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SCCO: Thermodiffusion for the Oil and Gas Industry



Guillaume Galliero, Henri Bataller, Jean-Patrick Bazile, Joseph Diaz, Fabrizio Croccolo, Hai Hoang, Romain Vermorel, Pierre-Arnaud Artola, Bernard Rousseau, Velisa Vesovic, Mounir Bou-Ali, José M. Ortiz de Zárate, Shenghua Xu, Ke Zhang, François Montel, Antonio Verga and Olivier Minster

Abstract The accurate knowledge of pre-exploitation fluid compositional profile is one of the necessary pre-requisites for a successful field plan development of a petroleum reservoir by the oil and gas industry. Thermodiffusion, leading to a partial diffusive separation of species in a mixture subject to thermal gradient, is thought to play an important role in oil and gas reservoir due to the geothermal gradient.

G. Galliero (✉) · H. Bataller · J.-P. Bazile · J. Diaz · F. Croccolo · H. Hoang · R. Vermorel · F. Montel

Laboratoire des Fluides Complexes et leurs Réservoirs - IPRA, UMR-5150 CNRS-TOTAL, E2S - Université de Pau et des Pays de l'Adour, Pau, France
e-mail: guillaume.galliero@univ-pau.fr

F. Croccolo

Centre National d'Etudes Spatiales (CNES), 2, Place Maurice Quentin, 75001 Paris, France

P.-A. Artola · B. Rousseau

Laboratoire de Chimie-Physique, UMR 8000, CNRS, Université Paris-Sud, Orsay, France

V. Vesovic

Department of Earth Science and Engineering, Imperial College London, London, UK

M. Bou-Ali

Mechanical and Industrial Manufacturing Department, Mondrago, MGEP Mondragon GoiEskola Politeknikoa, Arrasate, Spain

J. M. O. de Zárate

Departamento de Física Aplicada I, Universidad Complutense, Madrid, Spain

S. Xu

Key Laboratory of Microgravity (National Microgravity Laboratory), Institute of Mechanics, Chinese Academy of Sciences, No. 15 Beisihuanxi Road, Haidian District, Beijing 100190, China

K. Zhang

State Key Laboratory of Enhanced Oil Recovery (Research Institute of Petroleum Exploration & Development), CNPC, Beijing, China

F. Montel

TOTAL Exploration Production, Pau, France

A. Verga · O. Minster

European Space Agency, ESTEC, Noordwijk, The Netherlands

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6 Although major improvements in measuring, simulating and modelling thermodif-
7 fusion coefficients have been achieved in the last decades, the improvements are
8 mostly limited to binary liquid mixtures at atmospheric pressure. Thus, the need for
9 accurate data, that would prove invaluable as benchmark reference data for validat-
10 ing models and simulations, was one of the main drivers behind the project “Soret
11 Coefficient measurements of Crude Oil” (SCCO) which used a microgravity set-up
12 implemented in the SJ-10 satellite. This unique project, resulting from a partner-
13 ship between European Space Agency and China’s National Space Science Center
14 enhanced by collaboration among academics from France, Spain, United Kingdom,
15 China and industrialists from France and China, aimed to measure the thermodif-
16 fusion coefficients of multicomponent oil and gas mixtures under high pressures.
17 Within this framework, some results on thermodiffusion of one ternary oil mixture
18 and one quaternary gas condensate have been obtained in microgravity and have been
19 qualitatively confirmed by molecular simulations. More precisely, these microgravity
20 results have confirmed on multicomponent mixtures that thermodiffusion leads to a
21 relative migration of the lightest hydrocarbon to the hot region. These results support
22 the idea that, in oil and gas reservoirs, thermodiffusion is not negligible being able
23 to counteract the influence of gravity-driven segregation on the vertical distribution
24 of species.

25 **Keywords** Thermodiffusion · Segregation · Multicomponent mixtures · Oil and
26 gas · Molecular dynamics

27 1 Introduction

28 The ever increasing world-wide energy demand is putting severe pressure on our
29 ability to manage it effectively, while minimizing adverse climate effects. Although,
30 the renewable energy sources are making strong in-roads, gas and oil remain an
31 important part of the current and near-future energy landscape [1]. Natural gas and
32 crude oil, the two most well-known examples of reservoir fluids, are found, in gen-
33 eral, at depths greater than 500 m and require bringing to the surface in a controlled
34 manner. Reservoir fluids, that reside within the pores of petroleum bearing rocks
35 are the remnants of the transformation of organic matter (kerogen) over geological
36 timescales. They are chemically complex mixtures consisting of hundreds of dif-
37 ferent species, primarily hydrocarbons. In order to optimally exploit the available
38 resources, the petroleum industry creates a considerable demand for reliable values
39 of the thermophysical properties of reservoir fluids over extensive ranges of temper-
40 ature and pressure. The estimates of thermophysical properties of interest, mainly
41 density and viscosity, can be obtained by a number of standard methods [2].

42 The petroleum reservoirs are typically subjected to external pressure and/or
43 temperature fields so that gradients in chemical potentials are established leading
44 to diffusive fluxes and resulting in a non-uniform compositional profile. Knowl-
45 edge of such a profile, especially pre-exploitation profile, is one of the necessary

46 pre-requisites for a successful field plan development of a petroleum containing
47 reservoir.

