# Interfacial Properties at Elevated Pressures in Processes of Enhanced Oil and Gas Recovery

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**Abstract**

Interfacial properties play an important role in enhanced oil and gas recovery. The increased miscibility under reservoir conditions of elevated pressures and temperatures takes considerable influence on the efficiency of the recovery process. An interesting option from an economical point of view is the combination of enhanced oil recovery and sequestration of carbon dioxide. The interfacial tension is an experimentally accessible key quantity for characterizing the phase and interfacial behaviour of the existing complex fluid systems. It is directly related to the phase behaviour in liquid-fluid or liquid-liquid systems. Data of hydrocarbons in different fluid phases are presented at pressures of up to 15 MPa. Consequences of the observed results are shown regarding reservoir conditions and enhanced recovery techniques taking into account also dynamic effects.

## Introduction

In the course of improving recovery efficiencies of crude oil and natural gas, deeper insight into system properties and dominating mechanisms is required. Especially knowledge on interfacial and transport phenomena is essential for optimizing existing methods and developing innovative procedures. Up to now, mainly pure systems have been investigated regarding properties like interfacial tension, density, contact angle and diffusivity [1]. Real fluid systems are multicomponent mixtures composed of hydrocarbons, aqueous phases and sour gases. Mutual miscibility among coexisting fluid phases takes strong influence on these properties and varies to a great extent depending on the hydrostatic or lithostatic pressure within the rock formation. The interfacial tension reflects the miscibility behaviour and is therefore an interesting measure for determining the so-called minimum miscibility pressure (MMP) within production wells [2]. Further, mutual miscibility between two nearly

immiscible liquids may be enhanced by dissolving gases which on its turn changes the wetting angle on rock surfaces. Theoretical prediction of relevant system data is becoming increasingly relevant in view of costly experimentation under reservoir conditions and improved computational possiblities. Especially the density gradient theory based on the theory of Cahn and Hilliard [3] has proven to be a useful tool in this respect [4].

**Materials and Methods**

The materials listed in table 1 were used for the presented investigations.

| Name | Provider | Composition/Purity |
|------|----------|--------------------|
| Methane ($CH_4$) | Westfalen AG | 99.995 % |
| Carbon Dioxide ($CO_2$) | Westfalen AG | 99.999 % |
| n-pentane (C5) | Merck | > 99 % |
| n-heptane (C7) | Merck | > 99 % |
| n-decane (C10) | Merck | > 99 % |
| n-hexadecane (C16) | Merck | > 99 % |
| Water ($H_2O$) | Sigma Aldrich | HPLC quality |

**Table 1:** Materials for investigation including supplier and quality.

The experiments were performed in a high pressure view chamber described elsewhere [5]. A schematic of different configurations of the experimental setup is shown in figure 1, according to the specific aim.
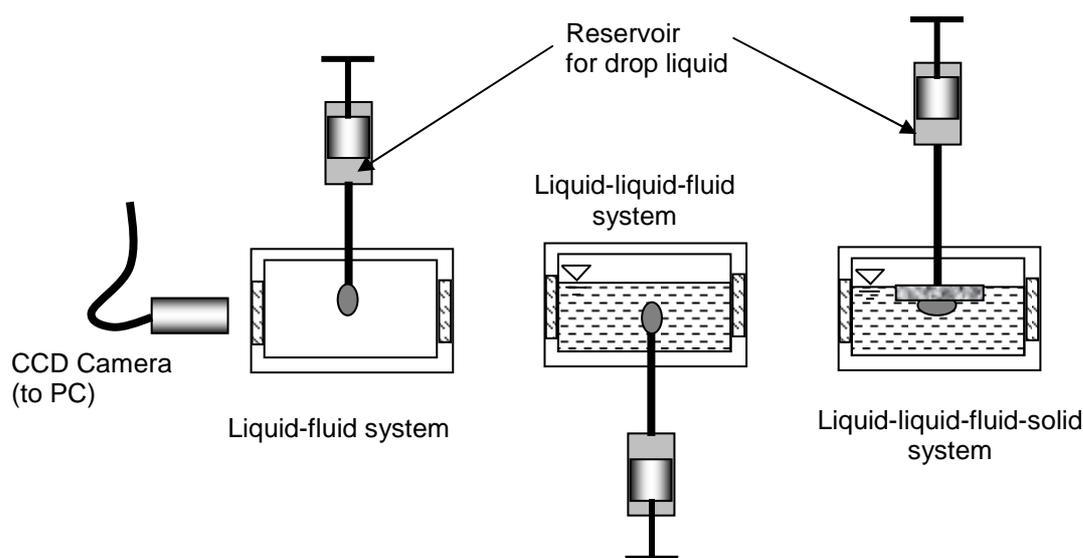


**Figure 1:** Experimental setup for measuring interfacial tension and contact angle.

**Results and Discussion**

At first, different reservoir fluids are classified according to their effect on interfacial tension. Subsequently, additional phases are added aiming to describe a real reservoir system as close as possible including rock surfaces as well. Finally, the density gradient theory is applied for describing pressure dependance of the IFT of liquid-fluid systems as a first step towards theoretical understanding of complex reservoir systems.

