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Multicomponent transport studies of crude oils and asphaltenes in DSC program

Crude oils have matured during ages in reservoirs under obvious non-equilibrium conditions. The resulting stratification and phases present can be predicted only with non-equilibrium thermodynamics tools. Possibly, convection is present and enforced by the Soret effect. These parameters are the focus of the MAP DSC (Diffusion and Soret Coefficients) multicomponent studies. Theoretical and ground based studies are completed by measurements performed in the SCCO experiments (Soret Coefficients of Crude Oils), of the DSC experiment on SODI facility (Beginning 2008). The problem is presented here in a simplified manner using Maxwell-Stéfan formalism, and is applied to some situations occurring in reservoirs and in the GATE experiment proposed for the study of growth conditions of asphaltenes.

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I. Introduction

Hydrocarbon fields explored present very different characteristics and evermore severe exploitation conditions. A good prediction of the extracting conditions is becoming mandatory and has consequences not only on the evaluation of the economic content of fields and reservoirs but also on the overall exploitation schemes. The importance of the analysis of reservoirs in this context is of growing importance.

These evaluations start with geological data, and proceeds during the exploitation of the reservoirs. Very costly drillings may be required to extrapolate from the samples the overall components distribution. Indeed, the material buried during geological ages in natural reservoirs results in a huge spectrum of hydrocarbons. They appear under many states, mainly liquid and gaseous, but also solid carboids, waxes, bitumens and asphaltenes. The latter form, still unexplained, aggregation under the variation of pressure and composition, causing important operational disturbances.

The catagenesis of this material as occurred under extreme thermodynamic conditions and the drillings performed up to depths of 7 km show pressures of more than one thousand bars and temperatures of 500 K. The analysis of such fantastic natural laboratories requires powerful thermodynamic tools. Phase envelopes can be predicted using finely tuned equations of state and mixing rules. Examples studied in the DSC program are shown on figure 1 and the corresponding compositions are given in figure 2. In addition to hydrocarbons are present nitrogen and acid gas components.

These analyses provide for instance the physico-chemical characteristics of the material as function of composition. To predict composition stratification, the gravity potential is implemented in the models. However, the so predicted stratifications do not fit at the desired level of accuracy very important reservoir characteristics, as the depth of the liquid-gas transition and the distribution of the gas to oil ratio (GOR). There are several reasons that may be responsible for it and the main arguments for a possible improvement of the analysis is that the reservoirs are maintained in obvious non equilibrium conditions. With this in mind, the static models have been reconsidered since the sev-

enties. It appears nowadays that, in addition to the static sedimentation and to the baro-diffusion, both included in these computations, dissipative transport couplings should also be considered in the evaluations. For instance, using reasonable theoretical estimates of the Soret coefficients, Montel [1] has obtained displacement of transition zone of more than hundred meters.

The evaluation of the state resulting from non-equilibrium constraints is a difficult question [2,3]. For *ab initio* estimations, convection, diffusion limited transport, chemical reactions are also to be included. In an explored field, characteristics of reservoir may have to be re-evaluated at any time of the exploitation. Operation of the installations may be stopped because of asphaltenes plugging.

In all these cases, a good prediction of the extracting conditions is a determinant factor. A scientific program funded by MAP (Microgravity Application Program) was undertaken with the related microgravity experiments. This Diffusion and Soret Coefficient (DSC) programme has the evaluation of the transport quantities as main task. It is indeed the cornerstone of the expected developments.

In addition to the expected financial return for oil companies, it is a domain of research with challenging problems and different disciplines involved. For instance, theoretical and molecular dynamics predictions are focused on the modelling; measurements are required to determine the Soret coefficients of actual crude oils; microgravity experiments are required to study processes as multicomponent diffusion and asphaltene growth.

In this paper we will shortly describe how the data obtained in microgravity experiments is implemented into models. The programmatic interlink of the microgravity programs and of the experiments is schematised on figure 3. The experiments concerned are the SCCO (Soret Coefficients of Crude Oils) experiment measuring the Soret coefficients on the unmanned FOTON satellites, the DSC (Diffusion and Soret Coefficients)

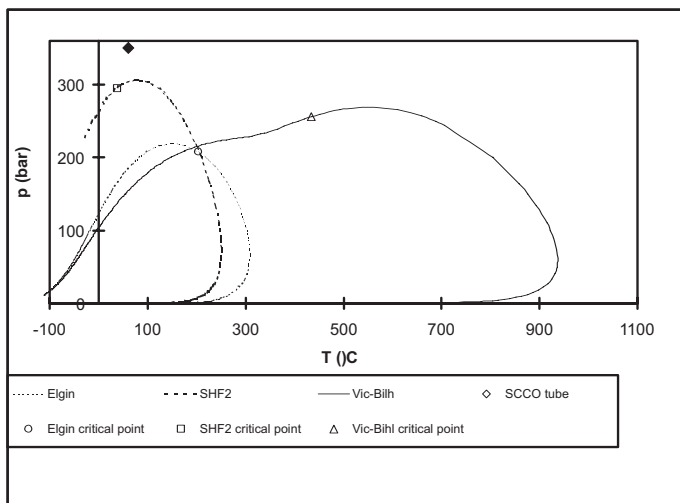


Fig. 1: phase envelopes for systems studied in the DSC program. The typical fluid of the SCCO experiment indicated on the figure by a diamond appears in slightly supercritical conditions.

