselves in an aporia.

On one hand, we had a lot of experimental confirm (from worldwide labs) of the "straight lines" behaviour. Besides, this behaviour seemed to be physically reasonable: the more the good solvent is present (higher X) the more the precipitant is needed (higher Y).

On the other hand, we must consider the description of the experiments in terms of the model: when a precipitant is added to the solution, there is an increase in the interaction parameter ($\chi$) and a decrease of the concentration (a decrease of the volume fraction $\varphi_2$). The first effect tends to de-stabilize the mixture, while the second one tends to keep asphaltene in solution. However, is predicted an effect of concentration that is not observed.

What had gone wrong?

## IT'S A LONG WAY...

A first possible explanation could be that the chosen physical model was not the right one. But we discharged this possibility for two main reasons:

(l) the physical system (i.e. the oil) is a liquid mixture, and asphaltene are similar, from a chemical-physic point of view, to the other oil components. This justifies the proposed approach, in which to the ideal entropy of mixing is added a regular solution's mixing enthalpy term;

(2) the other proposed models are more complex, with even more parameters. It seems that the physical behaviour is even simpler than the very simple model we adopted: other models would be unnecessarily complicated.

We started a long re-elaboration work, in order to reconnect the model and the experimental behaviour. A first observation was that the observed behaviour means that the onset of asphaltene precipitation happens at a fixed overall "solvent quality" (expressed in the model by the solubility parameter of the mixture), and that this condition does not depends on the asphaltene concentration [6]. This consideration leaded to the following onset condition:

$$\chi = \chi_{Cr} \qquad (11)$$

i.e., the onset of asphaltene separation corresponds to a critical value of the interaction parameter. When a n-paraffin is added to the mixture, both $\delta_1$ and $v_1$ change, according to Eq.s (9) and (10); in this way $\chi$ (Equation 5) increases. When $\chi$ is greater than a critical value, the asphaltene precipitation happens.

As critical value, on the basis of the polymer solutions theories, 0.5 was adopted. But, when we tried to fit experimental data with this model, a greater value was obtained: estimated values span in the range $0.8 \div 1.1$ [7]. By trying to explain this observation, we found that the instability condition $\chi \geq 1$ is equivalent to the condition:

$$\left[ \lim_{x_2 \to 0} \Delta \tilde{G}_{mix} \right] > 0 \qquad (12)$$

Equation (12) means that it is possible to obtain the observed instability condition by considering the Flory-Huggins expression of the enthalpy of mixing. If the solute is significantly bigger than the solvent (r > 10) and if the limit of

infinite dilution is considered, $\chi = 1$ is the condition at which the molar free energy of mixing is zero.

The physical consequences of this reasoning are remarkable. The onset of precipitation is reached by gradually adding a precipitant to the (stable) initial mixture. In doing this, the concentration of asphaltene ($\varphi_2$) decreases, and this is a stabilizing effect. The other effect that counteracts this one is the change of the "quality" of the solvent, expressed by the solubility parameter of the mixture ($\delta_1$). The onset happens when the overall solvent power of the mixture is such that asphaltene results to be perfectly immiscible (insoluble in the mixture). A strong implication of this is that at the onset a "pure asphaltene" phase precipitates out of the solution.

Currently we know that this is the physical behavior that is realized in the onset tests on stock-tank oils. In reservoir the destabilization of asphaltene happens in a slightly different way, and there could be another type of phase separation. Deposits formed under these conditions could contain significant amounts of non-asphaltenic constituents. This topic is still under investigation.

## WHAT ABOUT THE STRAIGHT LINES?

The model for the onset results to be:

$$@ \text{ onset: } \frac{v_1}{RT}(\delta_2 - \delta_1)^2 = 1 \qquad (13)$$

When trying to calculate the precipitant amount through Equation (13), a quadratic equation is obtained. However it is possible to show that, if the molar volumes of the pseudocomponents are similar, straight lines are recovered [6]. Besides, when the values of the properties are substituted into the equations, the straight lines are always found.

## BACK DOWN TO EARTH

The logical path described so far has a concrete motive. Working in the oil industry implies facing extremely complex and variable systems with very limited available information. Often it is not easy or possible to have samples to be directly analyzed, or it is impossible to directly make test at the desired conditions. For this reason is of paramount importance to have physically founded models. In this way it is possible to perform a limited number of tests in the laboratory, and then extrapolating the results to different conditions.

On the basis of this physical model of the onset, the following procedure was proposed to determine the region of instability in a (P,T) diagram, to forecast well bore asphaltene precipitation from stock tank oil measurements:

(l) Characterization of stock tank oil by means of lab measurements and previously developed empirical relationship. In this way it is possible to evaluate molar volume and solubility parameter of the stock-tank oil [8].

(2) Experimental determination of stock-tank oil precipitation onset. At the onset, the $\chi = 1$ has to be fulfilled. By imposing this condition, it is possible to calculate the asphaltene solubility parameter.