Liquid-fluid systems

In Figure 1, the interfacial tension of pentane in different gas phases is presented as a function of pressure. Nitrogen clearly has the least impact on the interfacial tension against pentane while carbon dioxide shows a tendency of complete miscibility below 8 MPa. Pentane – methane arrive at this state above 16 MPa. This behaviour illustrates the principle difference in different recovery techniques: displacement flooding, partly miscible flooding and miscible flooding. Further, these data are required for designing processing lines for cleaning and separation of gas condensates.
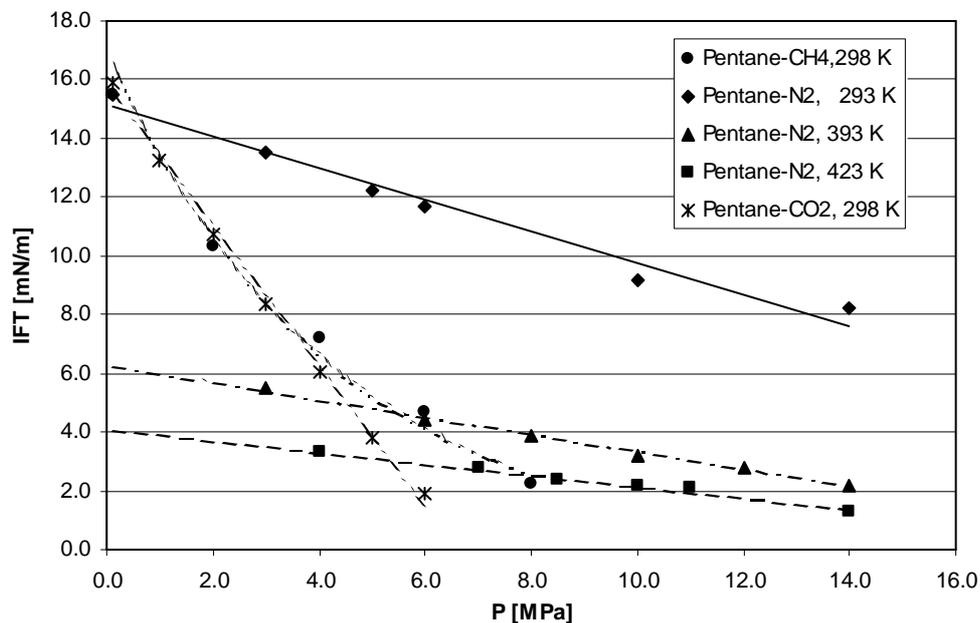
**Figure 2:** Interfacial tension of pentane in different fluid atmospheres.

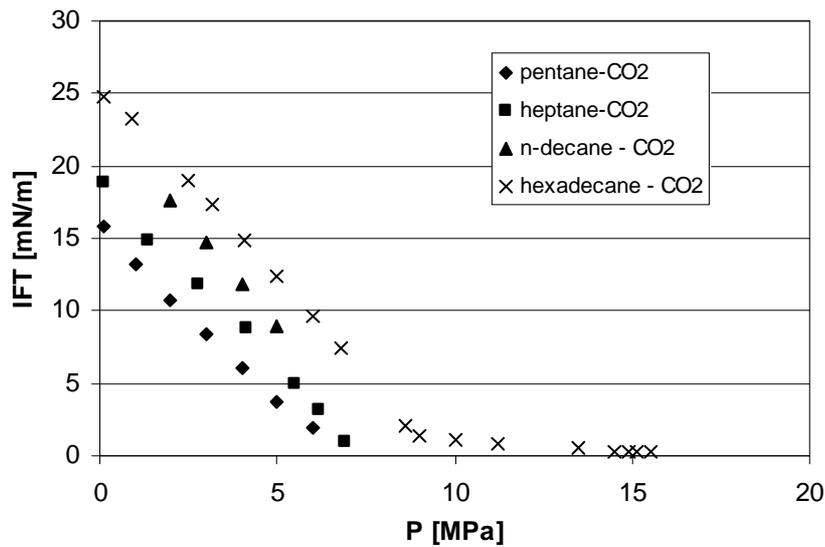In figure 2 the interfacial tension is shown for a series of alkanes in carbon dioxide.