48 The non-uniform distribution of species in the reservoir is known to be influ-
49 enced by a number of phenomena [3]; for instance, in a closed, convection-free
50 reservoir gravitational segregation is assumed to be the most important [4]. However,
51 if there is a temperature gradient within the reservoir, and most reservoir fluids are
52 subject to at least a vertical geothermal gradient of about 0.03 K/m [3], the coupling
53 of heat and mass fluxes [5] leads to a phenomenon known as thermodiffusion, which
54 is also referred to as Soret effect. Thermodiffusion has been shown to strongly
55 influence compositional distribution profile of species [3, 6, 7]. Indeed, there is some
56 evidence based on a number of reservoirs, that thermodiffusion can be as important
57 as gravitational segregation [6, 8–10].

58 In order to correctly model the thermodiffusion effects one needs a knowledge
59 of thermodiffusion coefficients [5]. Although, there has been a major improvement
60 in the accuracy and reliability in measuring thermodiffusion coefficients in the last
61 decades [11, 12], the improvements are mostly limited to binary liquid mixtures
62 at atmospheric pressure. Recently, the database of the available experimental data
63 has been enhanced by new measurements on ternary mixtures [12, 13] and under
64 high pressures [14–17]. As it is not possible to characterize all the relevant mixtures
65 experimentally, a major effort has been undertaken to develop reliable prediction
66 methods. Progress has been achieved both in the field of thermodiffusion simulation
67 [18] and modelling [12]. Nevertheless, progress has been scant as far as the oil and
68 gas at typical reservoir conditions are concerned, even when the reservoir fluids were
69 represented by synthetic multicomponent mixtures consisting of a few species. The
70 primary reason for this state of affairs can be traced to: (i) complexity of characterizing
71 the thermodiffusion in multicomponent mixtures and (ii) the small magnitude of
72 the thermodiffusion effect under normal laboratory conditions. The latter can be
73 addressed by performing measurements under microgravity conditions [9, 19–22].

74 The need for accurate data, that can serve as benchmark reference data that would
75 prove invaluable in validating models and simulations, was one of the main drivers
76 behind the project “Soret Coefficient measurements of Crude Oil” (SCCO). The
77 project aimed to measure the thermodiffusion coefficients of six multicomponent
78 fluid mixtures, of interest to reservoir applications, under high pressures used a
79 microgravity set-up implemented in the SJ-10 satellite [23]. The SCCO/SJ-10 project
80 is the result of a unique partnership between the European Space Agency and China’s
81 National Space Science Center [24] enhanced by collaboration among academics
82 from France (Université de Pau et des Pays de l’Adour, Université de Paris-Sud and
83 CNRS), Spain (Mondragon Unibertsitatea and Universidad Complutense), United
84 Kingdom (Imperial College London), China (Chinese Academy of Sciences) and
85 industrialists from France (TOTAL) and China (RIPED, CNPC).

86 In this chapter we aim to summarize some of the results of the project within
87 a context of a short thermodiffusion review and make them available to the larger
88 scientific community.

2 Quantifying Thermodiffusion

As already alluded to in the Introduction, a presence of temperature gradient within a convection-free fluid, generates a composition gradient in a mixture, that results in preferential migration of species towards either cold or hot sections. This separation effect occurs also when fluids are confined in a porous medium. It has been shown that the porous medium has a negligible effect on the magnitude of thermodiffusion, as long as one is not dealing with nano-pores [25]. Thus, the measurements of thermodiffusion coefficients in unconfined fluids can be used for most reservoir applications [26, 27].

The analysis of thermodiffusion is usually performed in the framework of non-equilibrium thermodynamics [5]. In this formalism, the macroscopic relation describing the transport of matter in a two-component mixture can be expressed as

$$\mathbf{J}_1 = -L_{1q} \frac{\nabla T}{T^2} - L_{11} \frac{\mu_{11}^w}{w_2 T} \nabla w_1 \quad (1)$$

where \mathbf{J}_1 is the mass flux of component 1, in a centre of mass reference frame, T is the temperature and μ_{11}^w is the derivative of the chemical potential of species 1 relative to its mass fraction, w_1 . The L_{ij} are the so-called *phenomenological* or Onsager coefficients, describing the proportionality between fluxes and thermodynamic forces. At the stationary state, i.e. at null mass flux, the partial separation of the species induced by thermodiffusion in binary mixtures is usually quantified by the Soret coefficient, that is defined by,

$$S_T = -\frac{\nabla w_1}{w_1(1-w_1)\nabla T} = -\frac{\nabla x_1}{x_1(1-x_1)\nabla T} \quad (2)$$

where x_1 is the mole fraction of component 1. Note that with the definition given in Eq. (2) the value of the Soret coefficient for a binary mixture is independent of whether mass or molar concentrations are used. By combining Eqs. (1) and (2), an expression of the Soret coefficient in terms of the L_{ij} 's can be given,

$$S_T = -\left(\frac{1}{w_1 \mu_{11}^w T} \frac{L_{1q}}{L_{11}} \right)_{\mathbf{J}_1=0} \quad (3)$$

In a multicomponent mixture, it is not possible to quantify thermodiffusion without specifying the reference frame. Although there is still some confusion in the literature, it is lately becoming more customary to quantify thermodiffusion in multicomponent mixtures by the so-called (molar) thermal diffusion ratio of each species, which is a dimensionless number defined by,

$$k_{T_i} = -T \frac{\nabla x_i}{\nabla T} \quad (4)$$

125 with temperature and composition gradients at steady state. The results of the SCCO
126 microgravity experiment will be reported in terms of these (molar) thermal diffusion
127 ratios.