microgravity experiment on SODI facility (Selectable Optical Diagnostics facility), to be flown on the International Space Station ISS (Beginning 2008) and aiming to analyse diffusion in model fluids, and the proposed GATE (Growth of Aggregates with Thermal Exchanges) experiment aiming to better understand the question of asphaltene growth, first proposed in the integrated proposal GANIMEDe (Growth of Asphaltenes in Nonequilibrium and Instrumental Microgravity Developments). The data obtained is directly implemented in the reservoir models at different levels of description, some aspects being provided in this paper.

2. Multicomponent Mass Transport

To describe processes occurring in reservoirs, a generalized form of the Maxwell-Stéfan [4] relations has been implemented [5]. Multicomponent dispersion fluxes, comparing the velocities v_i of components i having a mass fraction c_i with the one of component j , are defined by

$$\vec{J}_{ij} = \rho c_i c_j (\vec{v}_i - \vec{v}_j) = c_j \vec{J}_i - c_i \vec{J}_j \quad (1)$$

where ρ is the density of the mixture. They are caused by the generalized forces Y_i . The later can be decomposed into the thermal forces, involving a heat of transfer q_i of component i [5, 6], linked to Soret effect as will appear below, and the reversible component X_i :

$$\vec{Y}_i = \vec{X}_i + \frac{q_i}{T} \nabla T \quad (2)$$

where T is the temperature field. The reversible component for a species of molar mass M_i and chemical potential μ_i in a simplified description for the porous matrix of reservoirs in the gravity field is

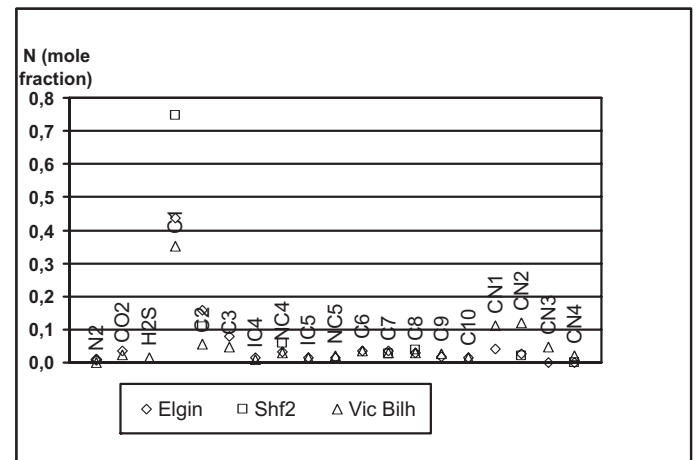


Fig. 2: composition of crudes studied in SCCO program. CN stands for cuts (number of carbons indicated on figure). Elgin is a North-Sea field, Vic-Bilh is a South East of France field and SHF2 is a synthetic crude oil.

$$\bar{X}_i = \bar{g} - \frac{1}{M_i} \nabla_T \mu_i \quad (3)$$

where subscript T on Nabla operator means that the gradient is taken at constant temperature. Using the total force defined by the

$$\bar{Y} = \sum c_i \bar{Y}_i = \bar{g} + \frac{q}{T} \nabla T \quad (4)$$

transport quantities are obeying to the relations

$$\sum_j \frac{\bar{J}_{ij}}{d_{ij}} = \rho \frac{c_i}{RT} (\bar{Y}_i - \bar{Y}) \quad (5)$$

where the d_{ij} are binary diffusion coefficients. These relations are equivalent to the Onsager relations [7], but present a more suitable form for several reasons developed elsewhere. In the case of reservoir modelling codes the chemical potentials will be directly related to the balances of forces. The distribution of components is deduced with the thermodynamic relations

$$\sum_j G_{ij} \nabla c_j = \nabla_{T,p} \mu_i \quad (6)$$

where the gradient of chemical potentials are at constant temperature and constant pressure. In case of non dispersive states (vanishing species fluxes) and after elimination of the pressure gradient assuming local mechanical equilibrium, it is obtained that

$$\sum_j G_{ij} \nabla c_j = \left(\frac{v_j}{v} - \frac{M_j}{M} \right) \bar{g} + \frac{q_i}{T} \nabla T \quad (7)$$