**Figure 3:** Interfacial tension of different alkanes in carbon dioxide. 313 K.

It is clearly seen that in case of short chain alkanes the MMP is achieved at moderate pressures while low volatiles arrive at low but still definite values of interfacial tension at elevated pressure. Crude oils are multicomponent mixtures of hydrocarbons of different molecular weight, structure and volatility explaining why complete miscibility is often not acchieved up to very high pressures.

Liquid-liquid-fluid systems

A number of authors presented interfacial tension data on liquid-liquid systems under conditions already during the past century [6]. In general it was found that immiscible liquid – liquid systems exhibit nearly unchanged values as a function of pressure. Recently it became more interesting to consider live oils which means crudes containing volatiles that are stored under reservoir pressures. In figure 4, IFT of the crude oil – water system is shown under carbon dioxide atmosphere. The absolute value of IFT varies according to the quality of the water and the type of crude. Anyhow, the general trend of slightly decreasing IFT at increasing pressure is the same.
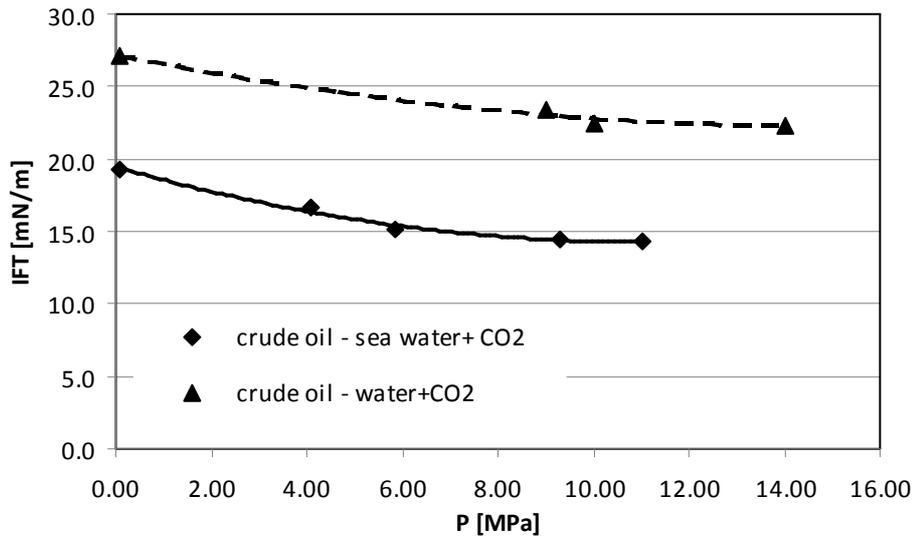
**Figure 4:** IFT of crude oil – water under carbon dioxide atmosphere, 323 K.


Liquid-liquid-fluid-solid systems

Real reservoir systems contain solid phases as rock surfaces take considerable influence on the principle system behaviour via wetting and capillarity. For investigating such systems it is important to consider the real situation in terms of continuous and dispersed phase. Figure 5 shows a sequence of oil drops in brine after being pressurized with carbon dioxide
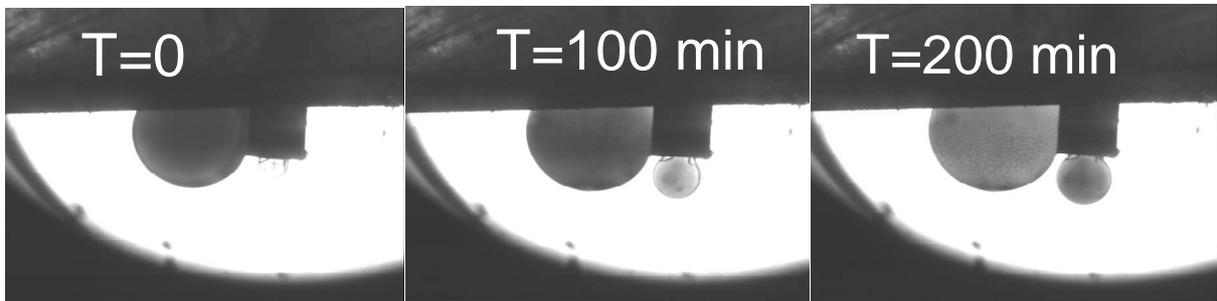