(3) Calibration of an equation of state (usually the Soave-Redlich-Kwong EOS [9]) by using the onset data. The oil is represented by means of components and
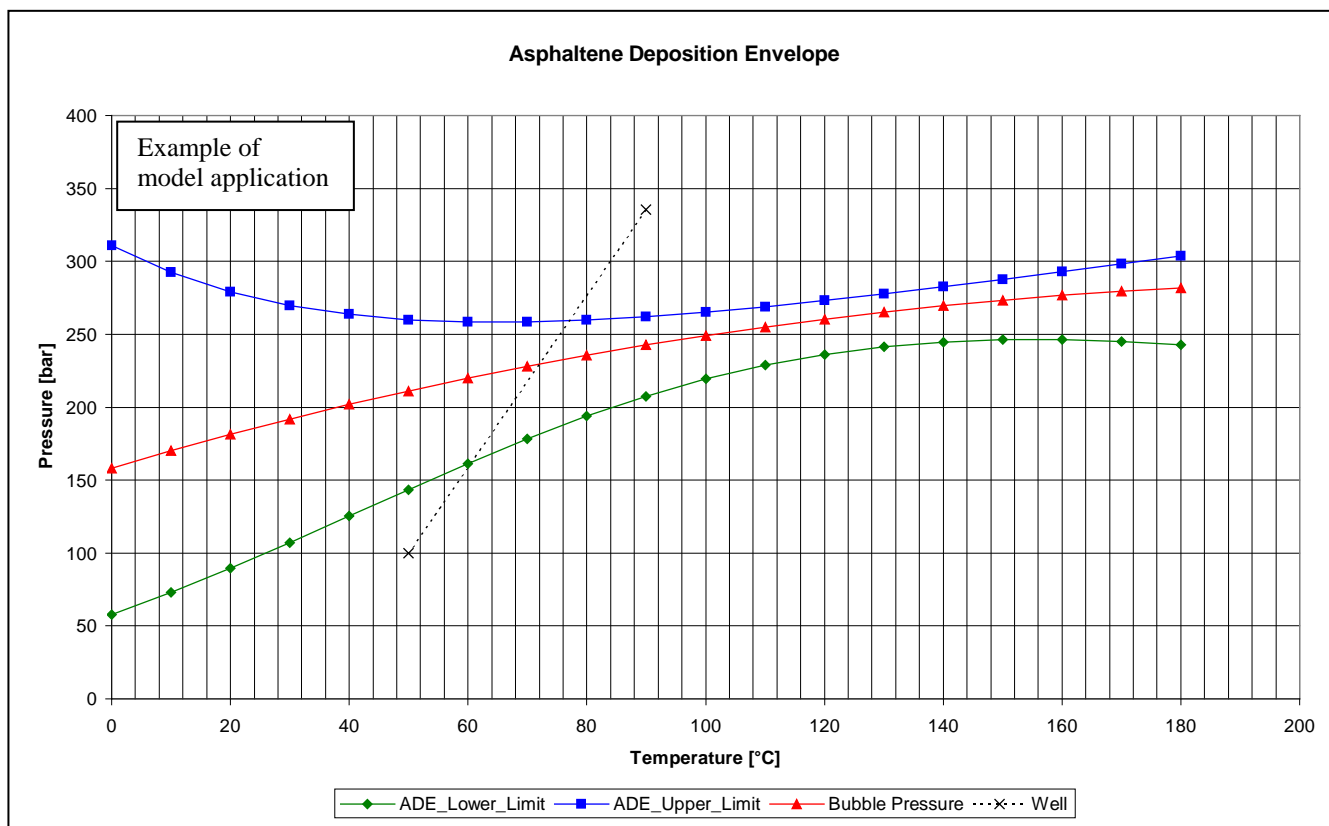
**Figure 3: Asphaltene Deposition Envelope**

pseudo-components, each one characterized by critical temperature (Tc), critical pressure (Pc) and acentric factor (ω). The parameters of the pseudocomponents can be evaluated from their boiling point and specific gravity by means of empirical relationships.

(5) Calculation of live oil molar volume and solubility parameter at different T and p conditions (up to reservoir conditions) by means of the calibrated equation of state.

(6) Calculation of asphaltene solubility parameter at the same conditions, by means of an empirical relationship.

(7) Determination of the asphaltene deposition envelope (ADE): at each pair (T, P), $\chi$ is calculated with Eq. [5]; if the oil conditions are inside the envelope ($\chi$>1), then at these conditions the asphaltenes are not stable.

An example of ADE determined with this procedure is reported in Figure 3. Therefore, with a relatively simple measurement of stock tank oil, it is possible to calculate an Asphaltene Deposition Envelope that identifies the pressure and temperature conditions in which there is a risk of asphaltene separation. If there is an area in the reservoir, the pipeline etc. where asphaltene enter the region of instability, asphaltene may deposit in that area.

This model has been employed in eni to assess the asphaltene deposition risk in many cases, with good results.

## CONCLUSIONS

The history of the eni's asphaltene deposition model has been here synthetically described. It is a model characterized by

a very limited number of parameters and by the strong adherence to experimental observations. The model, gradually built over the years, has been and is used to assess the risk of asphaltene deposition in well.

The work of these years allowed me to appreciate the elegance and ingenuity of the theory of regular solutions and Flory-Huggins theory for polymer solutions.

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