128 Thermodiffusion has been extensively studied, in particular in binary liquid hydro-
129 carbon mixtures, by experimental, modelling and simulation means. We present in
130 the following a brief review of recent approaches, in particular those developed by the
131 authors in connection with the SCCO project. The reader is referred to the literature
132 for more comprehensive reviews [12, 18, 28, 29] on this topic.

133 2.1 Experimental Investigations

134 When a temperature gradient is applied to a fluid, because of thermal expansion,
135 a density gradient appears. If the fluid is a mixture, the Soret effect will induce a
136 compositional gradient which will modify this density gradient. Depending on the
137 relative orientations of the density gradient and the gravity field, convection may
138 occur in terrestrial laboratories. There are two families of experimental set-ups to
139 measure the Soret effect: thermo-gravitational columns, which take advantage of
140 convection, and Soret cells, which work only in a quiescent, purely conductive heat
141 regime. In the framework of the SCCO project, measurements combining these two
142 techniques have been recently performed on binary mixtures of *n*-alkanes under high
143 pressure [16, 17].

144 2.1.1 Thermo-gravitational Columns

145 Following the ground-breaking experiments of Ludwig and Soret in U-shaped glass
146 tubes, the invention of the Clusius–Dickel tube and its application to liquid mixtures
147 [30] was an early milestone in the development of experimental devices capable of
148 accurate and reliable thermodiffusion measurements. The evolution of these devices
149 [31–33] has led to the method usually known as the Thermo-Gravitational Column
150 (TGC) technique. A TGC consists of two vertical plates or concentric cylinders
151 that are separated by a narrow gap, which contains the mixture, across which a
152 temperature gradient ∇T is maintained perpendicular to gravity [34–36]. Coupling
153 of thermodiffusion and solutal expansion induces thermo-solutal convection that
154 highly amplifies the top-bottom gravitational separation. In this technique, it is the
155 so-called thermodiffusion coefficient, D_T , which is directly measured. For a binary
156 mixture, D_T is expressed as the product of the mutual diffusion coefficient D and the
157 Soret coefficient (i.e. $D_T = S_T D$). The theory for concentric TGCs was originally
158 developed by Furry, Jones and Onsager in 1939 [37] and its validity limits have been
159 discussed, among others, by Valencia et al. [38].

160 TGCs have not only been used to measure thermodiffusion coefficients of binary
161 mixtures of small molecules at normal and high pressures [14], but also for mixtures
162 near the critical point [39]. More recently, the TGC technique has been extended to

163 ternary mixtures [40–43]. TGCs have also been filled with granular matter in order
164 to study the Soret effect in porous media, and to model the separation mechanisms
165 in situations more relevant for geochemical fluids [44, 45].

166 2.1.2 Soret Cells

167 A Soret cell is a sample volume bounded by two horizontal parallel plates with a
168 high thermal conductivity, typically copper. The plates have a vertical (z-direction)
169 spacing h and are kept at two different temperatures in order to generate a temperature
170 gradient ∇T parallel to gravity. The volume is laterally confined by a material of
171 low thermal conductivity, frequently glass thus allowing for optical observation in a
172 direction perpendicular to the temperature gradient [11, 12] which facilitates some
173 experimental techniques to measure thermodiffusion, like optical beam bending.
174 In this kind of cells, Soret coefficients (as well as other properties) can also be
175 measured by light scattering from non-equilibrium fluctuations, in which case optical
176 windows in the bounding plates are needed for optical access parallel to the gradient.
177 This approach was first demonstrated by Segre et al. [46] who investigated small-
178 angle Rayleigh light scattering due to temperature and composition fluctuations in a
179 toluene/*n*-hexane mixture subjected to a stationary temperature gradient.

180 According to fluctuating hydrodynamics [47, 48], the intensity of scattered light is
181 proportional to $(\nabla T)^2/q^4$ and, hence, it increases very strongly for small scattering
182 wave numbers q . The q^{-4} divergence at $q \rightarrow 0$ eventually saturates due to gravity
183 and finite size effects [49–51]. Building on the investigation of non-equilibrium
184 fluctuations in Soret cells, Crocco et al. [52] have recently obtained Soret and
185 diffusion coefficients of binary mixtures from dynamic shadowgraph experiments.
186 This shadowgraph technique in Soret cells has been extended to high pressures by
187 Giraudet et al. [15].

188 To apply the dynamic shadowgraph technique for ternary mixtures, theoretical
189 extensions were undertaken. Ortiz de Zárate et al. [53] extended the theory of
190 non-equilibrium concentration fluctuations spectra and their dynamics to micro-
191 gravity conditions, but without accounting for confinement effects. The valida-
192 tion was performed by comparing with the experimental results for a mixture of
193 tetralin/isobutylbenzene/*n*-dodecane under terrestrial conditions but at large wave
194 vectors, where gravity and confinement effects are negligible [54]. More recently,
195 and in the framework of the SCCO project, gravity has been included in the theory
196 [55]. There are several ongoing experimental verifications in this respect. The incor-
197 poration of confinement effects into the theory is currently being developed [56].