**Figure 5:** Drop of crude oil in brine + CO2 on calcite, 19.3 MPa, 323 K.


As can be seen from figure 4, an the oil drop changes its volume, contact angle and colour as carbon dioxide procedes through the aqueous phase towards the o/w interface and into the drop phase. If it was only the interfacial tension changing due to dissolution of carbon dioxide (compare section on liquid-liquid-fluid systems) the contact angle with respect to the drop phase should increase instead of decrease as shown in Fig. 5 fulfilling Young´s law:

$$\sigma_s = \sigma_{s,l} + \sigma_l \cdot \cos \Theta \tag{1}$$

Hence, also the interfacial energies of the rock surface towards the aqueous and oily phases is affected by the dissolving gas under elevated pressure. In order to estimate this effect, theoretical approaches for relating interaction forces and interfacial energies are required. Fowkes [7] devided the interfacial energy into a dispersive (non-polar) and a polar part. According to Fowkes the interfacial energy is composed of both parts as follows:

$$\sigma = \sigma_1 + \sigma_2 - 2\sqrt{\sigma^d_1 \sigma^d_2} - 2\sqrt{\sigma^p_1 \sigma^p_2} \qquad (2)$$

In [8] an expression was derived for determining the interfacial energy beween n-alkanes and reservoir rock surfaces under elevated pressure making use of the fact, that the interfacial tension of n-alkanes is only composed of a dispersive part. After having determined this dispersive part of the interfacial tension, the dispersive part of the interfacial energy of the solid-alkane interface and subsequently also its polar part may be determined. Fig. 6 shows the contact angle, the interfacial tension and the interfacial energy in the water - (hexadecane+methane) – dolomite – system.
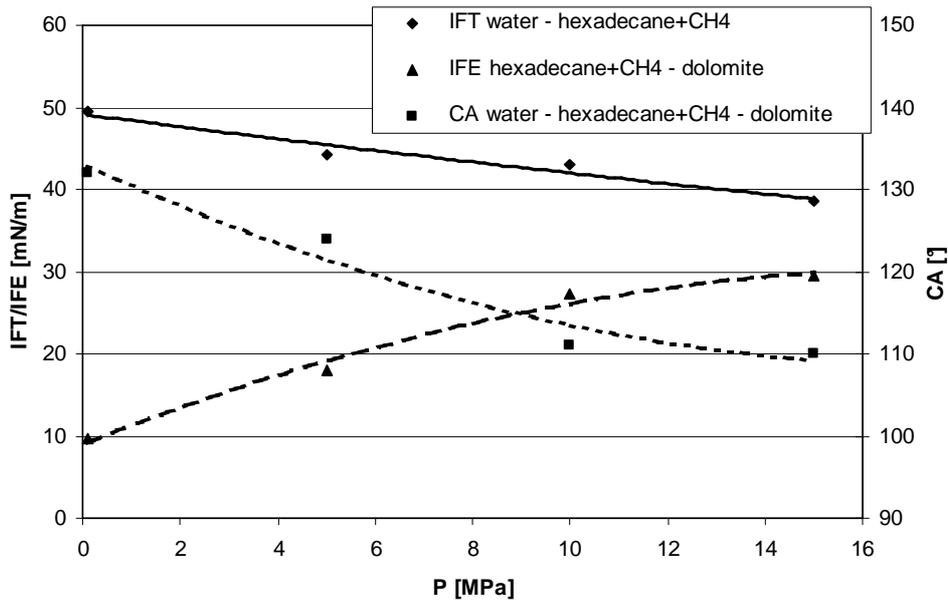


**Figure 6:** Contact angle, interfacial tension and energy in water/hexadecane+methane/dolomite, 298K.

At enhanced pressure an increased amount of methane is dissolved in the hexadecane leading to a decreasing density of the oily phase. While the dissolved methane enhances the interaction at the water – hydrocarbon interface resulting in a diminishing interfacial tension, the interaction forces are weakened at the solid interface resulting in an increasing value of the interfacial energy.