where v_j and v are the specific molar volume of component j and molar volume of the solution. This resulting distribution results from the superposition of sedimentation to Soret effect, but the specific effects are thermodynamically coupled. In addition to the thermodiffusion factors given by

$$k_{Ti} = \sum_j G_{ij} q_j \quad (8)$$

we introduce here the buoyancy numbers

$$a_i = \sum_j G_{ij} \left(\frac{v_j}{v} - \frac{M_j}{M} \right) \quad (9)$$

If these coefficients are kept constant, the distribution of components in a field with constant vertical gradient (z being the downwards position, i.e. the depth) is given by

$$\ln \left(\frac{N_i(z)}{N_i(z_0)} \right) = a_i g (z - z_0) + k_{Ti} \ln \left(\frac{T(z)}{T(z_0)} \right) \quad (10)$$

where N_i is the mole fraction of component i . In most apolar binary solutions, the Soret effect is “normal”, viz., the heavier component migrates towards the cold. In multicomponent systems, the “heavy” components are suitably defined as having a

positive buoyancy numbers. They may also present a “normal” Soret effect or not. The figure 4 illustrates the four possible combinations that appear when considering the possible signs of the thermodiffusion factors and buoyancy numbers.

3. Solutions With A Few Components

When the Soret effect is normal for most components of the solution, as expected, it has an effect on density opposed to sedimentation in the reservoir. This is a situation where the occurrence of a Bénard instability is favoured and enhanced by the composition distribution. Large Soret effect may have a very efficient effect to this respect [8].

However, the convective characteristic much depend on the characteristic times by which the fields relax. The analysis of it is a very complex task in actual crudes. The multicomponent diffusive behaviour of such systems is not known and a possible reverse diffusion may be observed [9] or critical behaviour of diffusion may occur. In the DSC experiment, to be carried in the SODI facility, a model ternary system will be studied. The composition profiles will be recorded with a Mach Zehnder optical set-up. All the Soret coefficients and the isothermal diffusion coefficients of the ternary solution will be obtained by applying periodically a thermal gradient.

This DSC experiment aims also to assess mixing rules, since deducing the values of solutions with n components from solutions with $n-1$ components is a possible iterative process that provides a great simplification in multicomponent studies and connects them to the equilibrium thermodynamic approaches. As an example, for the Soret coefficients, a guessed simplified mixing rule with mole fractions nowadays better assessed is

$$k_{Ti} = \sum N_j k_{Tij} \quad (11)$$

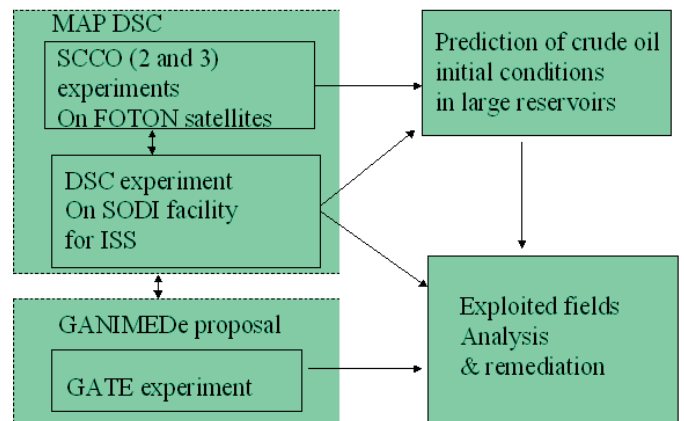


Figure 3: On the left, interlinks between the microgravity experiments and programs mentioned in the text and on the right the applications concerned.

4. Application to Crude Oils

Testing this mixing rule on an actual crude light fraction provides the results shown on figure 5. The composition providing this correlation (figure 2) is a light fraction of a crude sample (from TOTAL). Appears here an effect specific to the multicomponent systems: the heavy components are less discriminated than the light ones. The reason is here that the Soret effect appears as a cooperative process where the mole fractions of all the species are to be considered.

The distributions resulting by multicomponent Soret effect only (“elemental Soret effect”) deserves being studied in microgravity conditions to avoid convection that may be induced for instance by the reverse diffusion. Such a study is realised in the SCCO experiments flying on FOTON unmanned space platforms. The samples are processed in a fixed thermal gradient during about 200 hours. This large duration is selected because the actual relaxation time by which the Soret effect established depends on diffusion coefficients. Such a time diverges near multicomponent critical points, and the samples of interest are close from these regions of the reservoirs.