198 2.2 Modelling Developments

199 In the low density limit it is possible, by means of kinetic theory, to link thermodiffu-
200 sion to the intermolecular forces [57, 58]. However, and despite numerous efforts and

201 recent progress [12], there is still a lack of a universal microscopic picture explain-
202 ing thermodiffusion in condensed phases. The lack of an underlying theory is quite
203 general for transport properties [28], but for thermodiffusion it is compounded by its
204 extreme sensitivity to molecular interactions, in particular to cross interactions [59].

205 When dealing with dense atomic and molecular fluids, there are basically three
206 modelling approaches that have been proposed during the last century. The earliest
207 ones are based on adaptations of the kinetic theory to dense phases [58, 60–62]. They
208 were followed by ones based on pure equilibrium considerations of the phenomena
209 [63] and subsequently by the ones based on liquid states theory [64–66]. There exist
210 also some dedicated empirical approaches which lead to reasonable results when
211 dealing with *n*-alkanes [59, 61, 67].

212 In the oil and gas industry, the most popular models are probably those based on
213 equilibrium concepts as they can be linked with thermodynamics quantities readily
214 available in most PVT software packages that make use of Equations of States (EoS).
215 This is somewhat surprising as it is known that such models are not very accurate
216 because of their sensitivity to the choice of the EoS, as thermodiffusion quantifi-
217 cation requires second derivatives of thermodynamic properties [68]. Furthermore,
218 these equilibrium type models do not account correctly for the contribution due to
219 irreversibility, although this is not the dominant term in quasi-ideal mixtures, like
220 petroleum fluids [28]. In addition, equilibrium type models cannot take into account
221 properly the mass difference (“isotope”) effect which is well correlated with the Soret
222 coefficient in simple linear alkanes [67, 69].

223 At present, the most promising thermodiffusion models to apply to petroleum
224 fluids are probably those of Artola et al. [64] and of Würger [66] that contain con-
225 tributions from both equilibrium and irreversibility (through terms related to the
226 mobility of the species). However, these two models still need to be tested system-
227 atically against the available data on binary mixtures, in order to better understand
228 how the mobility is related to molecular parameters and thermodynamic conditions.
229 In addition, these models need to be extended to multicomponent mixtures [70], so
230 that they can be applied to real petroleum fluids.

231 2.3 Molecular Simulations

232 Equations (2) and (3) offer two different routes to compute the Soret coefficient in
233 binary mixtures by means of molecular dynamics simulations. In approaches
234 using Eq. (2), one mimics a real experiment by introducing a thermal gradient or by
235 imposing a heat flux in the simulation box. Such methods are classified as “boundary
236 driven non-equilibrium molecular dynamics” (BD-NEMD) methods [71, 72].

237 The other route, through Eq. (3), consists in directly computing the Onsager
238 coefficients L_{ij} either by using equilibrium molecular dynamics (EMD) and the
239 Green-Kubo formalism [73], or by the synthetic non-equilibrium molecular dynamics
240 (S-NEMD) algorithms proposed by Evans [74, 75] or Ciccotti [76]. One drawback in
241 the determination of S_T through the computation of L_{ij} is that additional quantities

242 are needed to relate the L_{ij} to the experimentally accessible S_T , namely, the value of
243 the thermodynamic factor μ_{11}^w . For isotopic or nearly ideal mixtures, one can use the
244 ideal value of μ_{11}^w as a first approximation. However, for a non-ideal mixture, μ_{11}^w
245 differs from the ideal value, strongly affecting the final value of the Soret coefficient.
246 Additional thermodynamic quantities also appear in the expression of L_{1q} , since in the
247 case of mixtures the heat flux J_q is not directly accessible by molecular simulation. In
248 particular, one needs the values of the partial enthalpies of the different components
249 to compute L_{1q} [76]. Therefore, BD-NEMD methods which provide directly Soret
250 coefficients (and thermal diffusion ratios) are becoming the main methods used to
251 obtain the Soret coefficient for realistic mixtures.

252 Molecular simulation of thermodiffusion has long been limited to the simplest
253 models, i.e. binary Lennard-Jones mixtures. As a result of advances in parallel com-
254 puting and adapted molecular dynamics simulation packages, it has now become
255 possible to produce quantitative predictions using realistic molecular models, of
256 interest to the crude oil industry. Simon et al. [77] and more recently Antoun et al.
257 [78] employed BD-NEMD to compute the Soret coefficients in alkane binary mix-
258 tures. Perronace et al. [79] performed an extensive study of Soret coefficients in
259 *n*-pentane–*n*-decane mixtures using EMD, S-NEMD and BD-NEMD simulations.
260 Their results were compared to experimental data and gave a satisfactory agreement.
261 Zhang and Müller-Plathe [80] applied BD-NEMD method to investigate thermodif-
262 fusion in benzene–cyclohexane mixtures at three different compositions. In a series
263 of articles, Polyakov and colleagues [81, 82] studied the behaviour of alkane/aromatic
264 mixtures in which they show that the Soret coefficient becomes larger with increas-
265 ing the degree of branching of the hydrocarbon, thus confirming the experimental
266 findings. Recently and in the context of the SCCO project, molecular simulations
267 have been used to study thermodiffusion in non-binary mixtures [70, 83], as well as
268 in coupling thermodiffusion with gravity segregation so as to mimic the behaviour
269 of a one-dimensional reservoir [9, 10].