<u>Theoretical Models</u>

Different theoretical approaches have been applied successfully that describe the concentration profile across fluid interfaces as a functional based on phase equilibrium data of the system under consideration. Among these, the density gradient theory (DGT) has proved to be a useful and predictive tool as long as single data on pure phase surface tension are available. Figure 7 shows calculations of pentane-fluid interfacial tension using the DGT and an appropriate EOS like the PCP-SAFT [9] for describing the phase equilibrium established within the adjacent bulk phases.
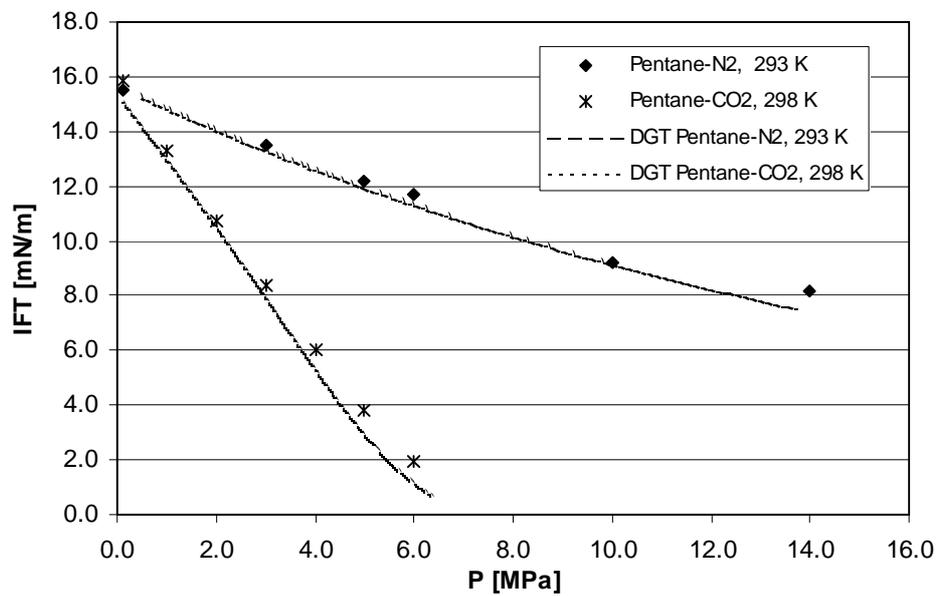


**Figure 7:** Interfacial tension of pentane in different fluid atmospheres compared to data calculated by DGT.

Reasonable accordance is achieved between experimental and predicted data. The only data required prior to calculations are the parameters of the EOS and one value of surface tension of each fluid under consideration, although taken at any condition of P/T.

**Conclusions**

The upcoming discussion of combining sequestration of carbon dioxide with techniques of enhanced oil recovery triggers investigation of its influence on interfacial and transport mechanisms in reservoir systems. Non of the conventional fluids in reservoir engineering shows such an impact on fluid interfaces like $CO_2$ due to its strong interactions with either

hydrocarbon and aqueous phases. New experimental and theoretical tools allow to describe, understand and predict the phase and interfacial behaviour also in dynamic situations.

**Symbols**

$P$ – pressure [MPa]

$T$ – temperature [K]

$\sigma$ - interfacial tension/energy = IFT/IFE [mN m$^{-1}$]

$\Theta$ - contact angle = CA [deg]

$s$ – solid

$l$ – liquid

**References**

[1] N. Nagarajan, R. L. Robinson, Equilibrium Phase Compositions, Phase Densities, and Interfacial Tensions for CO2 + Hydrocarbon Systems. 2. CO2 + n-Decane, J. Chem. Eng. Data 31 (1986), 168-171.

[2] D.N. Rao, J.I. Lee: Determination of Gas-oil miscibility conditions by interfacial tension measurements, Journal of Colloid and Interface Science 262 (2003) 474–482.

[3] J.W. Cahn, J.E. Hilliard: Free energy of a nonuniform system. I. Interfacial free energy, J. Chemical Physics 28 (1958) 258–267.

[4] O.G. Niño Amezquita, S. Enders, P.T. Jaeger, R. Eggers, Measurement and Prediction of Interfacial Tension of Binary Mixtures, Ind. Eng. Chem. Res. 49 (2010), 592–601.

[5] P.T. Jaeger, M. Alotaibi, H. Nasr-El-Din: Influence of Compressed Carbon Dioxide on the Capillarity of the Gas-Crude Oil-Reservoir Water System, J. Chem. Eng. Data 2010, 55, 5246–5251.

[6] A.S. Michaelis, E.A. Hauser: Interfacial Tension at Elevated Pressures and Temperatures II. Interfacial Properties of Hydrocarbon – Water Systems. J. Phys. Coll. Chem. 55 (1951), 408 – 421.

[7] F.M. Fowkes: Attractive Forces at Interfaces, Ind. Eng. Chem. 56 (1964) 12, 40-52.

[8] P.T. Jaeger, A. Pietsch, Characterization of Reservoir Systems at Elevated Pressures, J. Petrol. Sci. Eng. 64 (2009) 1-4, 20 – 24.

[9] J. Gross, G. Sadowski, Perturbedchain SAFT: an equation of state based on a perturbation theory for chain molecules, J. Ind. & Eng. Chem. Research 40 (2001) 1244–1260.