5. Application to Reservoirs

Close to such zones, the polyphasic equilibrium is not exactly realised, because of the applied non-equilibrium constraints. The gradients of the chemical potentials are small however. The relations that approach such a situation are obtained from equation (5). They are

$$\sum_j \frac{\bar{J}_{ij}}{d_{ij}} = \rho \frac{N_i}{RT} \left(\left(\frac{v_i}{v} - \frac{M_i}{M} \right) \bar{g} - \frac{q_i}{T} \nabla T \right) \quad (12)$$

Unless the Soret effect and the buoyancy exactly balance, what would be a quite exceptional circumstance, the relation shows that there must be a diffusion flux to compensate for the unbalance between the different forces.

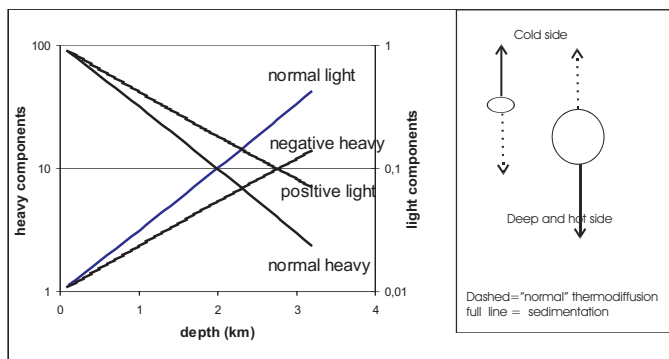


Fig. 4: profiles as function of depth for model compounds having unitary buoyancy and thermidiffusion numbers are unitary. The thermal gradient used is 40 K/km. Normal Soret is heavy towards cold and light towards hot, and sign defined is the reverse situation. Insert describes the “normal” case.

A similar situation occurs when asphaltenes grow, in as much as the resulting aggregates can be considered as a dispersed phase. Asphaltenes precursors are aggregates of a few nanometers of hydrocarbons associated mainly by polar links. They may grow in size dramatically in a window of high pressure (see [2,3] for instance) that is very sensitive to the ratio of normal parafines to aromatics [10].

The occurrence of such phenomena causes to oil industry detriments that have a direct impact on the price of the oil. A MAP proposal (GANIMEDe) was issued in answer to the 2004 AO of ESA to study this problem since the existing models of growth do not reach a reasonable consensus. For instance, it has been recently shown by calorimetric studies and survey of literature data that the concept of micellization does not apply to asphaltenes [11]. Models based on aggregates peptized by resins difficultly apply because the resins and asphaltenes form a nearly continuous spectrum of components [12]. Polymeric models have also been recently invoked to explain the high viscosity increase at high concentration of asphaltenes. Our proposal has as peculiarities, with respect to literature, to implement non-equilibrium effects and to use the benefits of microgravity conditions. The proposal can be reformulated into the following GATE experiment proposition where the components participating to the growth of asphaltenes are forced to migrate by Soret effect. The effect being tiny, the sensitivity of the growth to the composition could so be analysed with an unprecedented accuracy, the Soret effect acting as a chemical microscope. From another side, the relation (12) (with vanishing level of gravity) shows that the overall process can be quantified with quite simple diagnostics, the fluxes being in close correlation to the Soret effect and to the growth of the aggregates.

6. Conclusions

Multicomponent studies have a rich domain of experimentation and application in crude oil reservoirs. From the prediction of extracting conditions to the study of remediation of operational

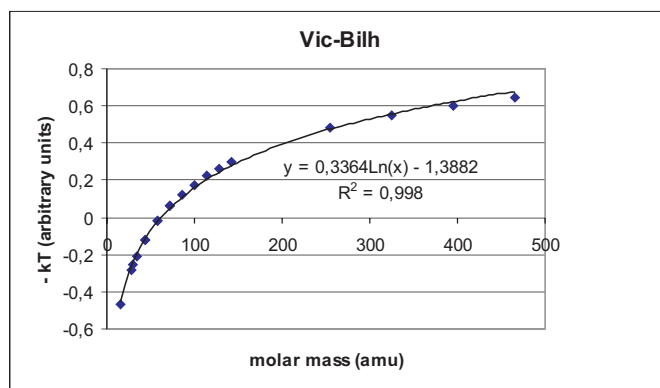


Fig. 5: thermidiffusion factors as a function of the molar mass of components, as computed with the mixing rule and on an actual crude oil whose composition is given in figure 2 (Vic-Bihl).

problems as the growth of asphaltenes, the non-equilibrium factors have to be implemented. The Soret effect in particular surely superposes to sedimentation in reservoirs and promotes Bénard convection and so has a probable indirect influence of the growth of asphaltenes during the exploitation of the reservoirs. It is also a tool proposed to study the unknown nature of the asphaltene growth and for the modelling of the multicomponent diffusive processes. Diffusion has to be considered in all cases as well.

The related microgravity (SCCO, DSC in SODI facility and the proposed GATE experiment) are linked together by the need to study the non-equilibrium transport and to characterise these processes in reliable conditions. We provided here a synthetic overview of the underlying physics by use of Maxwell-Stéfan formulation of transport.

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