270 3 The SCCO-SJ10 Experiment

271 The experimental set-up flown in SJ-10 consists of six small and sturdy titanium cells
272 developed for ESA by *Core Laboratories: Sanchez Technologies* (Paris, France) and
273 designed to operate at high pressures (HP). These HP cells are built by screwing two
274 titanium end parts to an initially open motorized cylindrical rotating ball valve which,
275 when closed, divides the inner volume into two exactly equal halves. The dimensions
276 of the inner cylinder of the HP cells are: a total length of $L = 40$ mm and a diameter
277 of $D = 6$ mm, which becomes a bit narrower in the channel that crosses the ball of the
278 valve, resulting in a total volume of about 1.2 mL. Kalrez 6375 O-ring were selected
279 as sealing materials for the titanium end parts and for the valve sealing stack. HP
280 cells have been certified for pressures up to 600 bars. For temperature control, two
281 aluminium blocks are attached (screwed) at the titanium end parts. Figure 1 shows one
282 of the SJ10-SCCO cells before integration. A cross-section schematic representation



Fig. 1 One of the HP cells flown in SJ10 before integration in its triad and in the C-Box. Note the two aluminium blocks attached at the titanium end parts

283 of an individual cell can be found in Ref. [23]. Electrical heaters are placed at the
284 two end aluminium blocks and the HP cells, thus fashioned, are attached to two
285 supporting triads and integrated into a hermetically sealed aluminium crate, named
286 C-box, see Fig. 2, which also contains the electronics for temperature control and
287 communications. During the orbital flight the two aluminium blocks of every HP cell
288 were maintained at different temperatures, so as to induce thermodiffusion inside the
289 fluid contained therein. Pt100 sensors with accuracy standard uncertainty of 0.05 K
290 placed at the two ends of each HP cell are used to monitor temperatures through the
291 duration of the experiment. Time-stamped temperature readings are stored in a flash
292 disk also contained in the C-Box. At the end of the experiment the central valves
293 in all HP cells were closed shut separating each fluid sample into two fractions (a
294 “hot” and a “cold” part), which, once recovered after re-entry, were forwarded to the
295 State Key Laboratory of Enhanced Oil Recovery (Research Institute of Petroleum
296 Exploration & Development) for composition analysis. The set-up is similar to the
297 one used during the Foton-M3 mission in 2007 and further details can be found
298 elsewhere [9, 21].

299 As already described [23] the SCCO-SJ10 experiment has been conducted on six
300 different synthetic mixtures that contain hydrocarbons found in reservoir fluids. The
301 samples were composed of linear alkanes: methane (C1), *n*-pentane (nC5), *n*-heptane
302 (nC7) and *n*-decane (nC10). Binary, ternary and quaternary mixtures containing the
303 aforementioned species have been studied under high pressure in a monophasic state.



Fig. 2 Left: The six HP cells contained in the C-box. Right: The C-box once closed

304 Table 1 summarizes the composition and pressures used in the six different experi-
 305 mental HP cells. Pressures correspond to the in-flight average temperature of 50.8 °C
 306 at which experiments were performed, as further elucidated in Sect. 2 of Chap. 3.
 307 The fluids in HP cells A–D are in a compressed liquid state, while HP cells E and F
 308 contain compressed gas, which on lowering the pressure produces a small amount
 309 of liquid. The latter mimics an important class of fluids of interest to the oil and gas
 310 industry, namely gas condensate, which is monophasic in reservoir conditions but
 311 diphasic (gas + “condensate”, i.e. liquid) at atmospheric conditions. Preparation and
 312 injection of the fluids mixture inside the HP cells have been performed in the State
 313 Key Laboratory of Enhanced Oil Recovery of the Research Institute of Petroleum
 314 Exploration & Development in Beijing as described in Sect. 1 of Chap. 3.

315 On April 6th at 01:38 local time, a Long March (Chang Zheng) 2D rocket lifted-
 316 off from China’s Jiuquan Satellite Launch Centre carrying the SJ-10 (Shi Jian 10)
 317 research spacecraft. The satellite’s scientific payload entailed of a variety of experi-
 318 ments including SCCO. SJ-10 landed on April 18th at 15:04, approximately 12.5 days
 319 after its launch, in the Inner Mongolia region north of Beijing. The SCCO C-Box
 320 was transported, within a day, to the State Key Laboratory of Enhanced Oil Recovery
 321 in Beijing. Additional technical details of the mission are provided in the sections
 322 below.

Table 1 Composition and pressure of the six SCCO HP cells embarked in SJ10 (adapted from Ref. [23])

HP cell	Pressure (MPa)	Composition (mole fraction)			
		C1	nC5	nC7	nC10
A	31.1	–	0.5	–	0.5
B	40.2	–	0.5	–	0.5
C	31.0	–	0.3333	0.3333	0.3334
D	40.1	–	0.3333	0.3333	0.3334
E	35.0	0.9649	0.0117	0.0117	0.0117
F	40.0	0.9649	0.0117	0.0117	0.0117

3.1 Fluid Preparation and HP Cell Filling Process

The experiments were performed at pressures given in Table 1 and at the flight operating average temperature of 50.8 °C [23]. In order to achieve these conditions, the HP cells were filled on the ground at 20 °C under a filling pressure that corresponds to the target pressure for each HP cell at the flight operating temperature. The required filling pressure was estimated by means of a Peng-Robinson equation of state [84], as the design of SCCO did not allow for pressure sensors inside the HP cells. Three STIGMA automatic pumps from Core Laboratories were used for sample preparation and HP cell filling procedures. Each pump controlled the injection pressure, the injected volume and temperature. Two different protocols [23], further described below, have been used depending on the mixture type, see Fig. 3.

3.1.1 Binary and Ternary (Liquid) Mixtures Preparation

The four liquid mixtures (A–D) were prepared by first introducing nC5 into pump 1, see Fig. 3 Then, the pre-evacuated pump 2 was filled with, either nC10 or with a nC7–nC10 premix by aspiration and weight control. The desired amount of nC5 was introduced into pump 2 from pump 1 and the mixtures were homogenized by integrated mechanical stirring and then injected into the SCCO HP cells. The cell volume was swept at least three times by the sample. The HP cell pressure was adjusted and controlled by pump 2.

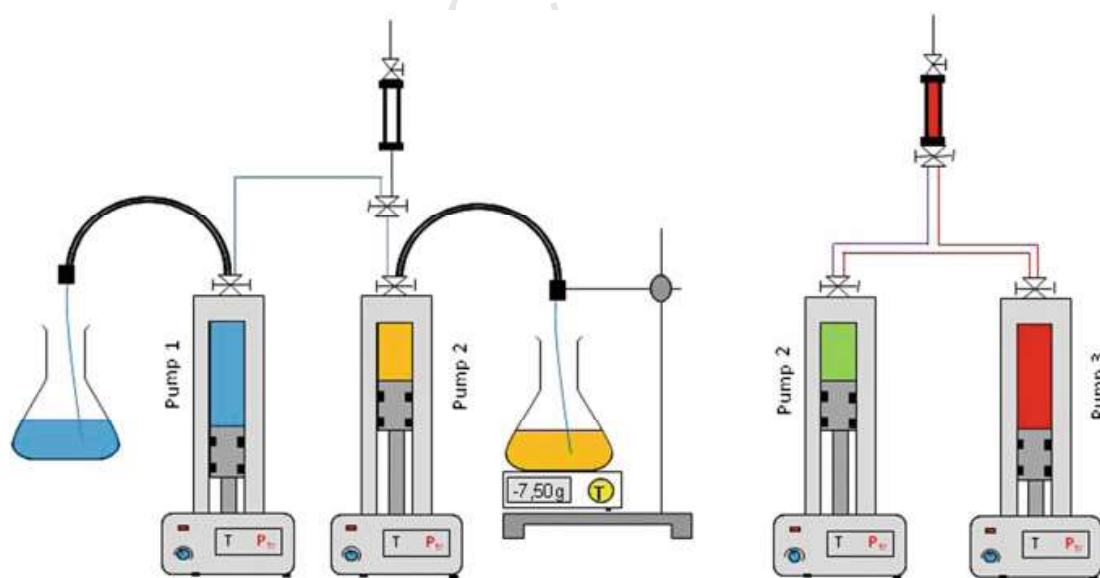


Fig. 3 Sketches of the protocol for the liquid mixture preparation (left figure) and gas-liquid mixtures (right figure) (adapted from Ref. [23])

Table 2 Average temperatures on the cold and hot plates during operational time of 270 h

HP cell ID	T cold side ($^{\circ}\text{C}$)	T hot side ($^{\circ}\text{C}$)
A	35.85	65.88
B	35.86	65.88
C	35.84	65.88
D	35.83	65.88
E	35.85	65.88
F	35.87	65.88

3.1.2 Quaternary Mixture (Gas Condensate) Preparation and Filling

The quaternary mixtures of HP cells E and F are single phase at the operating temperature and pressures of Table 1. However, at the filling temperature of 20 $^{\circ}\text{C}$ and corresponding filling pressures they are phase-separated. Hence, it is not possible to use the protocol described in Sect. 3.1.1 and a new protocol was designed. The SCCO HP cells were initially filled with methane (C1) at 20 MPa. The pump 2 was then filled with a C5–nC7–nC10 equimolar ternary mixture using the same procedure as described above, while pure methane was introduced into pump 3 at a pressure of 27.5 MPa. Then, from pump 3 the desired quantity of methane was transferred into pump 2. The quaternary mixture so obtained was homogenized and pressurized to 27.5 MPa and then transferred into the HP cells. The HP cells volume was swept at least five times by the sample. The HP cells pressure was adjusted and controlled by pump 2.

3.2 Conditions During the SJ-10 Orbital Flight

The SCCO experiment was powered on after SJ-10 reached its stabilized orbit, on April 7th at exactly 14:00. The segregation of chemical species occurred in a controlled environment where smooth and seldom orbital manoeuvres resulted in only very small residual accelerations. Inside the C-box, a set of heaters (one per HP cell) and Peltier's (one per triad) elements maintained a relatively stable temperature difference between approximately 36 and 66 $^{\circ}\text{C}$ at each of the six samples. After activation and the initial transitory phase, the target temperatures at the two triads were met in about 40 min. Actual temperatures measured at the HP cell sides are displayed in Fig. 4, illustrating that during the remaining operational time, about 270 h long, the temperatures at the hot and cold sides of each high pressure HP cell were stable to within ± 0.05 K. Average values of the temperatures measured at each side of the HP cells, after the short transient, are provided in Table 2.

Tightly attached to its SJ-10 cold plate, the C-Box containing the 6 HP cells kept a rather constant temperature of about 21 $^{\circ}\text{C}$ for the whole experimental run; it decreased to about 19 $^{\circ}\text{C}$ at the end of the orbital flight (see purple curves in

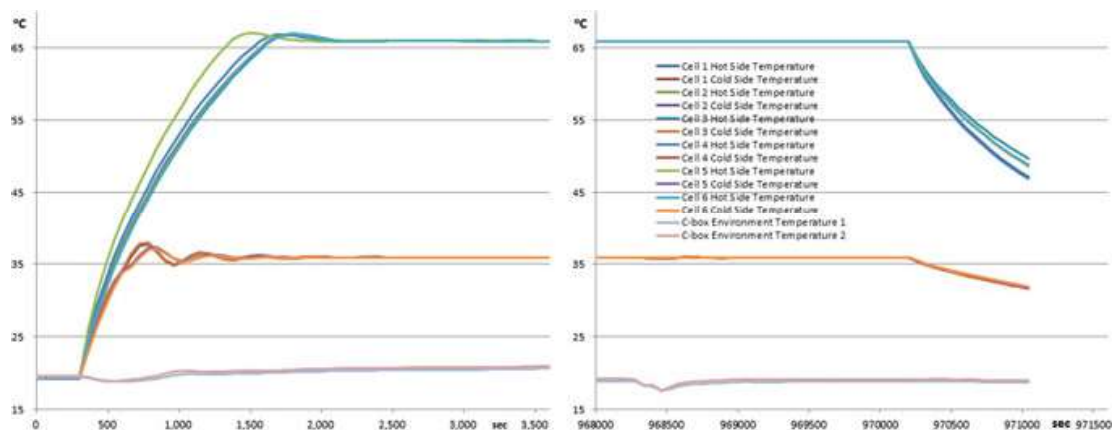


Fig. 4 Evolution of the temperature at the extremities of each HP cell, initial transient (left figure) and final transient (right figure)

371 Fig. 4). The C-Box is air tight and its inner pressure was continuously monitored.
 372 After a short, initial transient the pressure stayed at a relatively constant value of
 373 1.18 ± 0.05 bar.

374 On April 17th at 21:09, the temperature control at two extremities of the six HP
 375 cells was automatically switched-off, following the closure of the intercepting valves
 376 about 12 min earlier. The subsequent slow decrease in temperature at both extremities
 377 of the HP cells observed in Fig. 4, had no effect on the mixture composition as the
 378 fluids remained safely confined within the two separate halves of the HP cells. Typical
 379 diffusion coefficients in this kind of hydrocarbon mixtures are at least of the order
 380 of $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [17], which combined with a HP cell length $L = 4 \text{ cm}$ gives a
 381 maximum experimental characteristic time, τ_{max} , of about $2.5 \times 10^5 \text{ s}$. The duration
 382 of the runs, about $4\tau_{\text{max}}$, is so considered long enough for the separation inside the
 383 six HP cells to have attained steady state. Twenty-four hours after capsule recovery,
 384 the SCCO C-Box was brought back to the State Key Laboratory of Enhanced Oil
 385 Recovery in Beijing, where engineers and scientists were ready to split it apart and
 386 reach the valuable flown samples of alkane mixtures, in order to start the gamut of
 387 tasks for their post-flight sample analysis.

388 3.3 High Pressure Cell Analysis Process

389 Two Agilent Gas Chromatographs (GC) 6890 N with Agilent 19091Z-205 HP-1
 390 columns have been used to analyse the six samples; depending on the nature of the
 391 mixtures, two different protocols, as described previously [23], have been used.

3.3.1 Binary and Ternary Mixtures

For binary and ternary liquid mixtures (A–D) the HP cells were initially stored, at the CNPC laboratory, at $-15\text{ }^{\circ}\text{C}$ in order to limit evaporation of the lightest alkane (nC5). Following this pre-conditioning, the two compartments of each HP cell were emptied using dedicated syringes and the extracted fluids were then stored in Agilent vials with volume redactor. When the extracted volume was insufficient, the liquid samples were diluted in a solvent (carbon disulphide) which did not affect the analysis. Finally, the fluid samples were injected in the gas chromatograph and analysed.

3.3.2 Quaternary Mixtures

For quaternary gas condensate mixtures (E and F) the fluids contained in the two compartments of each HP cell, were initially diluted by using hydrogen, as to avoid phase separation. The resulting diluted mixtures were stored in a dedicated reservoir with a volume of 1 litre and subsequently transferred to the GC for analysis. The reservoirs were heated to the same temperature as the GC line, in order to avoid cold points.

3.4 Results and Discussions

From the gas chromatography analysis of all cold and hot compartments of each HP cell performed after the flight using the protocols above, it appeared that some HP cells have suffered from leakages yielding incoherent results. This conclusion is confirmed independently by accurate weighing of filled HP cells before and after the flight. The leakage may have many root causes, but most of them can be attributed to either unpredictable thermal effects at such high pressures inside the HP cells (more than 300 bar, See Table 1) or to unexpected landing shocks. In particular, HP cells A, B, D and F were found to be partially empty, to the extent that no sensible analysis could be performed and therefore they will not be discussed further. Results on the two exploitable HP cells (C and E), which contained a ternary and a quaternary mixture respectively, which have been presented previously [23], are displayed here in Table 3, for completeness and ease of discussion. The reported compositions in Table 3 have been estimated using normalized peaks-area computation and are an average between two different GC injections for each compartment. The associated error bars correspond to half the difference between the results of the two injections. The composition results were reproducible to within 2% of mole fraction of a given compound. It should be pointed out that the GC protocol has been tested on a HP cell that stayed on earth and was containing the same quaternary mixture as HP cells E and F.

Table 3 Measured GC compositions (in mole fraction) in the two exploitable HP cells after the flight. Initial compositions (before the flight) are shown in Table 1 (adapted from Ref. [23])

HP cell ID	Cold compartment				Hot compartment			
	Species	C1	nC5	nC7	nC10	C1	nC5	nC7
C	N/A ^a	0.3063	0.333	0.3607	N/A ^a	0.3585	0.3337	0.3078
		± 0.0151	± 0.0033	± 0.0185		± 0.0019	± 0.0025	± 0.0043
E	0.9612	0.0117	0.0138	0.0135	0.0969	0.0116	0.0096	0.0098
	± 0.0007	± 0.0002	± 0.0001	± 0.0008	± 0.0056	± 0.0003	± 0.0004	± 0.0049

^aN/A: Not applicable (Ternary mixture)

428 As shown in Table 3, compositions of the two compartments (cold and hot) of
 429 each exploitable HP cell are noticeably different, as expected. Furthermore, results
 430 clearly show that, in both liquid (HP cell C) and gas condensate (HP cell E) mixtures,
 431 the lightest species had a tendency to migrate (relatively to the heaviest) to the hot
 432 compartment, while the heaviest migrated towards the cold end. Such behaviour is
 433 consistent with what has been known qualitatively for a long time [85] and also
 434 with more recent experimental results on binary hydrocarbon mixtures [11, 12]. In
 435 addition, it appears that the intermediate species, nC7 in the ternary mixture and nC5
 436 in the quaternary mixture, is uniformly distributed showing only weakly migrating
 437 patterns. Such a trend is also consistent with what is known regarding mass effect
 438 in non-binary mixtures [69, 70]. The observed behaviour is also in agreement with
 439 molecular dynamics results on multicomponent hydrocarbon mixtures [9, 10, 58].
 440 More generally, these results confirm that, in oil and gas reservoirs composed of
 441 normal alkanes, thermodiffusion tends to counteract (and sometimes overcome) the
 442 influence of gravity-driven segregation on the vertical distribution of species [10].

443 From the compositional difference between the two compartments, and assuming
 444 a linear response, it is possible to quantify thermodiffusion in the studied mixtures
 445 by means of Eq. (4). Such a computation requires an estimation of the average
 446 temperature difference between the two compartments of each HP cell and following
 447 the work of Van Vaerenbergh [21], we estimated it to be equal to 12.45 ± 0.20 °C [23].
 448 As explained above, it is also implicitly assumed that the duration of the experiment
 449 (270 h) is long enough for the stationary state to be reached. Results, presented in
 450 terms of the thermal diffusion ratio, are provided in Table 4.

451 Experimental values of thermal diffusion ratios shown in Table 4, confirm quanti-
 452 tatively what is observed in terms of the compositional variations of the cold and hot
 453 compartments, i.e. thermodiffusion leads to a relative migration to the hot region of
 454 the lightest hydrocarbon in a given mixture. What is more surprising is the magnitude
 455 of the thermal diffusion factors [23]. The values obtained for the quaternary mix-
 456 tures, whose order of magnitude (about 0.1) is consistent with experimental results
 457 on non-polar binary mixtures [11, 12]. However, the thermal diffusion ratios for nC5

Table 4 Experimental measurements and molecular simulations results of thermal diffusion ratio of the various species in the two exploitable HP cells (adapted from Ref. [23])

HP cell ID	Thermal diffusion ratio per species (k_{T_i})							
	Experiments				Molecular simulations			
Species	C1	nC5	nC7	nC10	C1	nC5	nC7	nC10
C	–	-1.36 ± 0.47	-0.02 ± 0.14	1.38 ± 0.62	–	-0.09 ± 0.03	-0.09 ± 0.03	0.18 ± 0.04
E	-0.21 ± 0.17	0 ± 0.01	0.11 ± 0.09	0.1 ± 0.08	-0.16 ± 0.04	0.04 ± 0.01	0.05 ± 0.01	0.07 ± 0.02

458 and nC10 in the ternary liquid mixtures are one order of magnitude larger than those
459 of the quaternary mixture.

460 To complement these microgravity experiments Boundary Driven Non Equilib-
461 rium Molecular Dynamics computations of the thermal diffusion ratios of HP cells
462 C and E fluids have been performed using Mie Chain Coarse Grained molecular
463 models to represent the fluid molecules [86]. Simulations details can be found in
464 Ref. [23].

465 Simulations results, provided in Table 4, confirm what has been pointed out previ-
466 ously, i.e. microgravity experimental results on the ternary mixture are qualitatively
467 consistent, but quantitatively questionable, whereas experimental results on the qua-
468 ternary mixture are quantitatively consistent with molecular simulations results, rein-
469 forcing thus their reliability.

470 Dedicated on ground experiments and additional molecular simulations are in
471 progress in order to further analyse these very interesting experimental results
472 obtained in the microgravity environment of a space flight.

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